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Competition between Photoisomerization and Photocyclization of the Cis Isomers of *n*-Styrylnaphthalenes and -Phenanthrenes†

U. Mazzucato* and A. Spalletti

Dipartimento di Chimica, Università di Perugia, I-06123 Perugia, Italy

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The isomerization and cyclization photoreactions of the cis (Z) isomers of *n*-styrylnaphthalenes ($n = 1$ and 2), *n*-styrylphenanthrenes ($n = 1$, 2, 3, 4, and 9), and two related compounds, 3-styrylchrysene and 3-styrylbenzo[*c*]phenanthrene, were investigated by spectrophotometric and chromatographic techniques. The quantum yields of the two photoreactions were measured in aerated and deaerated nonpolar solvent at room temperature and compared with those reported in the literature for some of the molecules investigated and other related compounds. The combined use of high-performance liquid chromatographic and spectrophotometric techniques made easier the separation of the components of the photoreaction mixtures thus simplifying the study of the isomerization/cyclization competition and the measurement of the UV−vis absorption spectra and the thermal decay kinetics of the dihydrophenanthrene-type intermediates. The conformational equilibria in the ground state and the positional isomerism (*n* values) notably affect the prevalence of one or the other competitive photoreaction. Oxygen also plays an important role: practically it does not affect the quantum yield of the Z → E process but has a drastic effect on the formation of the final oxidation product which can proceed even in the presence of traces of air. In three cases, non-negligible formation of a side colorless product was detected. It was assigned to an isomer of the normal photocyclization intermediate (4a,4b-dihydrophenanthrene-type), formed by shift of one or both hydrogen atom(s) to other positions of the rings. Parallel ab initio calculations of the potential energy of the possible conformers helped to explain the structure effects on the competitive photoreactive relaxation pathways. Some correlations between the computed reagent/product energy difference in the ground state and the photocyclization yield and thermal stability of the intermediates were also verified.

1. Introduction

Extensive work on the photoreactions and conformational equilibria of the trans (E) and cis (Z) isomers of 1,2-diarylethenes containing naphthyl and phenanthryl groups has been carried out in various laboratories during the last decades.[1−22] Particular attention has been given to photocyclization (photochromic reaction competitive to photoisomerization) of the Z isomers leading to colored 4a,4b-dihydrophenanthrene-type (DHP) derivatives in trans stereochemistry. The latter are generally unstable: they back photoconvert to Z while thermally undergoing competitive ring opening and dehydrogenation to condensed-ring phenanthrene-type (P) arenes in the presence of suitable oxidants, such as iodine and oxygen.[12] While the geometrical E/Z isomerization can occur in both the lowest excited states of singlet and triplet multiplicity (S_1 and T_1), cyclization is known to occur in the singlet manifold only.[2,3]

Much attention has been paid in our laboratory to the photobehavior of geometrical, positional and conformational isomers of *E*-*n*-styrylnaphthalene, *n*-StN, and *E*-*n*-styrylphenanthrene, *n*-StP (for some representative papers see refs 17, 19, and 21). It is well-known that diarylethenes exist in solution as mixtures of two or more conformers (or rotamers), as generally revealed, for the fluorescent E isomers, by the effects of the excitation and emission wavelength (λ_{exc} and λ_{em}) on their fluorescence emission and excitation spectra, respectively.[17,23−30] Obviously, the study of the conformational equilibria of the Z isomers is complicated by the fact that their intrinsic emission is generally rather weak at room temperature.[30−35]

Recently, we focused our interest on the adiabatic mechanism of photoisomerization,[34,35] which takes place directly from one to the other excited isomer in a unique (singlet or triplet) potential energy surface, generally in the $^{1,3}Z^* \rightarrow {}^{1,3}E^*$ direction. Such a mechanism can often compete with the more common (reversible) diabatic mechanism implying $S_1 \rightarrow S_0$ internal conversion (IC) or $T_1 \rightarrow S_0$ intersystem crossing (ISC) at the perpendicular configuration (p) and relaxation to the ground-state isomers, $^{1,3}E^* \rightarrow {}^{1,3}p^* \rightarrow {}^1p \rightarrow \alpha{}^1Z + (1 - \alpha){}^1E$, where the partitioning factor α is assumed to be ~0.5 in most cases.[36] For the compounds here investigated, only for *Z*-2-StN a relatively small contribution of adiabatic mechanism to the overall yield of photoisomerization in the Z → E direction has been reported by Saltiel et al.[28] and later confirmed in our laboratory.[34,35] Mixed diabatic/adiabatic channels in the opposite direction were also reported for the photoisomerization and photocyclization processes of *E*-1,2-di(*n*-naphthyl)ethenes.[14]

The ratio of the isomerization/cyclization quantum yields ($\phi_{Z\rightarrow E}/\phi_{Z\rightarrow DHP}$) depends on the structure of ^1Z, specifically on the structure of each conformer. In the case of stilbene, the partitioning between the two photoreactions in nonpolar solvents is about 70/30% for isomerization/cyclization, respectively. However, only one-third of the latter decays to the metastable DHP while the rest reverts to Z leading to a Z → DHP quantum yield of 0.1 in nonpolar solvents.[3,9,37] Somewhat higher values ($\phi_{Z\rightarrow DHP} = 0.18$) were also reported.[38]

In principle, the conformers (s-trans and s-cis) of the Z isomers could give rise to more than one DHP photoproduct

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* To whom correspondence should be addressed: mazzucat@unipg.it.

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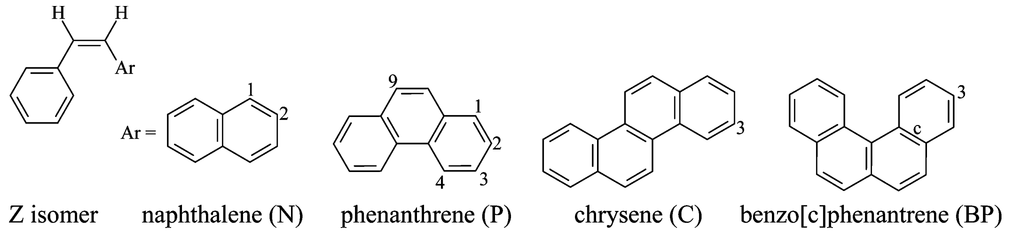
CHART 1: Compounds Investigated



(two in the case of the styrylarenes here investigated). It has to be recalled that an empirical rule, generally verified,[4−7,12,20,39] states that, apart from the relative conformer abundance, cyclization occurs only from those excited species whose "free valence number" ΣF_r^* exceeds the value of 1. In agreement with such a rule, only one DHP photoproduct has been often described in the literature, the other ones, if any, being hardly detectable.[12,20,37,40] Accordingly, the formation of DHP-like products having an anthracenic structure is often considered to be negligible in these compounds.

The present work describes the isomerization/cyclization competition for all positional isomers of *Z*-*n*-StN ($n = 1$ and 2) and *Z*-*n*-StP ($n = 1$, 2, 3, 4, and 5) and for two related (benzo-annelated) compounds, 3-styrylchrysene and 3-styrylbenzo[*c*]phenanthrene, whose photoreactivity has not been investigated hitherto, to our knowledge. This work will be followed by a further study aimed to ascertain if the contribution of the adiabatic mechanism to photoisomerization, reported for *Z*-2-StN, is a general phenomenon in this series of compounds and, if so, to what extent. Since the excited-state dynamics of the Z isomers, in our case the Z → E process, cannot be interpreted without considering the competitive cyclization channel,[37] a preliminary study was necessary to evaluate the isomerization/cyclization competition of the excited Z isomers and the spectral properties of the cyclization photoproducts. This information is not available in the literature since the abundant reported results generally concern one or the other of the two geometrical isomers and/or only some of the positional isomers of this series of compounds. The results are scattered and/or obtained in different experimental conditions; moreover they are focused on one or the other of the two main photoreactions (isomerization and cyclization) rather than on their competition. Therefore, a study of both photoreactions of this series of compounds in the same experimental conditions was needed to clarify their photobehavior.

The use of combined HPLC and spectrophotometric techniques allowed the complete UV−vis absorption spectra of DHPs to be also obtained. Parallel theoretical calculations of the absorption electronic transitions and formation enthalpies of the possible conformers helped to explain their role in the competitive photoreactions of the compounds investigated and to verify if a correlation exists between the computed reagent/product energy difference in the ground state and the photocyclization yield.

2. Materials and Methods

E/Z mixtures of the nine compounds here investigated (two *n*-StNs, with $n = 1$ and 2, five *n*-StPs, with $n = 1$, 2, 3, 4, and 9, and two analogous compounds, 3-styrylchrysene (3-StC) and 3-styrylbenzo[*c*]phenanthrene (3-StBP), see Chart 1) were prepared for previous works.[17,19,21] The geometrical isomers were separated from the synthesis mixture and carefully purified by preparative HPLC. The cyclization photoproducts (DHP analogues) and their dehydrogenation products (P analogues) were separated by HPLC (eluent deaerated by bubbling helium) and characterized by absorption spectrometry and, in many cases, by gas chromatography−mass spectrometry.

The solvent used was a mixture of 9/1 (v/v) methylcyclohexane/3-methylpentane (MCH/3MP) from Fluka, spectrophotometric grade, except as otherwise specified. The solvents were further purified by standard procedures.

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. For photochemical measurements (potassium ferrioxalate in water was used 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) and Prontosil 200−3-C30 (4.6 × 250 mm; 3 μm) columns and UV diode-array detector.

The procedure used to measure the photoreaction quantum yields was as follows. Diluted solutions of the Z isomers in deaerated (by bubbling nitrogen or argon) MCH/3MP were irradiated up to a maximum conversion percentage of 8% to minimize competition of the back photoreactions. Samples of the irradiated solutions, analyzed immediately after the removal of the irradiating source by combined HPLC and spectrophotometric techniques, generally contain four components: E, Z, DHP, and small amounts of P-type dehydrogenated arene. The air-equilibrated solutions were then left overnight in the dark to allow the decay of the DHP intermediates to go to completion. The residual components were separated by HPLC (using acetonitrile as eluent, a small addition of water being necessary in some cases to better separate the chromatographic peaks) and identified spectrophotometrically.

It has to be noted that the quantum yields of E and P formation ($\phi_{Z\rightarrow E}$ and $\phi_{Z\rightarrow P}$) measured at $\lambda_{exc} = 300$ nm, generally close to the maximum of the first absorption band, could be affected by changes in λ_{exc} because of the different absorption spectra of the two s-trans and s-cis conformers of the Z isomers when they have comparable abundances (i.e., in the case of compounds with the styryl group at positions 2 and 3 of the arene). In such cases, the quantum yields reported in the tables are to be considered mean values for the conformer mixtures.

The thermal stability of DHPs, usually expressed by the half-lives ($t_{1/2}$) at room temperature, was measured by following spectrophotometrically the disappearance of the visible absorption band in both aerated and deaerated (by bubbling nitrogen or argon) solutions of MCH/3MP. The quantum yields reported in the tables are averages of at least three independent experiments with mean deviations of ca. 10%. Higher uncertainty can be present for the compounds having very small cyclization yield (<1%).

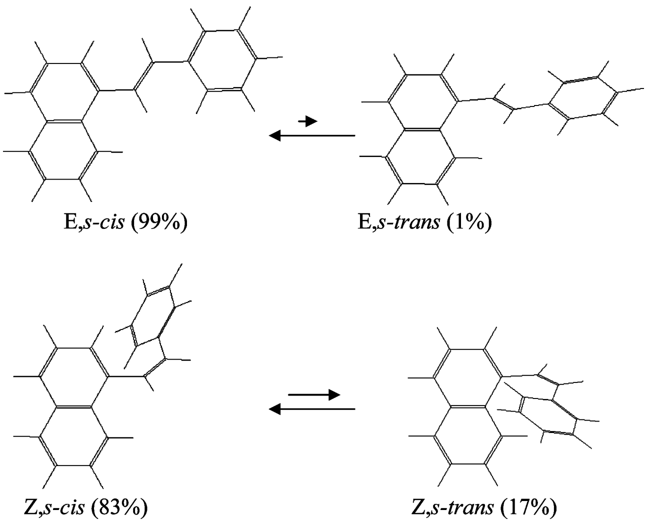
The theoretical calculations were performed using the HyperChem computational package (version 6.1). The total energy of the two conformers of each Z isomer was obtained for geometries optimized by ab initio calculations using a 3-21G

TABLE 1: Calculated Total Energy (*E*), Abundances in S_0 (%), and Electronic Spectra (Transition Energy, λ, and Oscillator Strength, *f*) for the Two Conformers of the Z Isomers Investigated

compound	conformer	*E*/kcal mol^{-1}	% (293 K)	λ/nm	*f*	
1-StN	s-cis	−430430.34	83	312	0.025	S_1
				291	0.39	S_2
				232	0.66	S_6
	s-trans	−430429.41	17	310	0.014	S_1
				280	0.32	S_2
				223	1.02	S_8
2-StN	s-cis	−430431.25	42	317	0.008	S_1
				292	0.31	S_2
				260	0.59	S_4
	s-trans	−430431.44	58	317	0.005	S_1
				283	0.63	S_2
				262	0.41	S_4
1-StP	s-cis	−525685.94	86	329	0.011	S_1
				294	0.54	S_2
				250	1.32	S_6
	s-trans	−525684.88	14	328	0.008	S_1
				288	0.32	S_2
				248	0.68	S_6
2-StP	s-cis	−525687.25	48	332	0.002	S_1
				291	0.35	S_2
				276	0.57	S_3
	s-trans	−525687.30	52	333	0.002	S_1
				290	0.41	S_2
				276	0.56	S_3
3-StP	s-cis	−525687.38	56	331	0.005	S_1
				301	0.46	S_2
				243	0.95	S_7
	s-trans	−525687.25	44	331	0.007	S_1
				298	0.76	S_2
				247	1.11	S_6
4-StP	s-cis	−525681.56	100	333	0.01	S_1
				293	0.23	S_2
				279	0.42	S_3
				254	0.80	S_6
	s-trans	−525567.19	0	315	0.03	S_1
				271	0.08	S_2
				267	0.41	S_3
9-StP	s-cis	−525686.13	85	329	0.009	S_1
				298	0.34	S_2
				249	1.09	S_6
	s-trans	−525685.13	15	327	0.008	S_1
				288	0.31	S_2
				247	1.34	S_7
3-StC	s-cis	−620940.88	66	343	0.003	S_1
				313	0.44	S_2
				276	0.78	S_4
	s-trans	−620940.50	34	344	0.002	S_1
				311	0.75	S_2
				276	1.18	S_4
3-StBP	s-cis	−620933.69	35	353	0.01	S_1
				314	0.29	S_2
				286	1.35	S_4
	s-trans	−620934.06	65	353	0.004	S_1
				312	0.35	S_2
				288	1.02	S_4

basis set. The electronic spectra (transition energy and oscillator strength) were calculated by ZINDO/S on the optimized geometries, the configuration interaction including 400 (20 × 20) singlet excited configurations. The formation enthalpy ($\Delta H_f°$) of Z and DHP for an estimation of their energy difference was obtained by the PM3 method. The conformational search was used to analyze the minimum energy structures of the DHP intermediates by using the Mm+ method.

CHART 2: Conformational Equilibria of the Geometrical Isomers of 1-StN



E,*s-cis* (99%) E,*s-trans* (1%)

Z,*s-cis* (83%) Z,*s-trans* (17%)

3. Results and Discussion

3.1. Theoretical Study. Table 1 contains the calculated total energies and electronic transitions for the optimized geometries of the Z isomers investigated in both s-trans and s-cis conformations. These results show that the bathochromic s-cis conformer is often (but not always) the most stable species, the energy gap between the two ground-state conformers being larger for some compounds (conformational equilibrium in the ground state S_0 largely shifted toward the s-cis species) while it is rather small for other positional isomers (comparable conformer abundance in S_0).

It has to be noted that the relative abundances of the two conformers of the Z isomers may be rather different than those of the corresponding E isomers, considering their larger deviations from planarity. The typical example of 1-StN is shown in Chart 2 where the abundances obtained from the calculations are reported. Contrary to the E isomers, whose lowest excited state S_1 has a B_u character, the Z isomers were found to have a S_1 state of forbidden nature ($f \leq 0.03$).

The parameters calculated for the two conformers are rather similar in each compound, but some small differences can be discerned: (i) the s-cis species is the most stable one when the styryl substituent occupies some specific positions of naphthalene ($n = 1$) and phenanthrene ($n = 1$, 4, and 9), where its abundance exceeds 80% (for $n = 4$, the enthalpy difference is so high that practically only the presence of the s-cis conformer can be expected), whereas comparable abundances were calculated when $n = 2$ and 3; (ii) the allowed (or partially allowed) $S_0 \rightarrow S_2$ transition of the s-cis species is always bathochromically shifted compared with that of the s-trans species; (iii) the related compounds with a benzo-annelated ring (3-StC and 3-StBP) behave as the corresponding naphthyl and phenanthryl derivatives bearing the styryl substituent in the analogous position (position 3 in the case of 3-StC and 3-StP, position 2 in the case of 3-StBP and 2-StP), but the prevalence of the most stable conformer tends to increase in favor of s-trans when $n = 2$.

3.2. Spectral Properties and Photoreactivity. As mentioned in section 2, at least four components (E, Z, DHP, and P) can be found in the solutions after irradiation of the Z isomers. Figure 1 shows, as an example, the spectra of the four species observed in the case of 3-styrylbenzo[*c*]phenanthrene (as to the possible formation of a second cyclized X photoproduct, see section 3.2.3).

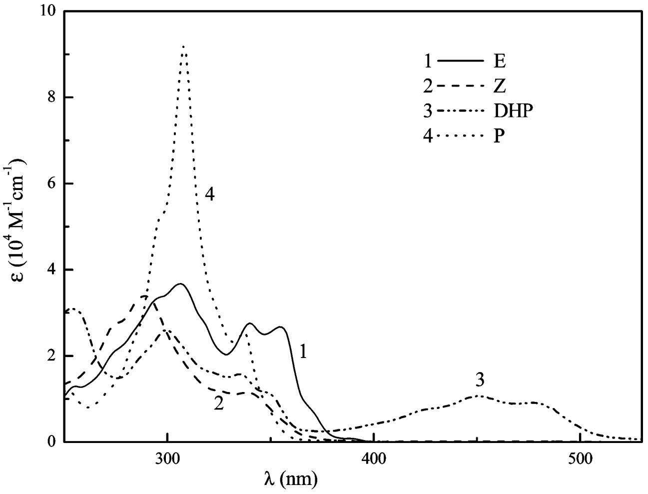


Figure 1. Absorption spectra in the eluent solvent (95/5, v/v, acetonitrile/water) of the four components (E, Z, DHP, and P) of the mixture obtained after UV irradiation of Z-3-styrylbenzo[c]phenanthrene in MCH/3MP.

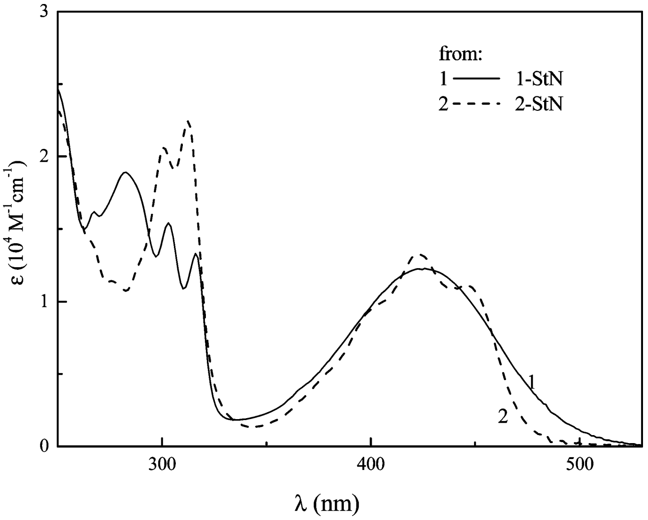


Figure 2. Absorption spectra of the DHP photoproducts of the Z isomers of n-StNs in 90/10 (v/v) acetonitrile/water.

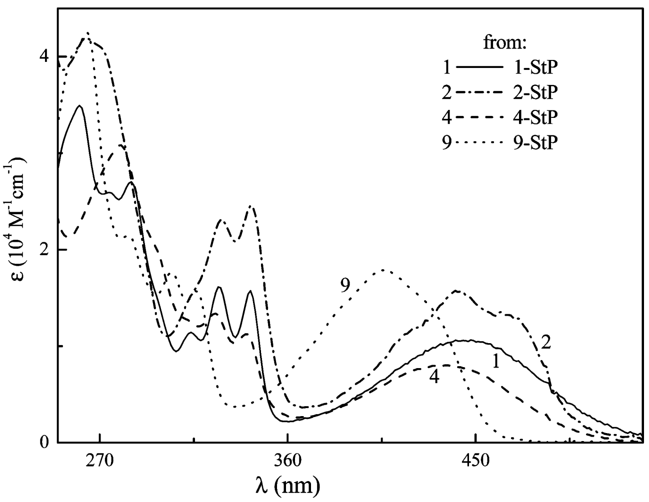


Figure 3. Absorption spectra of the DHP photoproducts of the Z isomers of n-StPs in 95/5 (v/v) acetonitrile/water.

The fact that all the four components absorb in the same UV region can strongly complicate the spectrophotometric measurements. In the present work, the separation of the chromatographic peaks by HPLC (equipped with a UV−vis diode array detector) allowed the spectral shape of each compound to be obtained. The presence of isosbestic points between the absorption spectra of DHP and P (the molar absorption coefficients of the P-type aromatic compounds were taken from the literature[41,42] and directly checked for a few compounds available in our laboratory) allowed the quantitative and complete (including the UV region) spectra of the metastable DHP photoproducts to be obtained (Figures 2 and 3). This procedure is correct for compounds where DHP gives the oxidation P product almost exclusively but is questionable for compounds where DHP gives not only P but also the back ring-opening to Z, as found for those bearing the styryl group at positions 2 and 3 of the aryl group (see below). However, the reasonable agreement of the spectral behavior with the theoretical calculations points to the reliability of the reported results. Comparison with literature data (shown in parentheses in Tables 2 and 3) is possible in a few cases, limited to the visible band. We refer to two styrylnaphthalenes (ref 9, including qualitative UV−vis spectra and absorption coefficients for the visible band only) and three styrylphenanthrenes (ref 18, only qualitative spectra, and ref 13 including qualitative UV−vis spectra and absorption coefficients for the visible band only). The comparison with the qualitative UV spectra found in the literature, obtained by extrapolation after a delicate procedure using iodine to achieve complete photocyclodehydrogenation,[9,13,18] is possible for the position of the band maxima (in this case the comparison is very good, differences being less than 1%, despite the different solvents). As to the absorption intensities, our coefficients of the visible band are always higher (from 8%, for the case of 1-StP, up to 35%, for the case of 1-StN) than those reported in refs 9 and 13, probably because of incomplete transformation of the photoproducts to stable products in their extrapolation procedure.

The absorption band in the visible region of DHPs formed by the less sterically hindered compounds, styryl-substituted at position 2 of the naphthyl and phenanthryl groups (and, even if at a lesser extent, at position 9 of the phenanthryl group), shows vibronic structure which is absent in the less planar compounds substituted at positions 1 and 4, in agreement with what was reported for styrylnaphthalenes[7] (see also section 3.2.5).

Tables 2−4 collect the isomerization/cyclization quantum yields of the excited Z isomers (solutions deaerated by bubbling nitrogen) and the spectral and kinetic properties of the DHP intermediates of the compounds investigated. Most of the revisited parameters in these tables are in agreement with the values previously reported and others differ substantially, probably because of the different solvent, deaeration efficiency, and measurement method (see section 3.2.4).

For stilbene,[1,12] it is generally assumed that ring-opening to Z is the only dark reaction of DHP in the rigorous absence of oxidants (in the literature such assumption is often considered to hold for stilbene-like molecules in general). In most of our solutions, deaerated by bubbling nitrogen, we found that the thermal decay of DHP is always due to competition between back ring-opening to Z and dehydrogenation to P (the stable oxidized compound), the formation of the latter being sometimes the fastest DHP decay. This aspect will be further discussed in section 3.2.4.

The photobehavior of the 1,2-diarylethenes investigated is described in detail below, separately for each group of compounds.

3.2.1. Styrylnaphthalenes. Figure 2 shows the spectra of the DHPs formed from the two isomeric Z-n-StNs. Chrysene and

TABLE 2: Photoisomerization and Photocyclization Quantum Yields of Z-*n*-StNs in MCH/3MP at Room Temperature (λ_{exc}= 300 nm)[c]

Z isomer	$\phi_{Z\to E}$	λ_{DHP}^{max}	ε_{DHP}^{max}	$t_{1/2}$	P-type product	$\phi_{Z\to P}$
1-StN	0.11 (0.04)[a]	425 (425)[a]	1.23 (0.80)[a]	85 (214)[b]	chrysene	0.15 (0.30)[a]
		316 (319)[a]	1.33			
		303 (306)[a]	1.54			
		282 (285)[a]	1.89			
2-StN	0.30 (0.30)[a]	422 (425)[a]	1.33 (1.10)[a]	61 (60)[b]	benzo[*c*]phenanthrene	0.02 (0.12)[a]
		312 (313)[a]				
		301 (302)[a]				

[a] Values in parentheses (in 2/1 MCH/2MP at 0 °C) are from ref 9 (the quantum yields are extrapolated from plots there reported). [b] Values in parentheses (in *n*-hexane at 25 °C) are from ref 7. [c] Spectral properties (λ_{DHP}^{max}/nm and $\varepsilon_{DHP}^{max}/10^4$ M^{-1} cm^{-1}) and thermal stability ($t_{1/2}$/min) of the corresponding DHPs are also reported.

TABLE 3: Photoisomerization and Photocyclization Quantum Yields (λ_{exc} = 300 nm) of Z-*n*-StPs and Thermal Stability ($t_{1/2}$/min) of the Corresponding DHPs in MCH/3MP at Room Temperature[c]

Z isomer	$\phi_{Z\to E}$	λ_{DHP}^{max}	ε_{DHP}^{max}	$t_{1/2}$	P-type product	$\phi_{Z\to P}$
1-StP	0.11	445 (445)[a]	1.06 (0.99)[b]	49 (320)[a] (35)[b]	picene	0.22 (0.05)[b]
		342 (343)[a]	1.57			
		327 (328)[a]	1.61			
		313 (314)[a]	1.14			
		285	2.70			
2-StP	0.12	440 (443)[a]	1.57 (1.20)[b]	5 (30)[a] (7)[b]	benzo[c]chrysene	0.004 (0.004)[b]
		342 (345)[a]	2.46			
		328 (330)[a]	2.31			
		264 (273)[a]	4.19			
3-StP	0.23			(0.1)[a]	dibenzo[c,g]phenanthrene	0.002 (0.005)[b]
4-StP	0.16	435	0.80	44	benzo[c]chrysene	0.15
		340	1.12			
		325	1.34			
		280	3.08			
9-StP	0.06	406	1.79 (1.22)[b]	27 (10)[b]	benzo[g]chrysene	0.20 (0.1)[b]
		316	1.57			
		304	1.77			
		284	2.15			

[a] In MCH, from ref 18. [b] In *n*-hexane, from ref 13. [c] Spectral properties (λ_{DHP}^{max}/nm and $\varepsilon_{DHP}^{max}/10^4$ M^{-1} cm^{-1}) in acetonitrile/water eluent are also reported and compared with literature values (in parentheses).

TABLE 4: Photoisomerization and Photocyclization Quantum Yields of the Z Isomer of 3-StC and 3-StBP in MCH/3MP at Room Temperature (λ_{exc}= 300 nm)[a]

Z isomer	$\phi_{Z\to E}$	λ_{DHP}^{max}	ε_{DHP}^{max}	$t_{1/2}$	P-type compound	$\phi_{Z\to P}$	$\phi_{Z\to X}$
3-StC	0.12				naphtho[2,1-*c*]chrysene	0.013	0.07
3-StBP	0.04	450	1.07	19	dibenzo[*c*,l]chrysene	0.06	0.02
		347^{sh}	1.16				
		335	1.57				
		299	2.60				

[a] Spectral properties (λ_{DHP}^{max}/nm and $\varepsilon_{DHP}^{max}/10^4$ M^{-1} cm^{-1}) and thermal stability ($t_{1/2}$/min) of the corresponding DHPs are also reported.

benzo[*c*]phenanthrene were obtained as oxidized aromatic products starting from 1-StN and 2-StN, respectively, in agreement with literature reports.[7,9] Data in Table 2 show that isomerization competes substantially with cyclization in 1-StN but becomes largely prevalent in 2-StN, as for stilbene.[37,38] Similar information can be also inferred by extrapolation from the plots of photoreaction quantum yields as a function of temperature reported by Fischer and co-workers.[9]

Only one DHP-like photoproduct (derived from the s-cis conformer) was detected in our experimental conditions for these two Z isomers, in agreement with the theoretical calculations that showed a net separation between the energy of the two conformers in the case of *Z*-1-StN (equilibrium largely shifted toward the most stable s-cis species) and with the rule cited above, which prevents cyclization of the s-trans conformer of *Z*-2-StN, that should lead to benzo[*a*]anthracene.[4−7,12,39] It has to be noted that a small formation (1%) of this side product was found by Mallory in the presence of high iodine concentration to favor the oxidative trapping with respect to the ring-opening of the corresponding DHP intermediate.[43]

The half-lives of DHPs in the dark, in reasonable agreement with those reported by Timmons and co-workers,[7] are similar to the value reported for stilbene (96 min)[3] and rather shorter than those of the widely investigated 1,2-dinaphthylethenes,[9,18] probably because of the higher energy content of the DHPs formed from our compounds (see section 3.2.5). Irradiation of 1-StN in aerated solution led to the same cyclization and isomerization quantum yields as those measured in deaerated solutions (by bubbling nitrogen, Table 2) whereas its oxidation to P was accelerated with increased oxygen concentration ($t_{1/2}$ = 27 min in aerated MCH/3MP).

3.2.2. Styrylphenanthrenes. Figure 3 shows the spectra of the DHPs formed by photocyclization of the isomeric *n*-StPs (*n* = 1, 2, 4, and 9). For *n* = 3, DHP was undetectable by static methods because of its too short half-life at room temperature (a value of 6 s has been estimated by flash photolysis measurements[18]).

Picene was the final aromatic compound formed from the s-cis conformer of *Z*-1-StP, in agreement with previous results.[13,18] Substantial yields of the two competitive photoreactions were found, with a prevalence of cyclization. The half-life of 1-StP (49 min) in deaerated (by bubbling nitrogen) solution, was quite different from those previously reported, i.e., much shorter than that reported in ref 18 (320 min) but slightly higher than that reported in ref 13 (35 min). This is a typical example of the extreme sensitivity of the system to the presence of oxidants (see section 3.2.4).

The final oxidized photoproducts of 2-StP and 3-StP (again in s-cis conformation) were benzo[*c*]chrysene and dibenzo[*c*,*g*-]phenanthrene, respectively, as previously reported.[13,18] For both compounds, the values of $\phi_{Z\to P}$ and $t_{1/2}$ are markedly smaller (particularly for $n = 3$) than those found for the other positional isomers. Interestingly, formation of a second cyclization product (P′) was detected under prolonged irradiation of these two compounds using a higher dose of polychromatic light. In both cases, these side photoproducts, separated by HPLC, were identified, on the basis of the known absorption spectra, as the corresponding anthracenic derivatives (dibenzo[*a*,*j*]anthracene and dibenzo[*a*,*h*]anthracene for $n = 2$ and 3, respectively), formed from the s-trans conformer of the corresponding Z isomers. The result for 2-StP is in agreement with a previous report where the formation of 1% of the anthracene derivative was detected.[44] It has also to be noted that a previous work on *n*-StPs with $n = 3$ tentatively assigned traces of a side photoproduct to 6a,14c-dihydropentahelicene (or 2a,10c-dihydrodibenzo[*c*,*g*]phenanthrene) formed from DHP by a hydrogen shift.[18]

The compound with $n = 4$, which practically exists as 100% *s-cis* conformation, photocyclizes to benzo[*c*]chrysene[45,46] with a substantial yield, approximately the same as that of photoisomerization. Its DHP intermediate has a relatively long $t_{1/2}$, similar to that of DHP formed from 1-StP.

The compound with $n = 9$ led to benzo[*g*]chrysene as final oxidized P product.[13,47] As in the case of 1-StP, a prevalent photocyclization yield was measured for this isomer while a slightly shorter $t_{1/2}$ was found for its DHP intermediate. By visible irradiation, the latter was converted to Z, similarly to the other compounds. A small but non-negligible amount of a second X photoproduct ($\phi_{Z\to X} = 0.04$) accompanied the formation of DHP.

The presence of this side product, which does not absorb in the visible, was detected by HPLC. It was relatively stable in the dark but converted to P by UV irradiation. The X product was also observed by gas chromatography−mass spectrometry and found to have the same mass as DHP. Since the colored band is no longer present for X, which absorbs at $\lambda_{max} = 269$ nm in 95/5 acetonitrile/water, one deduces that the π-electron system of conjugated double bonds, typical of DHP, is not present for this compound, probably due to intramolecular hydrogen shift from the primary 4,4′-DHP to 9,10-dihydrobenzo[*g*]chrysene (9,10-DHBC) or to an isomeric species with a hydrogen shift to other positions. The computed spectra of various positional isomers of DHP and their comparison with the experimental spectrum of X would indicate the compound where only one hydrogen atom shifts to position 8b (8b,14b-dihydrobenzo[*g*]chrysene, 8b,14b-DHBC, see Figure 4) as the most probable species. A sketch of the overall process is shown in Chart 3.

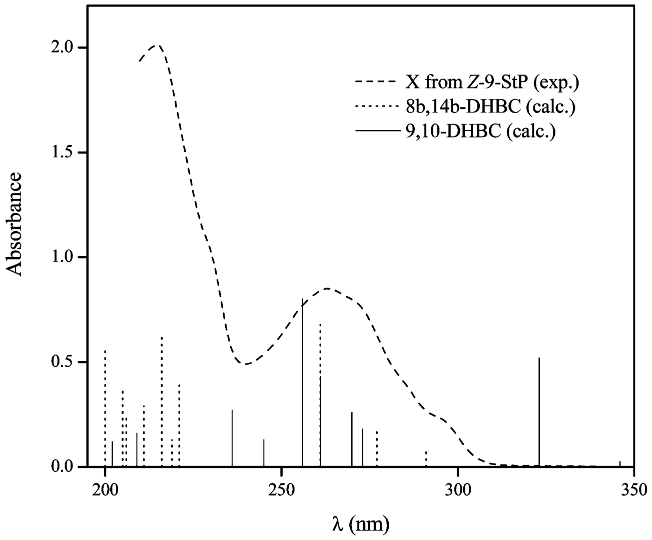


Figure 4. Experimental absorption spectrum of X formed from 9-StP (dashed line) compared with the computed spectra of 9,10-DHBC (full line) and 8b,14b-DHBC (dotted line).

3.2.3. Styrylchrysene and Styrylbenzophenanthrene. As shown in Table 4, UV irradiation of *Z*-3-StC and *Z*-3-StBP led to the final P products expected from the s-cis rotamers of both compounds, namely, naphtho[2,1-*c*]chrysene and dibenzo[*c*,l]chrysene, respectively. These two compounds display a different behavior since isomerization prevails for 3-StC, as for 3-StP, whereas cyclization slightly prevails in 3-StBP. The too short half-life of the DHP intermediate of *Z*-3-StC prevented us from its detection by HPLC, as in the case of 3-StP, namely, the compound bearing the styryl group in the same position of the polycyclic group.

For both compounds of Table 4, a second final compound, X, which did not absorb in the visible, was detected together with P (with a higher and smaller quantum yield for 3-StC and 3-StBP, respectively), similarly to that found for 9-StP. Its presence was observed in the HPLC measurements, where it was found to be relatively stable in the dark but easily converted to P by UV irradiation. However, in the case of these two compounds, X was no longer detected by chromatography−mass spectrometry, probably because of the thermal loss of the hydrogen atoms at high temperature, as indicated by the fact that the peak area of P corresponded to the sum of the peak areas measured for P and X by HPLC. This behavior showed several analogies with that of 9-StP (see above) and of the related molecule 2-StBP (where a common investigation of two groups[48−50] led to identification of X as *trans*-6a,16d-dihydrohexahelicene, implying the shift of only one hydrogen atom). We think it reasonable to identify X as an isomer of DHP produced by hydrogen shift also in this case.

3.2.4. Structure and Oxygen Effects on the Photoreaction. Perusal of Tables 2 and 3 indicates that the compounds styryl-substituted in positions 1, 4, and 9 are characterized by rather higher $\phi_{Z\to P}$ and longer $t_{1/2}$ values compared with the analogous compounds substituted in positions 2 and 3. The photocyclization efficiency depends markedly on the structure and can be drastically affected by the deaeration method, as observed above, since the ring-opening/dehydrogenation competition of DHPs can be substantially modified by the concentration of oxygen present in the solutions.

In some cases, the thermal stability of DHP ($t_{1/2}$ values of Tables 2−4) was found to be rather different from those reported in the literature (the typical example of 1-StP is described in

CHART 3: Sketch of the Photochemistry of 9-StP and Probable Structure of the X Product

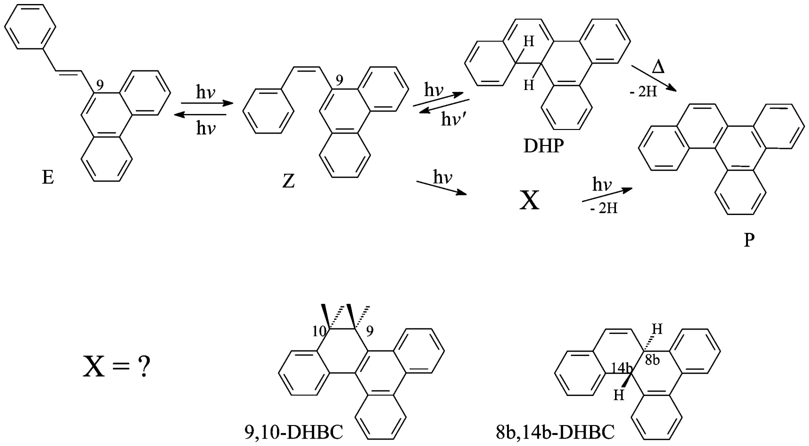


TABLE 5: Effect of Oxygen on the Photoreaction Quantum Yields of the Z Isomer of 1-StP, 2-StP, and 3-StBP in MCH/3MP at Room Temperature (λ_{exc} = 300 nm)[a]

	by bubbling O_2				by bubbling Ar			
Z isomer	$\phi_{Z\to E}$	$\phi_{Z\to P}$	$\phi_{Z\to X}$	$t_{1/2}$	$\phi_{Z\to E}$	$\phi_{Z\to P}$	$\phi_{Z\to X}$	$t_{1/2}$
1-StP	0.13	0.23		14.6	0.13	0.22		220
2-StP	0.14	0.03		4.9	0.14	0.005		12.6
3-StBP	0.09	0.11	0.01	5.0	0.031	0.05	0.03	19

[a] The thermal stability ($t_{1/2}$/min) of the corresponding DHPs is also reported.

section 3.2.2). Such unusual discrepancies, observed also for other compounds, are certainly caused by the oxidation mechanism leading to the fully aromatic compound.

To get a better insight in this behavior, we repeated the measurements of the photoreactivity of three typical compounds having substantial (1-StP) or very small (2-StP) or intermediate (3-StBP) cyclization yield, by bubbling oxygen and argon (Table 5). The half-lives of the corresponding DHP photoproducts are also reported.

The photoreaction yields of 1-StP, practically the same as those measured by bubbling nitrogen (Table 3), were found to not depend on oxygen thus indicating that the DHP → Z ring-opening does not compete with the P production. The half-life of DHP is drastically reduced in oxygen-saturated solution as expected from the fact that oxidation is the dominant reaction. In such a situation $\phi_{Z\to P}$ does practically correspond to the yield of the Z → DHP process. On the other hand, for 2-StP, only the yield of Z → E isomerization remained unchanged in oxygen-equilibrated and deaerated solutions whereas the yield of P formation increased by almost 1 order of magnitude in oxygen-saturated solutions. This indicates that the DHP → P oxidation can compete with the prevailing back reaction to Z. The case of 3-StBP is less straightforward and complicated by the formation of X which decreases by bubbling oxygen. Even here the oxidation yield increases (but to a smaller extent) in oxygen-saturated solutions, pointing to a competition of the two thermal processes. However, also the formation of the trans isomer increases in the presence of oxygen. An explanation could be offered by the fact that the condensed-ring group of *Z*-3-StBP could induce intersystem crossing to the isomerizable T_1 state, as found for the E isomer of 3-StBP;[51] therefore, the presence of oxygen can increase the ISC yield thus favoring photoisomerization in the triplet manifold. This oxygen effect, reported by different groups for analogous compounds,[52−54] implies that the S_1 lifetime is sufficiently long to be quenched by oxygen.

The contribution of dehydrogenation to the disappearance of DHP from 2-StP and 3-StBP leads also in this case to a reduction in half-lives (by ~3 times) by bubbling oxygen into the solution.

The unavoidable presence of oxygen traces left in the cell after deaeration[1,7,18] is certainly one of the reasons of the discrepancies among parameters measured by different laboratories, as demonstrated by the lengthening of the half-life on improving the deaeration method (bubbling argon instead of nitrogen or using more reliable degassing methods by freeze−pump−thaw cycles under vacuum). However, also other dehydrogenation channels, implying unknown adventitious catalysts, could be operative, as previously hypothesized.[18]

Examples of anaerobic trapping of DHP to give P were described to occur, for some particular structures of Z, through exothermic dehydrogenation or hydrogen shifts.[43] It is interesting to recall in this connection that irradiation of 2- and 4-styrylpyridine in solutions that had been degassed by multiple freeze−pump−thaw cycles was found to isomerize without detectable formation of cyclization product, whereas the same experiment on 3-styrylpyridine led to anaerobic photocyclization with regioselective formation of 2-azaphenanthrene.[55] This behavior was explained by a dark 1,7-hydrogen shift, i.e., by conversion of the primary DHP to a relatively stable 1,4-dihydropyridine intermediate, which then loses hydrogen to give the final azaphenanthrene.

As to the formation of the side X products, in contrast to literature reports about the hydrogen shift in DHPs, where the X formation is considered a sequential reaction from the primary DHP,[48−50] our results would indicate a parallel formation of X and DHP. It has to be recalled in this respect that photocyclization can be seen to occur by adiabatic formation of an excited intermediate, DHP′*, which would decay to a vibronically hot ground state DHP′ (a skewed geometry, was proposed for the latter),[1,8] from which partitioning to the ground state Z and DHP takes place.[8,37,38,56−58] Distorted geometries of such type can affect the weight of different allowed cyclization paths. On the basis of a similar reasoning, one could envisage that the parallel formation of two isomeric DHP-type photoproducts in S_0 proceeds from the DHP′ intermediate along the reaction coordinate from Z* to the ground state cyclized product(s). More recently, theoreticians have discussed the intimate mechanism by emphasizing the role of conical intersections along such a pathway,[59−61] but some open questions about the real pathway remain to be answered.

3.2.5. Correlations between Energy and Reactivity Parameters. A qualitative explanation of the ring-opening/dehydrogenation competition can be obtained by calculations of the

TABLE 6: Computed (PM3) Enthalpy Differences (kcal mol^{-1}) between the Rotamers of the Z Isomers and Their DHP Cyclization Photoproducts

Z isomer (rotamer)	ΔH_f^0(Z)	ΔH_f^0(DHP)	$\Delta E_{Z\text{-}DHP}$
1-StN(s-cis)	87.92	96.08	8.16
2-StN(s-cis)	86.79	99.14	12.35
2-StN(s-trans)	86.92	112.77	25.85
1-StP(s-cis)	104.10	113.70	9.60
2-StP(s-cis)	102.72	117.12	14.40
2-StP(s-trans)	102.97	123.03	20.06
3-StP(s-cis)	102.59	122.30	19.71
3-StP(s-trans)	102.86	123.03	20.17
4-StP(s-cis)	108.40	117.91	9.51
9-StP(s-cis)	104.04	110.16	6.12
3-StC(s-cis)	119.95	136.71	16.86
3-StC(s-trans)	120.54	140.36	19.88
3-StBP(s-cis)	126.02	139.12	13.10
3-StBP(s-trans)	126.14	145.94	19.80

relative potential energy of the species involved. In fact, on the basis of a comparative study of the DHPs derived from 1,2-dinaphthylethenes and the isoskeletal ones derived from *n*-StPs with $n = 1$, 2, and 3,[18] it was proposed that the half-lives of the DHP intermediate depend on the difference between the energy levels of Z and DHP ($\Delta E_{Z\text{-}DHP}$).

It has to be noted in this respect that an interesting series of papers on sterically hindered DHPs, disubstituted at the 4- and 5-positions[62,63] or benzoannelated at the [*c*] and [*g*] bonds,[64,65] reported that two interconvertible DHP intermediates, a bathochromic one (antiperiplanar, ap) and a hypsochromic one (anticlinal, ac), can be observed, particularly below room temperature. The primarily photoproduced ap conformation (typical of unhindered species) undergoes twisting about the 4a−4b bond, giving the less planar ac conformation which is generally the most stable species characterized by a structured visible band. We did not observe such a phenomenon in our styryl derivatives studied at room temperature by stationary spectrophotometry. However, a theoretical study of our compounds, by using the Hyperchem Conformational Search program for the search of minimum energy conformations, showed that two potential energy minima, separated by non-negligible energy differences, are indeed obtained for four moderately hindered compounds, namely, 2-StN, 2-StP, 9-StP, and 3-StBP. This is in agreement with the spectral behavior of DHPs of Figures 1−3, showing that these compounds present a structured visible band (ac structure) whereas the **1** and **4** derivatives have the broad band typical of the ap structure of unhindered compounds.[65] In any case, the computed data (see Table 6 below) always refer to the most stable conformations to be compared with the experimental results of Tables 2−4.

It is interesting to note that the discovery that $t_{1/2}$ of DHPs can be prolonged by replacing the phenyl rings of stilbene by thiophene rings[66] and the related observation that the ring-opening in S_0 has to overcome energy barriers which are small when $\Delta E_{Z\text{-}DHP}$ is large and vice versa, led researchers to synthesize diarylethenes characterized by very small $\Delta E_{Z\text{-}DHP}$ (such as dithienylethene analogues) in order to have DHP analogues with $t_{1/2}$ of months or years, the so-called "bistable" photochromic compounds, very interesting for their potential use as memories and switches in optoelectronics.[67−69] The thermal stability of the photoproduced DHP depends then on the $\Delta E_{Z\text{-}DHP}$ value in S_0, which correlates with the aromatic stabilization energy of the side aryl groups, being large when the resonance energy is large.

On the basis of these observations, calculations of the potential energies of the relatively large series of molecules under study, to be possibly correlated with the aromatic stabilization which characterizes the opening process, can be very useful for discussing the experimental parameters ($\phi_{Z\rightarrow P}$ and $t_{1/2}$) collected in Tables 2−4 and to verify if some relationships exist with the energetic parameters. The $\Delta E_{Z\text{-}DHP}$ values calculated for our compounds are shown in Table 6.

Comparison of the $\Delta E_{Z\text{-}DHP}$ values with the experimental quantum yields in Tables 2 and 3 indicates that compounds displaying substantial $\phi_{Z\rightarrow P}$ values (>10%) have smaller $\Delta E_{Z\text{-}DHP}$ (6−10 kcal mol^{-1}) whereas those with $\phi_{Z\rightarrow P} \leq 2\%$ have higher $\Delta E_{Z\text{-}DHP}$ values (12−19 kcal mol^{-1}). A correlation, even if less clear, was found also with the half-lives, which tend to become shorter for compounds with larger $\Delta E_{Z\text{-}DHP}$ values. Indeed, in the case of 3-StP and 3-StC, the too short half-lives at room temperature made the DHP intermediates practically undetectable. These results are consistent with the Hammond−Leffler postulate.[70,71]

For the 2- and 3-substituted compounds, where both possible conformers have important abundance, the energy calculations were carried out for both conformations. As expected, higher $\Delta E_{Z\text{-}DHP}$ values ($\geq$20 kcal mol^{-1}) were obtained for the s-trans species, which practically do not photocyclize.

4. Conclusions

The use of combined HPLC and UV spectrometry techniques allowed the separate spectra of the four components of the mixture formed under irradiation of each Z isomer to be measured. A general view of the reactive relaxation processes was then obtained for the series of styryl-substituted naphthalenes and phenanthrenes and their chrysene and benzophenanthrene analogues.

For all compounds investigated, the sum of the parallel isomerization/cyclization quantum yields, considering only a diabatic pathway (with $\alpha = 0.5$) for the Z → E process, remains substantially below 100% pointing to the presence of significant radiationless relaxations. An important role of the thermal/photochemical back DHP → Z process was found for compounds styryl-substituted at positions 2 and 3; for the other compounds with $n = 1$, 4, and 9, having a substantial yield of P formation, the role of the back ring-opening is almost negligible also in anaerobic conditions.

The structure effects on the photocyclization quantum yields was reasonably explained by potential energy calculations of the species involved. The changes in the resonance energy accompanying the reversible Z-DHP process are an important factor for the thermal stability of DHP since they reflect the energy barrier to ring-opening of DHP and are then related to the more or less efficient competition with the oxidation to P. The rough correlations verified between the yields of P formation and the DHP half-lives, on one hand, and the enthalpy difference between Z and DHP in the ground state, on the other, proved to be useful to describe the competition between the two main processes which characterize the disappearance of the DHP intermediate.

As to the role of adiabatic Z → E photoisomerization, we can anticipate that preliminary information from the fluorescence of the E isomers, observed since the beginning of irradiation of most of the Z isomers here investigated, proved that the occurrence of adiabatic photoisomerization mechanism (production of E* under excitation of Z) in competition with the usual diabatic mechanism, is a general phenomenon for the series of styrylnaphthalenes and -phenanthrenes. A quantitative study of the contribution of the adiabatic mechanism to the overall photoisomerization process is under study and will be reported in a next paper.

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