specified in Table VII where the shortest distances $I^-\cdots I^-$ and $I^-\cdots N^+$ are given.

Acknowledgment. We are grateful to the Belgian National Science Foundation for two fellowships (J.V. and J.P.D.) and for financial support. We acknowledge the assistance of Dr. S. Toppet for the interpretation of the NMR spectra and of Mrs. J. Feneau-Dupont for preparation of the manuscript.

Registry No. I, 13341-40-7; II, 1135-32-6; III, 73048-52-9; IV, 62141-47-3; V, 73048-53-0; VI, 73048-54-1; VII, 73048-55-2; VIII, 73048-56-3; IX, 24274-78-0; *t*-3,3′-DPyE, 14987-84-9; *t*-3,4′-PyiQE, 73048-57-4; *t*-2,4′-PaiQE, 73048-58-5; 4-isoquinolylcarboxaldehyde, 22960-16-3; (4-isoquinolinemethylene)triphenylphosphonium chloride hydrochloride, 73048-59-6; 4-(hydroxymethyl)isoquinoline, 73048-60-9; 4-(chloromethyl)isoquinoline hydrochloride, 73048-61-0; 2-pyrazinecarboxaldehyde, 5780-66-5; (3-pyridinemethylene)triphenylphosphonium chloride hydrochloride, 34377-83-8; 2-methylpyrazine, 109-08-0; 3-pyridylcarboxaldehyde, 500-22-1; *c*-3,2′-PyPaE, 73048-62-1; (2-pyrazinylmethylene)triphenylphosphonium chloride, 73048-63-2; *t*-4,4′-DPyE·CH_3I, 73048-64-3; *t*-4,4′-DPyE·$(CH_3)_2SO_4$, 73048-65-4; *t*-2,2′-DPyE·$(CH_3)_2SO_4$, 73048-66-5.

Supplementary Material Available: Full X-ray data for compounds I–IX, including final atomic parameters, temperature factors, and bond lengths and angles (9 pages). Ordering information is given on any current masthead page.

Azastilbenes. 2. Photodimerization

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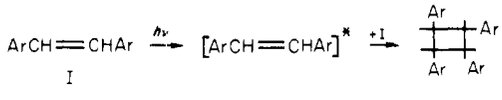
Received July 2, 1979

The photochemical behavior of several azastilbenes has been followed in concentrated solution and in the solid state. In acetonitrile and benzene isomerization and dimerization occur, the reactions being generally faster in acetonitrile. In methanol, however, photoreduction as well as photoaddition of the solvent intervene and are important processes. With irradiation in the solid state, dimerization occurs only for some azastilbenes and their quaternary salts, depending on the orientations of the molecules within the crystal lattice and the distances between adjacent double bonds (3.5–4.2 Å). X-ray analysis has shown that *trans*-1,2-di(2-pyrazinyl)ethylene crystallizes in two distinct modifications of which only one has a crystal stacking suitable for topochemical dimer formation. The dimers were characterized by ^1H and ^{13}C NMR, IR, and mass spectroscopy. The crystalline and molecular structures of five of them were determined by X-ray diffraction, namely, cyclobutane dimers of 1,2-di(4-pyridyl)ethylene, 1,2-di(2-pyridyl)ethylene, 1,2-di(2-pyrazinyl)ethylene (all three *r-ctt* dimers), and 1-(3-pyridyl)-2-(2-pyrazinyl)ethylene (*r-ctt* head-to-head and head-to-tail dimers).

The photodimerization of stilbenes and azastilbenes is a concerted $[{}_\pi 2_s + {}_\pi 2_s]$ cycloaddition allowed by the principle of orbital symmetry conservation.[1] It can be represented by



Such dimerization can be carried out in relatively concentrated solutions, in the solid state, in monolayers, and in polymer matrices. Different dimers or dimer ratios can be obtained, depending on the reaction conditions. As such, this reaction can be used for the synthesis of difficultly accessible 1,2,3,4-tetraarylcyclobutanes, for the synthesis of high molecular weight polymers,[2] for photocross-linking of polymers,[3,4] and eventually as a photochromic system.[5,6] The photodimerization of 1,2-diarylethylenes has already been described for several compounds: stilbene,[7–13] thienylarylethylenes,[11,14] stilbazoles and their quaternary salts,[5,15–24] (benzo)isoquinolylarylethylenes,[25–29] styrylpyrazine,[30] distyrylbenzene ana-

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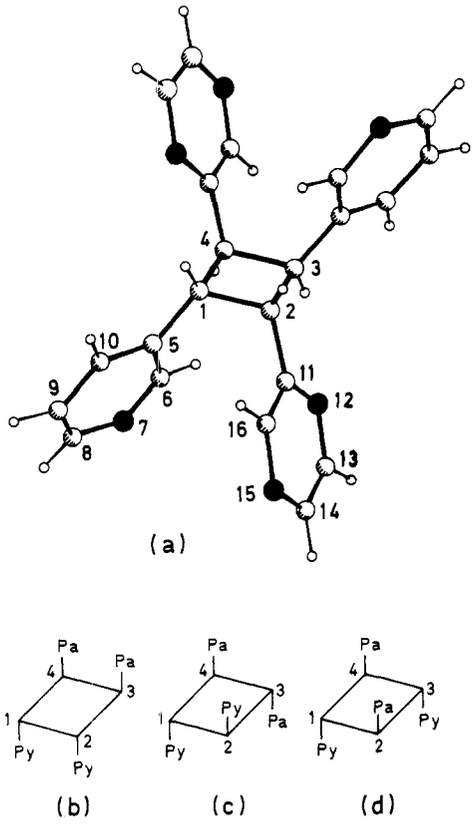

Figure 1. Numbering of atoms, nomenclature, and abbreviations used for the azastilbene dimers.[32] (a) *r*-1,*t*-3-di(3-pyridyl)-*c*-2,*t*-4-di(2-pyrazinyl)cyclobutane [*r-ctt* htt dimer]; (b) *r*-1,*c*-2-di(3-pyridyl)-*t*-3,*t*-4-di(2-pyrazinyl)cyclobutane [*r-ctt* hth dimer]; (c) *r*-1,*t*-2-di(3-pyridyl)-*c*-3,*t*-4-di(2-pyrazinyl)cyclobutane [*r-tct* hth dimer]; (d) *r*-1,*c*-3-di(3-pyridyl)-*t*-2,*t*-4-di(2-pyrazinyl)cyclobutane [*r-tct* htt dimer].

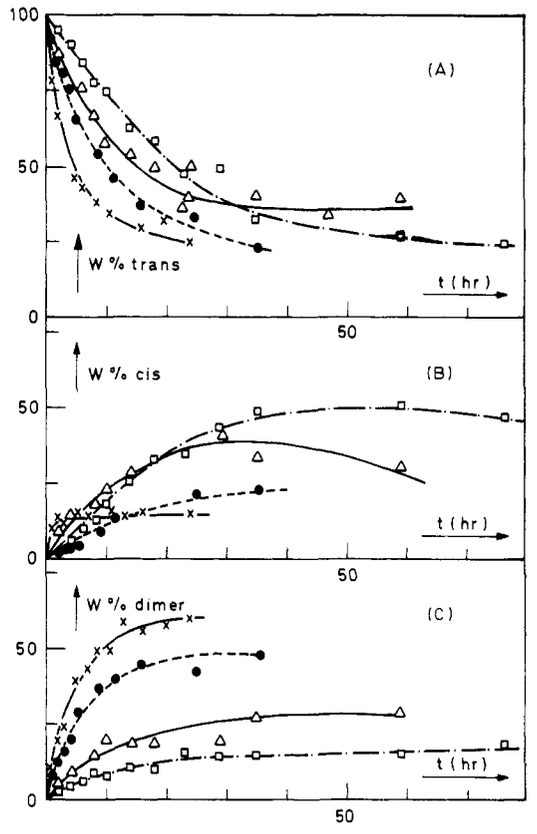

Figure 2. Disappearance of the trans isomer (A), formation of the cis isomer (B), and dimerization (C) as a function of the time of irradiation (350 nm, solvent acetonitrile). *t*-3,2′-PyPaE (0.55 M) (×); *t*-3,3′-DPyE (0.55 M) (●); *t*-2,2′-DPyE (0.55 M) (△); *t*-4,4′-DPyE (0.37 M) (□).

logues,[2,31] etc.

In the present paper, the structure of the dimers is designated according to IUPAC rules[32] as illustrated in Figure 1. For almost all compounds, dimerization occurs readily in concentrated solutions;[9] with the exception of 1,2-di(β-naphthyl)ethylene for which dimerization of cis isomers was observed,[33] the dimers result from the reaction of a trans molecule in the excited state with another trans molecule in the ground state. This process can lead to the formation of four different dimers (see Figure 1).

Reaction in the solid state is only possible when the monomer molecules are properly oriented within the crystal lattice and when the distances between the double bonds lie between 3.5 and 4.2 Å. When these requirements are met, the "topochemical" dimer will be formed upon irradiation.[34,35] In some cases a second, nontopochemical dimer is formed, probably at dislocations (surface defects) or regions where the crystal is already disturbed by dimer formation.[11,12,34] This case has been nicely illustrated by 9-cyanoanthracene which crystallizes in cis geometry but forms only trans dimer upon irradiation. Since the formation of cis dimer is energetically unfavorable, the excitation energy is transferred from one molecule to another until it becomes trapped at a crystal defect, where the molecular orientation may be appropriate for dimerization.[34] It should be noticed that even when the structure of the monomer crystal is suited for topochemical dimerization, it is still not certain whether the dimerization will occur according to a homogeneous (i.e., inside the bulk) or heterogeneous (i.e., at defects) mechanism. Thus, Hasegawa[2] and Jones[36] assume a homogeneous photopolymerization for 2,5-distyrylpyrazine, while Wegner et al.[37,38] suggest that the photopolymerization of this compound starts at macroscopic defaults (edges and cracks), the crystalline structure being progressively broken up as polymerization proceeds. According to Green et al.[11] some correlation should exist between the photodimerization behavior in the solid state and the reaction mechanism in solution: monomers dimerizable in the crystalline state yield in solution mainly *r-ctt* dimers; the other monomers, stable in the solid state, can form *r-tct* as well as *r-ctt* dimers in solution.

In the present paper we will consider the photodimerization of 1,2-dipyridylethylenes (DPyE) and their

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(32) IUPAC rules [*Pure Appl. Chem.*, **45**, 13 (1976)] stipulate that when alternative numberings of the ring are permissible, that numbering is chosen which gives a cis attachment at the first point of difference. When one substituent and one hydrogen atom are attached at each of more than two positions of a monocycle, the steric relations of the substituents are expressed by adding *r* (for reference substituent), followed by a hyphen, before the locant of the lowest numbered of these substituents and *c* or *t* (as appropriate), followed by a hyphen, before the locants of the other substituents to express their relation to the reference substituent.
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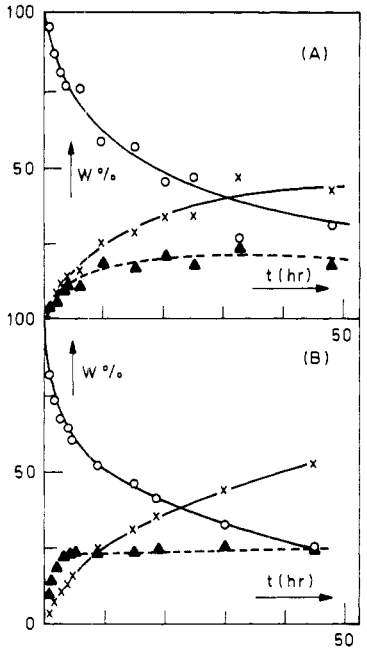

Figure 3. Disappearance of the trans isomer (○), formation of the cis isomer (▲), and dimerization (×) as a function of the time of irradiation (350 nm) for (A) *trans*-stilbene in benzene (0.56 M) and (B) *t*-2,2′-DPaE in chloroform (0.21 M).

quaternary salts, 1,2-di(2-pyrazinyl)ethylene (DPaE), and recently synthesized azastilbenes (see part I).

Photodimerization in Solution

Concentrated solutions of diarylethylenes were irradiated in a merry-go-round apparatus inside a Rayonet (350 nm). The composition of the solutions after irradiation was determined by ^{1}H NMR analysis. Table I gives a survey of the experiments and indicates the weight percent of each compound as a function of the time of irradiation. Additional data are given in Figures 2 and 3. It is obvious that the overall reaction proceeds almost similarly for all compounds. In methanol and acetonitrile, the overall rate is much higher than in benzene; in benzene and acetonitrile, isomerization and dimerization are the only reactions observed. However, in methanol side reactions (addition and reduction) occur and are important for 2,2′- and 4,4′-DPyE.[39-41] The *initial* rate of isomerization trans → cis is usually greater than the rate of dimerization. The overall rate of conversion of the trans isomer as well as the rate of dimerization are in the following decreasing order (Figures 2 and 3): 3,2′-PyPaE > 3,3′-DPyE > 2,2′-DPyE > 4,4′-DPyE.

3,3′-DPyE, however, has the slowest rate of isomerization ($t \rightarrow c$). Solubility difficulties made it impossible to carry out the experiments for *trans*-stilbene and *t*-2,2′-DPaE under identical conditions; comparison of curves 3A and 3B is therefore inappropriate though their shapes are similar. Quantum yields of dimerization and isomerization were determined in acetonitrile or chloroform solution (λ_{irrad} 300 nm, 23 °C). The results are reported in Table II.

As expected, all dimers have *r-ctt* or *r-tct* configurations (see Experimental Section). Dimerization therefore arises either from two cis or from two trans monomers. However, on irradiation of a mixture rich in cis isomer, dimerization

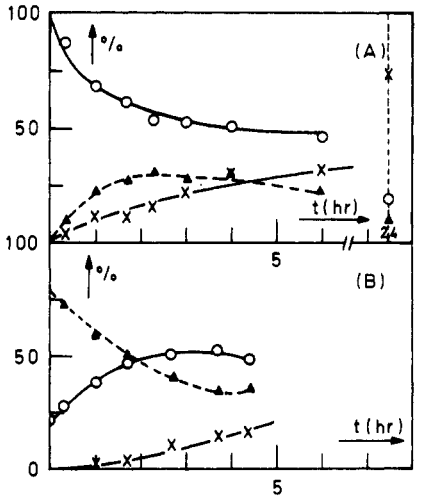

Figure 4. Variation of trans (○) and cis (△) isomers and formation of the *r-ctt* dimer (×) as a function of the time of irradiation starting from *t*-2,2′-DPaE (A) and cis-rich 2,2′-DPaE (B), both in chloroform (0.14 M).

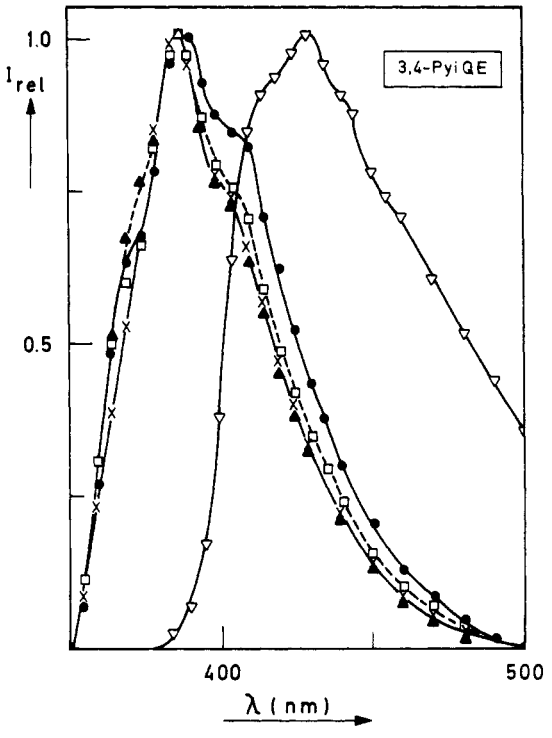

Figure 5. Fluorescence spectra (λ_{exc} = 332 nm) of *t*-3,4-PyiQE in the solid state (▽) and in acetonitrile: 6.8 10^{-2} mol/L (●), 6.8 10^{-3} mol/L (□), 6.8 10^{-4} mol/L (×), and 6.8 10^{-5} mol/L (▲).

only begins when approximately 50% of the trans isomer is formed, while irradiation of the pure trans isomer under similar conditions gives immediate dimerization (Figure 4).

It is therefore assumed that dimers are formed by interaction of an excited-state trans molecule with a trans isomer in the ground state (excimer) as shown already for *trans*-stilbene.[8,9,42] The dimerization should therefore result from a competition between isomerization (trans → cis) and cyclization: dimer ← trans ⇌ cis. As a consequence of the reversibility of the isomerization $t \rightleftharpoons c$, when pure trans isomer is irradiated, the cis-isomer concentration increases in the first stage of the reaction. With increasing dimer formation, however, the isomerization equilibrium is shifted to the trans isomer, and a progressive

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Table I. Photodimerization of Stilbene and Azastilbenes in Solution

monomer	concn, mol/L	solvent	irradiation time, h	reaction mixture, wt % trans	cis	r-ctt dimer	r-tct dimer	phenan-throline	addn prod.
trans-stilbene	0.28	CH_3CN	4.1	77	14	7	2		
			8.0	62	20	13	5		
			24.0	37	27	20	8	8	
	0.56	$CHCl_3$	4.1	79	12	6	3		
			8	68	20	8	4		
			24	38	33	13	9	7	
	0.78	$CDCl_3$	16	56	18	16	10		
			39	38	23	26	13		
			61.7	38	15	27	14	6	
			84.7	40	10	29	15	6	
t-2,2'-DPyE	0.56	CH_3OH	7.9	86	6	6	2		
			22	29		35	12		24
			47.2			45	14		41
	0.27	C_6H_6	7.9	90	9	(0.6)	(0.4)		
			22.0	51	37	9	3		
			47.2	44	39	12	5		
t-3,3'-DPyE	0.55	CH_3OH	6.2	59	5	31	5		
			23	34	7	44	6	9	
	0.55	C_6H_6	6.2	79	6	12	3		
			23	62	12	16	7	3	
t-4,4'-DPyE	0.55	CH_3OH	22	39	21	23	6		11
			47.2	18	20	25	7		30
	0.28	C_6H_6	22.0	72	23	4	1		
			47.2	47	37	6	3		7
t-4,4'-DPyE·$(CH_3O)_2SO_2$	0.32	Me_2SO-d_6	2.2	86		14			
			16.2	62		38			
			23.2	58		42			
			38.8	51		49			
			49.8	55		45			
3,2'-PyPaE	0.55	CH_3OH	4.0	59	11	30			
			8.2	31	15	54			
			17.4	35	13	52			
	0.55	C_6H_6	4	71	11	18			
			8.2	56	19	25			
			17.4	50	17	33			

Table II. Quantum Yields of Dimerization and t → c Isomerization of Azastilbenes in Solution[a]

compd	solvent	concn, 10^2 mol/L	$\Phi_{t\rightarrow c}$	$\Phi_{t\rightarrow r\text{-}ctt}$	$\Phi_{t\rightarrow r\text{-}tct}$
3,3'-DPyE	acetonitrile	35	0.08	0.07	0.015
		17	0.12	0.05	0.01
		8.7	0.13	0.03	~0.006
		4.4	0.23	0.01	<0.004
		3.7	0.24	0.02	NM
		0.87	0.25	0.003	NM
		0.2	0.25	NM[b]	NM
3,2'-PyPaE	chloroform	55	0.47	0.10[c]	
		27.5	0.49	0.06[c]	
		13.8	0.40	0.03	
		6.9	0.42	0.02	
		1.4	0.29	<0.002	
		0.28	0.25	NM	
4,4'-DPyE	chloroform	55	0.09	0.02	0.003
		27.4	0.12	0.01	NM
		13.7	0.15	0.007	NM
		6.9	0.18	~0.004	NM
		1.4	0.24	<0.001	NM
		0.17	0.18	NM	NM
2,2'-DPyE	chloroform	55	0.20	0.03	0.015
		27.4	0.17	0.01	~0.004
		15.7	0.17	~0.005	<0.001
		6.9	0.17	~0.004	NM
		1.4	0.10		NM
		0.17	0.05	NM	NM

[a] λ_{irr} 300 nm, analysis with ^1H NMR and GLC for *c* and *t* mixtures. [b] NM = not measurable. [c] *r-ctt* head-to-head:head-to-tail ± 50:50.

decrease of the cis-isomer concentration is indeed observed (see Figures 2 and 4).

The intermediate formed in the course of the dimerization may be either an excimer or an encounter complex. With 3,4'-PyiQE additional experiments suggest excimer formation; at 3.6×10^{-5} and 3.6×10^{-2} mol/L its radiative lifetimes calculated from single-photon counting amount to 0.8 and 1.3 ns, respectively. Moreover, as can be seen from Figure 5, the fluorescence spectra in acetonitrile solution show a weak bathochromic broadening above 10^{-2}

Table III. Half-Life Time of Dimerization of Azastilbenes and Some Quaternary Salts in KBr Pellets

monomer	$t_{1/2}$
t-2,2′-DPyE	±70 min
t-3,3′-DPyE	±185 min
t-4,4′-DPyE	±160 min
t-2,2′-DPaE triclinic	27 s
monoclinic	stable
t-4,4′-DiQE	stable
t-2,4′-PaiQE	30 s
t-3,4′-PyiQE	105 s
t-3,2′-PyPaE	stable
t-4,4′-DPyE·2CH_3I	stable[a]
t-2,2′-DPyE·2CH_3I	stable[a]
t-2,2′-DPyE·$(CH_3)_2SO_4$	1 s
t-2,2′-DPyE·CH_3I	15 s[b]
t-4,4′-DPyE·$(CH_3)_2SO_4$	7 s
t-4,4′-DPyE·CH_3BF_4	3 s
t-4,4′-DPyE·CH_3I	±10 min[a]

[a] In agreement with Horner.[49] [b] According to Horner's results,[49] this dimer has a *r-ctt* head-to-tail structure.

mol/L. Similar observations were previously mentioned for *trans*-β-styrylnaphthalene.[43] On the contrary, with 3,3′-DPyE no excimer emission can be detected, and the fluorescence spectra in acetonitrile remain unchanged from 3×10^{-5} to 0.2 mol/L. In this case we are therefore unable to ascertain the structure of the dimerization intermediate.

As far as concentration effects are concerned, dimerization occurs even at 10^{-2} mol/L. 3,3′-DPyE and 4,4′-DPyE behave like stilbene;[42] due to self-quenching and dimer formation the quantum yield of isomerization decreases on increasing the initial monomer concentration. On the contrary, the $t \rightarrow c$ isomerization quantum yields of 2,2′-DPyE and 3,2′-PyPaE increase with increasing monomer concentration. A possible interpretation could be an increased formation of triplet-excited trans molecules (t^T*) from the excimer and subsequent efficient isomerization to the cis isomer.[39,44-47] The photochemical behavior of quaternary salts of 4,4′-DPyE has also been examined in concentrated solution; irradiation of the bismethiodide salt in D_2O gives an adduct with the solvent almost quantitatively. On the other hand, irradiation of the methosulfate and monomethiodide salts produces only *r-ctt* (head-to-tail) dimer, as already mentioned.[48,49]

Photodimerization in the Solid State

One of the few methods which permits a uniform irradiation of crystals and an efficient thermostatization is the irradiation of a suspension in a liquid in which the crystals are insoluble. This method is, however, inappropriate for the azastilbenes on account of their partial solubility in almost all solvents. Therefore the solid-state dimerization was carried out in KBr pellets and pure crystals.

(a) In KBr Pellets.[50] The KBr pellets (2 mg of monomer/180 mg of KBr) were irradiated above 320 nm, except for *t*-4,4′-DPyE which was irradiated at 280 nm for absorption reasons. The degrees of conversion were followed by infrared spectrometry by using monomer and dimer absorption bands (see Experimental Section). From conversion vs. time plots, half-life times of dimerization were calculated; these values were considered to be a measure of the dimerizing ability of the corresponding monomer in the solid state. The results are summarized in Table III.

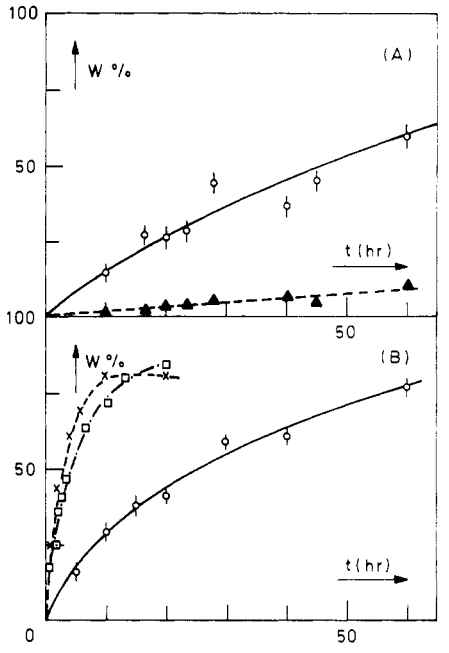

Figure 6. Weight % dimer vs. time of irradiation of azastilbene crystals (320 nm). (A) *t*-3,4′-PyiQE: (○) *r-ctt* hth and (▲) *r-ctt* htt dimers, (B) *t*-2,2′-DPaE (○), *t*-4,4′-DPyEMe$^+$$SO_4Me^-$ (×), and *t*-2,2′-DPyEMe$^+$$SO_4Me^-$ (□).

On the basis of the distances measured by X-ray analysis (see part 1) it was expected that *t*-2,2′-DPaE (monoclinic), *t*-4,4′-DiQE, *t*-3,2′-PyPaE, and the bismethiodides of *t*-2,2′-DPyE and *t*-4,4′-DPyE would not dimerize in the solid state, and indeed these compounds are stable under irradiation. Though an identical behavior was expected for *t*-2,2′- and *t*-4,4′-dipyridylethylenes, a very slow dimerization was nevertheless observed for all three dipyridylethylenes. In view of the fact that DSC measurements show phase transitions around 68 and 90 °C for *t*-2,2′-DPyE and *t*-4,4′-DPyE, respectively, it is assumed that the mechanical preparation of the pellets might cause local heating of the samples and consequently a modification of the crystal structure.

The very short half-life times of *t*-2,2′-DPaE (triclinic) and *t*-2,2′-DPyE·CH_3I correspond to the favorable X-ray distances which allow topochemical dimerization. The high dimerization reactivities of *t*-2,4′-PaiQE, *t*-4,4′-DPyE·$(CH_3)_2SO_4$, *t*-4,4′-DPyE·CH_3BF_4, *t*-2,2′-DPyE·$(CH_3)_2SO_4$, and probably *t*-3,4′-PyiQE also suggest crystalline structures favorable for a topochemical reaction, though these structures were not yet established by direct X-ray measurements. In the case of *t*-3,4′-PyiQE it is worthwhile to note the strong bathochromic shift of the fluorescence spectrum in the solid state compared to that in solution; it confirms that the molecules are properly oriented for excimer (and dimer) formation (Figure 5).

(b) Crystal Irradiation. Direct irradiation of monomer crystals was carried out between two quartz plates; the reaction was followed by NMR analysis after the product was dissolved in Me_2SO-d_6. In agreement with the KBr-pellet experiments no dimer formation was detected even after more than 8-h irradiation (λ_{irrad} >320 nm) for *t*-2,2′-DPyE, *t*-4,4′-DPyE, *t*-3,2′-PyPaE, *t*-2,2′-DPaE

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Table IV. Photodimerization of Azastilbenes

azastilbene	d between ethylenic bonds, A	solution: dimer ratio, r-tct/r-ctt	solution: remark	solid state: KBr pellets[b]	solid state: direct irradiation
stilbene	6.8				stable[c]
c-4,4′-DiQE	6.40	-			
t-4,4′-DiQE	7.40	-		stable	-
t-2,2′-DPyE	6.09	1/2		slow	stable
t-3,3′-DPyE	NM[a]	1/10		slow	stable[c]
t-4,4′-DPyE	5.77	1/2		slow	stable
t-2,2′-DPaE monoclinic	5.46		only r-ctt	stable	stable
triclinic	3.85		only r-ctt	fast	r-ctt
t-3,2′-PyPaE	5.39		only r-ctt (37.4 htt and 33.7 hth)	stable	stable
t-3,4′-PyiQE	NM	94% r-ctt-htt[d] 6% r-tct-hth		fast	85% r-ctt-hth 15% r-ctt-htt
t-2,4′-PaiQE	NM	only r-ctt-htt		fast	NM
t-2,2′-DPyE·CH_3I	3.76			fast	r-ctt-htt
t-2,2′-DPyE·$2CH_3I$	7.02			stable	stable
t-4,4′-DPyE·$2CH_3I$	6.27		add D_2O	stable	stable
t-4,4′-DPyE·$(CH_3)_2SO_4$	NM			very fast	r-ctt
t-4,4′-DPyE·CH_3BF_4	NM			very fast	NM
t-2,2′-DPyE·$(CH_3)_2SO_4$	NM			very fast	dimerizes
t-4,4′-DPyE·CH_3I	NM			slow	stable

[a] NM = not measured. [b] See Table III. [c] Traces of dimer after prolonged irradiation. [d] htt = head-to-tail, hth = head-to-head.

(monoclinic), and the bismethiodides of t-2,2′- and t-4,4′-DPyE. After 7.5-h irradiation, t-3,3′-DPyE contains around 1.5 wt % dimer, and *trans*-stilbene contains traces of r-tct dimer, formed very likely at lattice dislocations. On the other hand, t-2,2′-DPaE (triclinic), t-3,4′-PyiQE, t-4,4′-DPyE·$(CH_3)_2SO_4$, t-2,2′-DPyE·$(CH_3)_2SO_4$, and t-4,4′-DPyE·CH_3BF_4 dimerize readily, as can be seen from Figure 6 where the percent dimer is plotted against the time of irradiation.

In the case of t-3,4′-PyiQE, the occurrence of 15% of a second dimer (r-ctt head-to-tail) clearly shows the presence of defects in the crystal structure which permit dimer formation.

The reactivities found in this type of measurement match very well with the order of reactivities based on the half-life times obtained from the KBr experiments; thus t-4,4′-DPyE·$(CH_3)_2SO_4$ $\simeq$ t-4,4′-DPyE·CH_3BF_4 $\simeq$ t-2,2′-DPyE·$(CH_3)_2SO_2$ $\gg$ t-2,2′-DPaE (triclinic) > t-3,4′-PyiQE. It should be mentioned that X-ray powder diagrams of samples of t-3,4′-PyiQE and t-2,2′-DPaE (triclinic) show, on irradiation, only a decrease in intensity of existing reflections, but no new reflections are observed. Thus the crystalline structure of the solid is progressively broken up as irradiation proceeds, thus confirming the heterogeneous mechanism proposed by Meyer.[37,38]

Discussion

All azastilbenes isomerize and dimerize when irradiated in concentrated acetonitrile or benzene solution. In methanol, where dimerization proceeds at the highest rate, the reactions are complicated by photochemical reduction and addition reactions with the solvent.

The data summarized in Table IV show clearly that in the solid state the compounds with an intermolecular distance smaller than 4.2 Å readily dimerize, while those such as the bismethiodides of t-2,2′- and t-4,4′-DPyE, with a longer distance, do not have a crystalline structure appropriate for a topochemical reaction. Almost surely t-3,4′-PyiQE, t-2,4′-PaiQE, t-4,4′-DPyE·$(CH_3)_2SO_4$, t-4,4′-DPyE·CH_3BF_4, and t-2,2′-DPyE·$(CH_3)_2SO_4$ must have an adequate position in the crystal lattice.

Azastilbenes which do not dimerize in the solid state should yield both r-ctt and r-tct dimers in variable amounts, following the assumption of Green;[11] such is the case of 2,2′-, 3,3′-, and 4,4′-DPyE. One exception, however, is represented by 3,2′-PyPaE which gives only r-ctt dimers in equal amounts of head-to-head and head-to-tail isomers in solution and behaves as an easily dimerizable monomer in the solid state.

If the azastilbenes which dimerize in the solid state are considered, two of them, namely, 2,2′-DPaE and 4,4′-DPyE·Me_2SO_4, behave according to Green's rule. On the contrary, two asymmetric isoquinoline azastilbenes, 3,4′-PyiQE and 2,4′-PaiQE, give only the r-ctt head-to-tail dimer in solution which represents one-sixth of the r-ctt dimers produced in the solid state (Table IV). The results clearly prove that no general correlation exists between solution and solid-state behavior of these azastilbenes. This statement is reinforced by the existing dimorphism of t-2,2′-DPaE and 1-(2,4-dichlorophenyl)- and 2-(3-methylphenyl)ethylene.[51]

Structural Assignment of Dimers

(a) NMR Assignment of Dimer Structures. Structural assignment of the dimers by ^1H NMR is based on two semiempirical rules. Ben-Efraim and co-workers[52] showed that the cyclobutane protons of r-tct-1,2,3,4-tetraarylcyclobutanes have chemical-shift values (or in the case of AA′BB′ systems, midpoints shift values) about 0.8 ppm lower than the corresponding r-ctt compounds (δ 3.6 to 3.9 and δ 4.5 to 5, respectively). The same difference was observed in our case (see Table V). Moreover, the aromatic protons in the r-ctt cyclobutane display diagnostic upfield shifts compared to the corresponding protons in the monomer or in the r-tct dimer (see Table VI), this effect being due to the mutual influence of the magnetic anisotropy of aromatic rings in a cis position.

For photodimers of unsymmetrical azastilbenes, further distinction between head-to-head (hth) and head-to-tail (htt) structure is unambiguously made by analysis[53] of the

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Table V. Chemical Shifts, N Parameters ($J_{AB} + J_{AB'}$), and Frequency Differences between Protons A and B in Azastilbene Dimers

azastilbene	Ar	Ar′	*r-ctt* dimers, δ	*r-tct* dimers, δ
4,4′-DPyE	4-Py	4-Py	4.5	3.7
2,2′-DPyE	2-Py	2-Py	5.1	4.4
3,3′-DPyE	3-Py	3-Py	4.55	3.75[b]
2,2′-DPaE	2-Pa	2-Pa	5.16	
3,4′-PyiQE	3-Py	4-iQ	hth: 5.16 (N = 7 Hz, $\Delta\nu_{AB}$ 56 Hz) htt: 5.5 (N = NM[a] $\Delta\nu_{AB}$ = 5 Hz)	hth: 4.38 (N = 10 Hz, $\Delta\nu_{AB}$ = 30 Hz)
2,4′-PaiQE	2-Pa	4-iQ	htt: 5.5 (N = 17 Hz, $\Delta\nu_{AB}$ = 27 Hz)	
3,2′-PyPaE	3-Py	2-Pa	hth: 4.85 (N = 7.6 Hz, $\Delta\nu_{AB}$ = 25 Hz) htt: 4.9 (N = 17 Hz, $\Delta\nu_{AB}$ = 15 Hz)	

[a] NM = not measurable because of the weak intensity of the outer lines in an AA′BB′ system with $\Delta\nu_{AB}$ = 5 Hz. [b] Not isolated.

AA′BB′ pattern of the cyclobutane ring protons. The value of $N = J_{AB} + J_{AB'}$ is easily measured on the spectrum: for htt dimers, N is the sum of two vicinal coupling constants ($N > 15$ Hz), whereas for hth dimers, N is the sum of one vicinal and one four-bond coupling ($N < 10$ Hz). All these NMR data are summarized in Tables V and VI. The two *r-ctt* dimers and the *r-tct* dimer mentioned in these tables can be represented as in Figure 7.

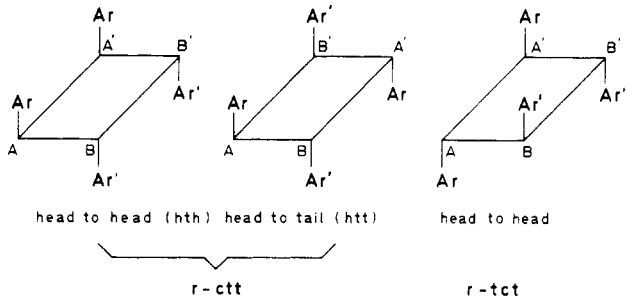


Figure 7. Assignment of the AA′BB′ patterns to the *r-ctt* dimers and the *r-tct* hth dimer.

(b) X-ray Structures of Azastilbene Dimers. Crystalline and molecular structures of five dimers have been determined by X-ray diffraction, namely: (A) *r*-1,*c*-2,*t*-3,*t*-4-tetra(4-pyridyl)cyclobutane; (B) *r*-1,*c*-2,*t*-3,*t*-4-tetra(2-pyridyl)cyclobutane; (C) *r*-1,*c*-2,*t*-3,*t*-4-tetra(2-pyrazinyl)cyclobutane; (D) *r*-1,*t*-3-di(3-pyridyl)-*c*-2,*t*-4-di(2-pyrazinyl)cyclobutane; (E) *r*-1,*c*-2-di(3-pyridyl)-*t*-3,*t*-4-di(2-pyrazinyl)cyclobutane.

The details of these determinations are given as supplementary material in the microfilm edition. The crystallographic data, the experimental conditions, and the

Table VI. Significant Chemical Shifts of Aromatic Protons of Some Monomers and Dimers

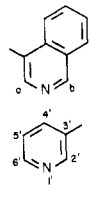
compd			$H_{6'}$	$H_{4'}$	$H_{3'}$	$H_{5'}$	
	2,2′-DPyE	trans mono	8.63	7.65	7.4	7.15	
		r-ctt dim	8.4	7.35	7.06	6.88	
		r-tct dim	8.64	7.54	7.24	7.1	
compd			$H_{2'}$	$H_{6'}$	$H_{4'}$	$H_{5'}$	
	3,3′-DPyE	trans mono	8.74	8.53	7.84	7.3	
		r-ctt dim	8.4	8.38	7.4	7.1	
compd			$H_{2'}$	$H_{6'}$	$H_{5'}$	H_a	H_b
	3,4′-PyiQE	trans mono	8.82	8.55	7.33	8.75	9.18
		r-ctt hth	8.6	8.41	7.13	8.55	8.96
		r-ctt htt	8.46	8.17	6.88	8.70	9.08
		r-tct hth	8.64	8.52	(7.25)	8.92	9.18

Table VII. Crystallographic Data and X-ray Data of Azastilbene Dimers

	A	B	C	D	E
formula unit	$C_{24}H_{20}N_4$	$C_{24}H_{20}N_4$	$C_{20}H_{16}N_8$	$C_{22}H_{18}N_6$	$C_{22}H_{18}N_6$
system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	*Pccn*	*C*2/*c*	*C*2/*c*	$P\bar{1}$	*C*2/*c*
unit cell, *a*, Å	9.389 (5)	16.129 (5)	15.339 (7)	8.459 (4)	15.974 (5)
b, Å	14.012 (6)	5.598 (3)	5.837 (3)	7.670 (3)	5.640 (3)
c, Å	14.155 (5)	21.437 (7)	21.454 (8)	8.090 (3)	21.094 (7)
α, deg				104.08 (2)	
β, deg		102.15 (2)	109.62 (3)	114.44 (2)	103.11 (2)
γ, deg				81.10 (2)	
V, Å^3	1862.2 (1.4)	1892.2 (1.3)	1809.3 (1.4)	462.6 (0.3)	1850.9 (1.3)
Z	4	4	4	1	4
D_x, g cm^{-3}	1.30	1.28	1.35	1.32	1.32
independent reflections					
measured	1389	1400	1341	1472	1370
observed	782	1232	773	1404	980
final conventional *R* factor	0.047	0.127	0.043	0.056	0.140

interpretation of the diffraction spectra for all compounds are given in Table VII. For all five dimers, the structure determined by NMR was confirmed by X-ray analysis.

Experimental Section

All dimers were prepared by irradiation of the monomers in concentrated solution, except for the *r-ctt* hth dimer of 3,4′-PyiQE, which was obtained from solid-state experiments. The mixtures obtained after irradiation were separated by high-performance LC on silica gel. The home-built apparatus consists of a Waters Model 6000 pump, a Waters Model U6K injector (2 mL loop), 4 columns of 30 cm (o.d. ~9.5 mm; i.d. ~7.7 mm), and a Waters R.I. type 403 detector for the semipreparative-scale separations and a LDC UV monitor for analytical purposes. The separations were performed on Li Chromosorb Si60 silica gel (Merck) with methanol–acetonitrile mixtures ranging from 10:90 to 30:70 (v/v). NMR spectra were recorded on JEOL MH-100 (100 MHz), Varian EM 360 (60 MHz), or Varian XL 100 spectrometers operating at 100 MHz in the CW mode for ^1H and at 25.16 MHz in the FT mode for ^{13}C. All spectra were taken in $CDCl_3$; chemical shifts refer to tetramethylsilane internal standard. IR spectra were taken in KBr pellets on a PE 521 grating IR spectrophotometer. Mass spectrometric data were obtained with a AEI MS 9025 spectrometer.

Photodimerization of Azastilbenes in KBr Pellets. All irradiations were carried out with a Hoya UV 32 filter (50% T at 320 nm), except for *t*-4,4′-DPyE for which a Hoya UV 28 filter (50% T at 280 nm) was used. Irradiation of *t*-2,2′-DPyE and *t*-4,4′-DPyE leads to changes in the IR spectrum, and comparison with the IR spectra of the corresponding pure dimer indicates the formation of the *r-ctt* dimer. In the case of *t*-3,3′-DPyE, the pellet was extracted with dichloromethane after 4 h of irradiation, and the product was subjected to mass spectral analysis without any purification. The presence of a peak at *m/e* 364 (M^+) clearly indicates the formation of dimer. For *t*-2,2′-DPaE, the IR spectrum obtained at the end of the photolysis (±5 min) is identical with that of the pure *r-ctt* dimer. For *t*-3,4′-PiQE, the correspondence with the IR spectrum of *r-ctt* hth was also very good; moreover, the mass spectrum shows peaks corresponding to *m/e* 464 (2%, M^+), 282 (3.9%, *t*-4,4′-DiQE), 232 (100%, $M^+/2$). The peak at 282 clearly confirms the hth conformation of this dimer. The changes in the IR spectrum of *t*-3,2′-PyPaE show that dimerization occurs but that it is probably not the only occurring reaction. For the quaternary salts, the half-life period was determined from the decrease of the intensity of the trans absorption (970–990 cm^{-1}) and the increase of the intensity of the aliphatic CH bands (around 3000 cm^{-1}). The only compound for which the observed changes of the IR spectrum did not correspond to dimerization is *t*-4,4′-DPyE·CH_3I; consequently, this compound does not have a crystal structure suited for topochemical dimerization.

Photodimerization of Azastilbenes in Solution and Pure Crystals. The formation of each dimer as a function of the time of irradiation is given in Table I and Figures 2, 3, and 6. Most dimers were isolated from the combined fractions of the semipreparative-scale experiments. They were separated by high-performance LC and crystallized once from benzene or benzene/cyclohexane mixtures. We were, however, unsuccessful in obtaining the *r-tct* dimer of 3,3′-DPyE.

Dimerization of 2,2′-DPyE. Two dimers are obtained. ***r-ctt* dimer**: mp 187–190 °C; IR 3037, 3005, 2969, 2953, 2938, 2900 (CH aliphatic) (other specific bands absent in the monomer), 925, 826, 768, 762, 712, 648, 612, 497 cm^{-1}; mass spectrum, *m/e* 364 (M^+), 272 (M – HC – Py), 182, 181, etc.; ^1H NMR δ 8.4, (H_7, dq), 7.35 (H_9, td), 7.06 (H_{10}, dt), 6.88 (H_8, ddd), 5.1 (H_1, s); ^{13}C NMR δ 160.8 (C_5), 149.1 (C_7), 135.6 (C_9), 123.5 and 120.9 (C_{10} and C_8), 47.2 (C_1). Anal. Calcd: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.22; H, 5.61; N, 15.34. The numbering of the C atoms is that indicated in Figure 1; the structure was proved by X-ray analysis. ***r-tct* dimer**: mp ~120 °C; IR bands absent in the spectrum of the *r-ctt* dimer, 741 (m), 532 and 529 (m) cm^{-1}; mass spectrum *m/e* 272 (M – HC – Py, 100); ^1H NMR δ 8.64 (H_9, dq), 7.54 (H_8, td), 7.24 (H_{10}, td), 7.1 (H_8, ddd), 4.4 (H_1, s); ^{13}C NMR δ 161.9 (C_5), 149.9 (C_7), 136.3 (C_9), 123.1 and 121.7 (C_{10} and C_8), 50.2 (C_1). In methanol additional reaction products are formed: **2,3-Di(2-pyridyl)propanol** [^1H NMR δ 8.55 ($H_{6'}$), 7.58 ($H_{4'}$), 7–7.4 ($H_{3'}$, $H_{5'}$), 5.1 (OH), 3.94 (H_1), 3.2–3.6 (H_2 and H_3); ^{13}C NMR δ 64.8 (C_1), 48 (C_2), 40.7 (C_3)] and **1,2-di(-2-pyridyl)ethane** [^1H NMR δ 3.25 (s, CH_2)].

Dimerization of 3,3′-DPyE. Only *r-ctt* dimer was isolated; ^1H NMR δ 8.4 (H_6, d), 8.38 (H_8, dd), 7.4 (H_{10}, dt), 7.1 (H_9, dd), 4.55 (H_1, s).

Dimerization of 4,4′-DPyE. *r-ctt* dimer: mp 234–237 °C; IR 3066, 3025, 2989, 2960, 2907, 2896, 1375, 1136, 779, 764, 750, 709, 602 cm^{-1}; mass spectrum, *m/e* 364 (3.7, M^+), 309 (0.6, M – H – HCN), 272 (1.0, M – CH – Py), 182 (100, $M^+/2$), 181; ^1H NMR δ 8.44 (H_7, H_9, d), 7 (H_6, H_{10}, d), 4.5 (H_1, s); ^{13}C NMR δ 150.5 (C_7, C_9), 147.8 (C_5), 123.2 (C_6, C_{10}), 46 (C_1). Anal. Calcd: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.01; H, 5.47; N, 15.38. The structure was confirmed by X-ray analysis. ***r-tct* dimer**: mp ~180 °C; IR typical bands absent in the *r-ctt* dimer, 2931, 870, 790, 646 cm^{-1}; ^1H NMR δ 3.71 (H_1, s), 7.16 (H_6 and H_{10}, d), 8.55 (H_7 and H_9, d). Two side products are formed in methanol: **1,2-di(4-pyridyl)ethane** [^1H NMR δ 8.44 ($H_{2'}$, $H_{6'}$, d), 7.04 ($H_{3'}$, $H_{5'}$, d), 2.95 (CH_2, s)] and **2,3-di(4′-pyridyl)propanol** [^1H NMR δ 8.46, 8.36 ($H_{2'}$, $H_{6'}$), 7.14, 7.06 ($H_{3'}$, $H_{5'}$), 3.86 (H_1), 2.9–3.4 (H_2, H_3); ^{13}C NMR δ 64.9 (C_1), 49 (C_2), 37.2 (C_3)].

Dimerization of 2,2′-DPaE. Only ***r-ctt* dimer** is formed: mp 200 °C; IR 3075, 3060, 3007, 2958, 2943, 1260, 1236, 950, 930, 802, 769, 728 cm^{-1}; UV (THF) λ_{max} 318 (ε 340), 264 (16 000) nm; mass spectrum, *m/e* 368 (4.2, M^+), 367 (0.7, M – H), 289 (6.7, M – Pa), 276 (17.0, M – CH – Pa), 275 (100, M – CH – Pa), 209 (3.8, M – H 2Pa), 197 (6.0, M – CH – Pa – Pa), 184 (84.4, $M^+/2$), 183; ^1H NMR δ 8.2–8.5 (H_{10}, H_8, and H_7), 5.16 (H_1, s). Anal. Calcd: C, 65.21; H, 4.38; N, 30.42. Found: C, 65.21; H, 4.49; N, 30.32. The structure was confirmed by X-ray diffraction methods.

Dimerization of 3,4′-PyIQE. *r-ctt* hth dimer was the only one prepared in the solid state: ^1H NMR δ 8.96 (H_{14}, s), 8.6 (H_6, d), 8.55 (H_{12}, s), 8.41 (H_8, dd), 7.13 (H_9, dd), 5.16 (H cyclobutane, m), 7.4–8 (H_{10} and iQ protons). In solution the following two dimers were obtained: ***r-ctt* htt dimer** [mp ~330 °C; IR 3065, 3048, 2975, 2933, 1571, 1322, 897, 842, 719 cm^{-1}; ^1H NMR δ 9.08 (H_{14}, s), 8.7 (H_{12}, s), 8.46 (H_6, d), 8.17 (H_8, dd), 6.88 (H_9, dd), 5.12 (H cyclobutane, m), 7.6–8 (H_{10} and iQ protons). Anal. Calcd: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.50; H, 5.44; N, 12.07] and ***r-tct* hth dimer** [mp ~110 °C; IR 3016 (w), 2912 (w), 2840 (vw), 2232 (w), 875 (w, br), 837 (w), 602 (s) cm^{-1}; ^1H NMR δ 9.18 (H_{14}, s), 8.92 (H_{12}, s), 8.64 (H_6, d), 8.52 (H_8, dd), 4.38 (H cyclobutane, m), 7.2–8 (H_9, H_{10}, and iQ protons)].

Dimerization of 2,4′-PaiQE. *r-ctt* htt dimer: mp ~250 °C; IR 3042 (w), 3022 (w), 2995 (vw), 2918 (w), 2845 (vw), 2238 (vw), 1558 (s), 1412 (s), 1400 (s), 1362 (m), 1001 (vs), 875 and 864 (w), 698 (vs) cm^{-1}; mass spectrum, *m/e* main peaks 233 and 232; 466, 387, 373, 324, 282; ^1H NMR δ 8.4–7.4 (Pa and iQ), 5.5 (cyclobutane, m).

Dimerization of 3,2′-PyPaE yields two dimers: ***r-ctt* hth dimer** [mp ~183–187 °C; IR 3056 (w), 3040 (w), 3025 (m), 3005 (w), 2935 (m), 2909 (w), 1572 (w), 925 (vw), 776 and 763 (vw), 718 (m) cm^{-1}; ^1H NMR δ 8.2–8.5 (H_{12}, H_{14}, H_{10}, H_8, H_7), 7.44 (H_{16}, dt), 7.1 (H_{15}, dd), 4.85 (H-cyclobutane, m)] and ***r-ctt* htt dimer** [mp ~173–175 °C; IR 3045 (w), 3024 (m), 3005 (w), 2935 (w), 2915 (vw), 1573 (vw), 702 (s), 580 (s) cm^{-1}; ^1H NMR δ 8.2–8.5 (H_{12}, H_{14}, H_{10}, H_8, H_7), 7.48 (H_{16}, dt), 7.07 (H_{15}, dd), 4.9 (H-cyclobutane, m). Anal. Calcd: C, 72.11; H, 4.95; N, 22.94. Found: C, 71.96; H, 5.03; N, 23.01]. The structure of both dimers was ascertained by X-ray analysis.

Acknowledgment. The authors are grateful to the Belgian National Science Foundation for equipment and two fellowships (J.V. and J.P.D.). They acknowledge financial support of the Ministry of Scientific Programmation and are also indebted to Mrs. J. Feneau-Dupont for the preparation and discussion of the manuscript.

Registry No. *trans*-Stilbene, 103-30-0; *cis*-stilbene, 645-49-8; stilbene *r-ctt* dimer, 54515-63-8; stilbene *r-tct* dimer, 54515-64-9; *trans*-2,2′-DPyE, 13341-40-7; *cis*-2,2′-DPyE, 14802-37-0; 2,2′-DPyE *r-ctt* dimer, 73069-90-6; 2,2′-DPyE *r-tct* dimer, 73069-91-7; *trans*-3,3′-DPyE, 14987-84-9; *cis*-3,3′-DPyE, 14802-42-7; 3,3′-DPyE *r-ctt* dimer, 73069-92-8; 3,3′-DPyE *r-tct* dimer, 73069-93-9; *trans*-4,4′-DPyE, 13362-78-2; *cis*-4,4′-DPyE, 14802-45-0; 4,4′-DPyE *r-ctt* dimer,

62415-98-9; 4,4'-DPyE *r-tct* dimer, 73078-76-9; *trans*-3,2'-PyPaE, 73048-52-9; *cis*-3,2'-PyPaE, 73048-62-1; *r*-1,*c*-2,*t*-3,*t*-4-tetra(2-pyrazinyl)cyclobutane, 73069-94-0; *r*-1,*t*-3-di(3-pyridyl)-*c*-2,*t*-4-di(2-pyrazinyl)cyclobutane, 73078-81-6; *r*-1,*c*-2-di(3-pyridyl)-*t*-3,*t*-4-di(2-pyrazinyl)cyclobutane, 73069-95-1; *trans*-2,2'-DPaE, 62141-47-3; *trans*-4,4'-DiQE, 73048-54-1; *trans*-2,4'-PaiQE, 73048-58-5; *trans*-3,4'-PyiQE, 73048-57-4; *trans*-4,4'-DPyE $2CH_3I$, 24274-78-0; *trans*-2,2'-DPyE $2CH_3I$, 73048-55-2; *trans*-2,2'-DPyE $(CH_3)_2SO_4$, 73048-66-5; *trans*-2,2'-DPyE CH_3I, 73048-56-3; *trans*-4,4'-DPyE $(CH_3)_2SO_4$, 73048-65-4; *trans*-4,4'-DPyE CH_3BF_4, 73069-97-3; *trans*-4,4'-DPyE CH_3I, 73048-64-3; 3,4'-PyiQE *r-ctt hth* dimer, 73069-98-4; 3,4'-PyiQE *r-tct hth* dimer, 73089-62-0; 3,4'-PyiQE *r-ctt htt* dimer, 73069-99-5; 2,4'-PaiQE *r-ctt hth* dimer, 73070-00-5; 2,3-di(2-pyridyl)propanol, 73070-01-6; 1,2-di(4-pyridyl)ethane, 4916-57-8; 2,3-di(4-pyridyl)-propanol, 73070-02-7; 4,4'-DPyE·$(MeO)_2SO_2$ *r-ctt* dimer, 73070-04-9; 1,2-di(2-pyridyl)ethane, 4916-40-9.

Supplementary Material Available: Results and discussion of the X-ray structure determination of five azastilbene dimers plus full X-ray data for these compounds. (17 pages). Ordering information is given on any current masthead page.

Polymer-Based Sensitizers for Photochemical Reactions. Silica Gel as a Support

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Received October 2, 1979

Silica gel has been converted to silylated derivatives which can be converted to sensitizers for singlet oxygen formation. The silica gel sensitizers, [P_{Si}]-rose bengals,[1] are versatile and useful in both polar and nonpolar media. [P_{Si}]-Rose bengal has been studied as a source of singlet oxygen and its uses in reactions of sulfite ion, tryptophan, and 2,3-diphenyldioxene are reported. Results are compared with unbound and polystyrene-based rose bengal ([P]-rose bengal).

Silica gel has attracted considerable attention in the petroleum industry as a low cost support for the anchoring of heavy metal catalysts. In view of our continuing interest in the use of polymers in organic photochemical synthesis[2] and in view of our already described supported reagent for singlet oxygen genesis based on styrene–divinylbenzene copolymer beads,[3a] the development of a polymer-supported sensitizer for singlet oxygen genesis in which the polymer support was solvent versatile, rather than solvent limited, seemed obvious.

Accordingly, we have developed a pair of sensitizers for singlet oxygen formation: [P_{Si}]-rose bengal and [P_{Cl}]-rose bengal, the former supported on silica gel, the latter supported on cellulose. Silica gel adsorbed (in contrast to covalently attached) sensitizers have been studied before[3b] and have been acknowledged to have numerous disadvantages;[4] therefore the silica gel bound materials were designed to add the versatility of the support to the stability of the bound reagent.

Silica gel rose bengal, [P_{Si}]-rose bengal, was prepared by the following reactions:

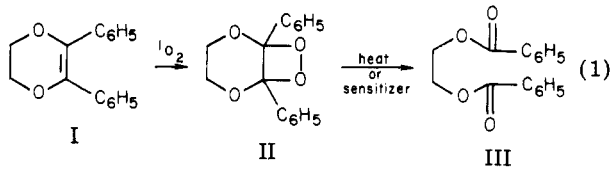
$$Cl_3Si(CH_2)_3Cl + EtOH \xrightarrow[C_6H_6]{Et_3N} (EtO)_3Si(CH_2)_3Cl$$

$$[P_{Si}]\text{–}OH + (EtO)_3Si(CH_2)_3Cl \xrightarrow[150\ ^\circ C]{\text{xylene}} [[P_{Si}]\text{–}O]_3Si(CH_2)_3Cl$$

$$[[P_{Si}]\text{–}O]_3Si(CH_2)_3Cl + \text{rose bengal} \xrightarrow[135\ ^\circ C]{DMF} [[P_{Si}]\text{–}O]_3Si(CH_2)_3\text{–rose bengal}$$

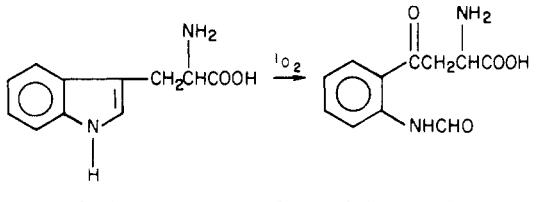
The silica gel obtained was cherry red and withstood continuous Soxhlet extraction for several days with the following solvents in succession: MeOH, THF, chloroform, and benzene. Following the Soxhlet extraction, the polymer was washed with methylene chloride for 24 h and methanol for 24 h, and it was dried in a vacuum oven at 50 °C overnight.[5]

[P_{Si}]-Rose bengal was tested as a source of singlet oxygen in three diagnostic reactions: the cycloaddition reaction of 2,3-diphenyldioxene (eq 1),[6] the oxidation of sulfite ion (eq 2)[7] in phosphate buffer, and the oxygenation of tryptophan (eq 3)[8] as well as its sodium salt. In general, it



(1)

$$SO_3^{2-} \xrightarrow{^1O_2} SO_4^{2-} \qquad (2)$$



(3)

is observed that [P_{Si}]-rose bengal is as effective as is [P]-rose bengal in forming singlet oxygen in nonpolar solvents, but unlike [P]-rose bengal, which one would expect to agglomerate in water because of the hydrophobicity

(1) The common symbol for polymer support systems, circled characters, has been replaced by brackets because of composition difficulties.

(2) For leading references to our work see (a) Blossey, E. C.; Neckers, D. C. "Benchmarks in Photochemistry"; Dowden, Hutchinson, and Ross: Stroudsburg, PA; (b) Neckers, D. C. *CHEMTECH* **1978**, *8*, 108; (c) Card, R. J.; Neckers, D. C. *Isr. J. Chem.* **1979**, *17*, 269.

(3) (a) Marketed under the trade name "Sensitox", Hydron Laboratories, New Brunswick, NJ. (b) Williams, J. R.; Orton, G.; Unger, L. R. *Tetrahedron Lett.* **1973**, 4303. Takeshita, H.; Hatsui, T. *J. Org. Chem.* **1978**, *43*, 3081.

(4) Srinivasan, V. S.; Neckers, D. C. unpublished results. Blossey, E. C.; Neckers, D. C., unpublished results.

(5) It was also possible to prepare a silica gel rose bengal by the reaction of silica gel first with thionyl chloride, and then with rose bengal. This silica gel rose bengal was not as stable to hydrolysis as that described above, so it was tested as a source of singlet oxygen (which it is) and then not further utilized.

(6) Bartlett, P. D.; Mendenhall, G. D.; Schaap, A. P. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 79.

(7) (a) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1969**, *244*, 6056. (b) Misra, H. P.; Fridovich, I. *Ibid.* **1972**, *247*, 3170.

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