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Azastilbenes. 1. Synthesis, Characterization, and Structure

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The synthesis of several symmetric and asymmetric azastilbenes is described, and their spectral characteristics (NMR, mass, UV, IR) are given. Four of them are new compounds, namely, 1,2-di(4-isoquinolyl)ethylene, 1-(3-pyridyl)-2-(2-pyrazinyl)ethylene, 1-(3-pyridyl)-2-(4-isoquinolyl)ethylene, and 1-(2-pyrazinyl)-2-(4-isoquinolyl)ethylene. The molecular structure and crystalline stacking of some of these azastilbenes and of the quaternary salts of 1,2-di(2-pyridyl)ethylene and 1,2-di(4-pyridyl)ethylene have been determined by X-ray diffraction on single crystals and their characteristic parameters indicated.

Azastilbenes can undergo several photochemical reactions such as cis-trans isomerization, cyclodimerization into cyclobutane compounds (part II), and intramolecular cyclizations with formation of dihydroazaphenanthrenes.[1-12] It was the aim of the present work to synthesize several symmetric and asymmetric azastilbenes and to examine the influence of their structure on their photochemical behavior. In the present paper the synthesis of these compounds will be considered, as well as their structural characterization. Py (pyridyl), Pa (pyrazinyl), iQ (isoquinolyl), D (di-), and E (ethylene) will be used as abbreviations.

Synthesis and Characterization

The three usual paths for the synthesis of azastilbenes are (i) Perkin condensation followed by decarboxylation,[1,9] (ii) Wittig reaction,[13-17] and (iii) condensation of an aryl aldehyde with an active methylene aryl compound.[12,18,19] They are illustrated in Figure 1.

The synthesis of 3,3′-dipyridylethylene by path i is known from the literature.[20,21] Its main disadvantage is the decarboxylation step, during which much product is lost. Method ii gives satisfactory yields for 3,3′-DPyE, 2,2′-DPaE, 3,2′-PyPaE, and 3,4′-PyiQE; the corresponding yields of Table I refer only to the Wittig condensation step. Method iii was only used for the pyrazine derivatives in which the methyl group is activated by the ortho ring nitrogen atom. Table I summarizes the results of the syntheses carried out in the present study.

The diarylethylenes obtained in these syntheses are usually mixtures of cis and trans isomers. On treatment with iodine in nitrobenzene[22,23] the mixture is completely transformed into the trans compound. All new diarylethylenes were analyzed by ^{1}H and ^{13}C NMR, infrared, and mass spectrometry. In view of their dimerization in the solid state, X-ray diffraction was measured on single crystals.

Experimental Section

The numbering of atoms in the rings is indicated in Table I.

3,3′-DPyE and 2,2′-DPaE were synthesized as described in the literature.[1,18,20,21] **2,2′-** and **4,4′-DPyE** were commercially available (Aldrich).

4,4′-Diisoquinolylethylene (4,4′-DiQE). 4-Isoquinolylcarboxaldehyde was obtained by the reaction of 4-isoquinolyllithium with dimethylformamide.[24] It was condensed with (4-isoquinolinemethylene)triphenylphosphonium chloride hydrochloride, prepared by the following three steps:

(a) 4-(Hydroxymethyl)isoquinoline. 4-Isoquinolylcarboxaldehyde (0.074 mol), dissolved in 50 g of dry methanol, was hydrogenated on 1 g of Pd catalyst (10% Pd/Al$_2$O$_3$) until an equimolar amount of hydrogen was taken up. The catalyst was filtered off and the product crystallized from ethanol or methanol to give colorless plates (88%): mp 166 °C; NMR (Me$_2$SO-d_6D$_2$O; (Me$_3$Si)$_2$O) δ 8.92 (H$_1$, s), 8.37 (H$_3$, s), 7.0–8.0 (H$_5$–H$_8$, m), 4.60 (CH$_2$, s).

(b) 4-(Chloromethyl)isoquinoline Hydrochloride.[25] 4-(Hydroxymethyl)isoquinoline (8.75 g) was dissolved in a minimum volume of dry methanol. Dry ether saturated with HCl (25 mL) was added in several portions. After the solution was cooled, the hydrochloride precipitated (92%) as a white powder. It was dissolved in 60 mL of SOCl$_2$, and the solution refluxed for 3 h. After evaporation, 50 mL of benzene was added and the mixture was again evaporated to dryness. The residue was treated with 60 mL of benzene and 15 mL of dry ether saturated with hydrochloric acid. The solid (95%, 4-(chloromethyl)isoquinoline hydrochloride) was filtered off.

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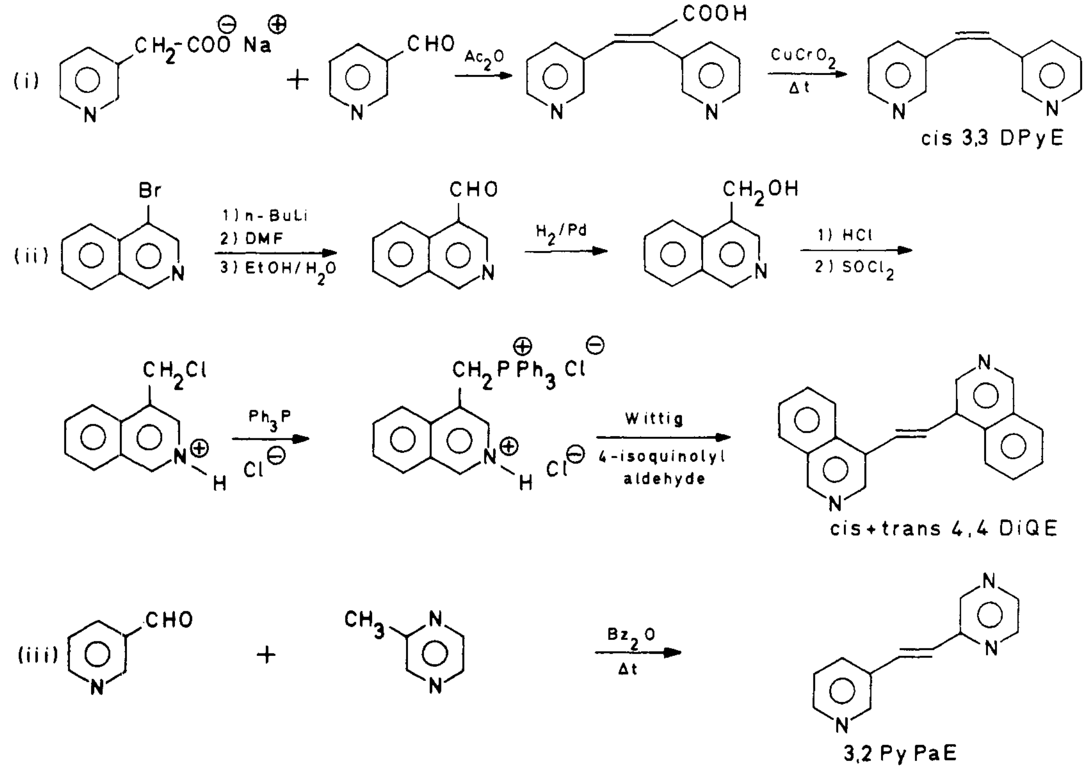
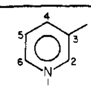
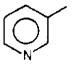
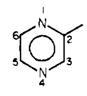
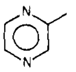
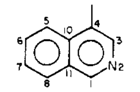
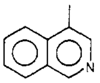
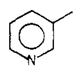
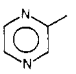
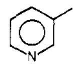
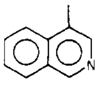
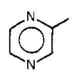
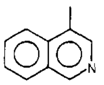


Figure 1. Syntheses of azastilbenes.

Table I. Preparation of Azastilbenes ($Ar^1CH{=}CHAr^2$)

compd	no.[a]	Ar^1	Ar^2	% yields for method of synthesis		mp, °C, trans isomer
				ii	iii	
3,3'-DPyE				40-45		89-90
2,2'-DPaE	IV			60-70	50	190-194
4,4'-DiQE	V_{cis} VI_{trans}			20		(cis: 196-198) 243
3,2'-PyPaE	III			45	50	93-95
3,4'-PyiQE				67		98-102
2,4'-PaiQE				50	5-10	82-85

[a] Roman numerals refer only to molecules described in the X-ray section.

(c) (4-Isoquinolinemethylene)triphenylphosphonium Chloride Hydrochloride was prepared according to E. C. Taylor and T. Kobayashi.[26] 4-(Chloromethyl)isoquinoline hydrochloride (0.083 mol) and triphenylphosphine (0.106 mol) in 80 mL of dry DMF were stirred for 3 h at 80–90 °C. After the mixture was cooled, the precipitate was filtered off. Crystallization from methanol yielded only 35–50% of the product: NMR (D_2O/$(CH_3)_3Si(CH_2)_3SO_3^-Na^+$) δ 5.60 (CH_2, d, J_{HP} = 15 Hz); Me_2SO-d_6, 6.34 (CH_2, d); IR 1438, 1000–1110 (P^+–Ph), and 2600 (=NH—$^+$) cm^{-1}. Treatment of a solution of this salt with concentrated NH_3 and extraction with CH_2Cl_2 gave free (4-isoquinolinemethylene)triphenylphosphonium chloride: mp 285 °C (after crystallization from acetone); NMR (Me_2SO-d_6/D_2O) δ_{HMDS} 5.54 (CH_2, d); IR, same as above, except the band at 2600 cm^{-1} is absent.

(d) *t*-4,4'-DiQE was obtained from (4-isoquinolinemethylene)triphenylphosphonium chloride hydrochloride and 4-isoquinolylcarboxaldehyde in the presence of potassium *tert*-butoxide in THF at 0 °C[27,28] (path ii). The crude reaction mixture was crystallized from acetonitrile or DMF to yield approximately 20% of *trans*-4,4'-DiQE. Purification was carried out by high-performance LC on silica gel (CH_3CN–CH_3OH, 85:15). ***t*-4,4'-DiQE**: mp 243 °C; IR 1624 (m), 1580 (w), 1508 (w), 1313 (m), 1262 (s), 1217 (w), 972 (s), 805, 790 (s), 750 (vs); UV_{max} (cyclo-

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hexane) 340 (ϵ 18 600) and 230 (41 900) nm; mass spectrum, m/e 282.1127 (77.5, M$^+$), 225.0976 (7.9, M − HCN), 254.0913 (17.8, (17.8, M − H − HCN), 227.0696 (1.9, M − H − 2HCN), 226.0742 (5.1, M − 2H − 2HCN); ^{1}H NMR ($CDCl_3/Me_4Si$) δ 9.2 (H_1, s), 8.84 (H_3, s), 8.2–7.5 (H_5, H_6, H_7, H_8), 7.8 (H_9, s); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 152.9 (C_1), 141.3 (C_3), 134.2 (C_{10}). Anal. Calcd: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.95; H, 5.13; N, 9.80. ***cis*-4,4′-DiQE**: mp 196–198 °C; IR 1625 (s), 1580, 1570 (m), 1505 (s), 1380 (m), 1228 (m), 970 (vw), 926, 920 (s), 840 (s), 812, 798 (vs), 754 (vs); UV_{max} (cyclohexane) 331 (ϵ 8500), 283 (7400) nm; mass spectrum, m/e 282.1142 (84.5, M$^+$), 280.3391 (1.2, M − 2H, cyclization?), 255.1000 (8.0, M − HCN), 254.0937 (19.5, M − H − HCN), 227.079 (2.8, M − H − 2HCN), 226.0787 (5.0, M − 2H − 2HCN); ^{1}H NMR ($CDCl_3/Me_4Si$) δ 8.92 (H_1, s), 7.96 (H_3, s), 8–7.4 (H_5, H_6, H_7, H_8), 7.3 (H_9, s); ^{13}C NMR ($CDCl_3/Me_4Si$) δ 152.1 (C_1), 143 (C_3), 134.7 (C_{10}).

3,2′-Pyridylpyrazinylethylene (3,2′-PyPaE) was prepared from 2-pyrazinecarboxaldehyde and (3-pyridinemethylene)triphenylphosphonium chloride hydrochloride in the presence of potassium *tert*-butoxide. The crude reaction mixture was treated with I_2 in nitrobenzene to yield 45% pure *trans*-3,2′-PyPaE after crystallization. The product was obtained (50% yield) from 2-methylpyrazine and 3-pyridylcarboxaldehyde in benzoic anhydride, according to method iii. ***trans*-3,2′-PyPaE**: mp 93–96 °C; IR, all bands appearing in the spectra of 3,3′-DPyE and 2,2′-DPaE are present; UV_{max} (acetonitrile) 267 (ϵ 16 500), 317 (21 700) nm; mass spectrum, m/e 183 (37.5, M$^+$), 182 (100, M − H), 156 (4.4, M − HCN), 155 (16.5, M − H − HCN), 130 (9.3, ?), 129 (10.7, M − 2HCN), 128 (5.4, M − H − 2HCN). Anal. Calcd: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.10; H, 5.02; N, 22.80. In the case of 3,2′-PyPaE as well as that of 3,4′-PyiQE (see below), the assignment of each olefinic proton was made possible by observation of differences in their line width due to benzylic type couplings with one or two neighboring aromatic protons; by selective decoupling of one or the other of these aromatic protons, it was possible to sharpen the corresponding olefinic proton. For 2,4′-PaiQE, assignment is only tentative; ^{1}H NMR ($CDCl_3/Me_4Si$) (prime signs refer to the pyrazine ring) δ 8.8 (H_2, d), 8.65 ($H_{3'}$, d), 8.57 ($H_{6'}$, d), 8.57 ($H_{6'}$, H_6), 8.45 ($H_{5'}$, d), 7.9 (H_4, d tr), 7.75 (H_7, d), 7.3 (H_5, d d), 7.20 ($H_{7'}$, d), $^3J_{H_7H_{7'}}$ = 16 Hz; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 150.8 ($C_{2'}$), 150.1 and 149.6 (C_2 and C_6), 143.7, 144.3 and 144.8 ($C_{3'}$, $C_{5'}$, and $C_{6'}$), 133.7 (C_4), 132.1 (C_3), 131.8 and 126.4 (C_7 and $C_{7'}$), 124 (C_5). ***cis*-3,2′-PyPaE** is a liquid: UV_{max} (acetonitrile) 265 (ϵ 10 100), 292 (11 100), nm; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 8.6–8.4 (H_2, H_6, $H_{3'}$, $H_{5'}$, and $H_{6'}$, m), 7.72 (H_4 d tr), 7.23 (H_5, d d), 6.78 and 6.92 (H_7, d and $H_{7'}$, d), $^3J_{H_7H_{7'}}$ = 12.5 Hz; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 151.6 ($C_{2'}$), 150.3 and 149.1 (C_2 and C_6), 145.4, 144.3 and 143 ($C_{3'}$, $C_{5'}$, and $C_{6'}$), 136.2 (C_4), 132.2 (C_3), 132.4 and 128.8 (C_7 and $C_{7'}$), 123.2 (C_5).

3,4′-Pyridylisoquinolylethylene (*t*-3,4′-PyPiQE) was prepared from 4-isoquinolylcarboxaldehyde and (3-pyridylmethylene)triphenylphosphonium chloride hydrochloride. After treatment with I_2 in nitrobenzene and crystallization from benzene/cyclohexane (10:90) an overall yield of 67% was obtained: mp 103 °C; IR, all bands characteristic of *t*-3,3′-DPyE and *t*-4,4′-DiQE are present; UV_{max} (cyclohexane) 332 (ϵ 17 600), 257 (13 800) and 224 (30 400) nm; mass spectrum m/e 232 (100, M$^+$), 231 (92, M − H), 205 (17, M − HCN), 204 (39, M − H − HCN), 203 (10, M − 2H − HCN), 178 (3.3, M − 2HCN), 177 (5.5, M − H − 2HCN), 176 (10, M − 2H − HCN); ^{1}H NMR ($CDCl_3/Me_4Si$) (prime signs refer to the pyridine ring) δ 9.12 (H_1, s), 8.80 ($H_{2'}$, d), 8.75 (H_3, s), 8.55 ($H_{6'}$, dd), 8.1–7.5 (H_5, H_6, H_7, H_8, $H_{4'}$), 7.70 ($H_{7'}$, d), 7.3 ($H_{5'}$, dd), 7.1 (H_9, d), $^3J_{H_9H_{7'}}$ = 16 Hz; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 152.7 (C_1), 149.4 and 149 ($C_{2'}$ and $C_{6'}$), 140.9 (C_3). Anal. Calcd: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.65; H, 5.36; N, 12.03.

2,4′-Pyrazinylisoquinolylethylene (2,4′-PaiQE) was prepared from (2-pyrazinylmethylene)phosphonium chloride[26,29] and 4-isoquinolylcarboxaldehyde in approximately 50% yield as fine white needles, mp 82–85 °C. Anal. Calcd: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.04; H, 4.68; N, 17.89. Condensation of 2-methylpyrazine with 4-isoquinolylcarboxaldehyde in benzoic anhydride (method iii) gave less than 10% yield: IR, same bands as those of *t*-2,2′-DPaE and *t*-4,4′-DiQE; UV_{max} (acetonitrile) 340 (ϵ 19 500) and 230 (22 200) nm; mass spectrum m/e 233 (37, M$^+$), 232 (100, M − H), 206 (9, M − HCN), 205 (19, M − H − HCN), 179 (1, M − 2HCN); ^{1}H NMR ($CDCl_3/Me_4Si$) (prime signs refer to the pyrazine ring) δ 9.12 (H_1, s), 8.76 (H_3, s), 8.62 ($H_{3'}$, d), 8.56 ($H_{6'}$, d d), 8.42 ($H_{5'}$, d), 8.36 (H_9, d), 8.2–7.5 (H_5, H_6, H_7, H_8, m), 7.20 ($H_{7'}$, d), $^3J_{N_{7'}H_8}$ = 16 Hz; ^{13}C NMR ($CDCl_3/Me_4Si$) δ 153.1 (C_1), 151 ($C_{2'}$), 144.8, 144.4 and 143.7 ($C_{3'}$, $C_{5'}$, and $C_{6'}$), 141.1 (C_3), 134 (C_{10}).

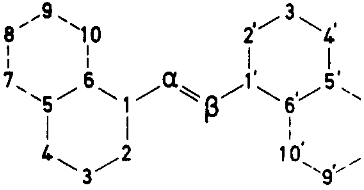

Figure 2. Numbering of atoms in azastilbenes.

Quaternary salts of dipyridylethylenes were prepared by treating the azastilbene with methyl iodide, or dimethyl sulfate in chloroform or acetonitrile.[30,31]

(a) *t*-4,4′-DPyE·CH_3I: mp 233–235 °C; ^{1}H NMR (Me_2SO-d_6/Me_4Si) (primes for quaternized ring) δ 9.02 ($H_{2'}$, $H_{6'}$, d), 8.72 (H_2, H_6, d), 8.35 ($H_{3'}$, $H_{5'}$, d), 8.06 and 7.80 (H_7 and $H_{7'}$, 2 d), 7.72 (H_3, H_5, d), 4.35 (CH_3, s), $J_{H_7H_{7'}}$ = 16.5 Hz; ^{13}C NMR (Me_2SO-d_6/Me_4Si) δ 151.3 ($C_{4'}$), 150.3 (C_2, C_6), 145.3 ($C_{2'}$, $C_{6'}$), 142.0 (C_4), 137.4 and 127.4 (C_7, $C_{7'}$), 124.2 ($C_{3'}$, $C_{5'}$), 121.7 (C_3, C_5).

(b) *t*-4,4′-DPyE·$(CH_3)_2SO_4$: mp 160–163 °C; ^{1}H NMR (Me_2SO-d_6/Me_4Si) δ 8.96 ($H_{2'}$, $H_{6'}$, d), 8.73 (H_2, H_6, d), 8.30 ($H_{3'}$, $H_{5'}$, d), 8.00 and 7.74 (H_7, $H_{7'}$, 2 d), 7.70 (H_3, H_5, d), 4.32 (CH_3, s).

(c) *t*-4,4′-DPyE·2CH_3I: slow decomposition above 320 °C; ^{1}H NMR (Me_2SO-d_6/Me_4Si) δ 9.09 (H_2, H_6, d), 8.41 (H_3, H_5, d), 8.21 (H_7, s), 4.37 (CH_3, s); ^{13}C NMR (Me_2SO-d_6/Me_4Si) δ 150.6 (C_4), 146.0 (C_2, C_6), 133.8 (C_7), 125.1 (C_3, C_5).

(d) *t*-2,2′-DPyE·CH_3I: mp 212–216 °C; ^{1}H NMR (Me_2SO-d_6/Me_4Si) δ 9.08 ($H_{6'}$, d), 8.78 ($H_{6'}$, d), 8.65 ($H_{3'}$, $H_{4'}$, m), 8.06–7.85 ($H_{5'}$, H_7, $H_{7'}$, H_3, H_4, m), 7.50 (H_5, dt), 4.44 (CH_3, s).

(e) *t*-2,2′-DPyE·$(CH_3)_2SO_4$: mp 158–159.5 °C; ^{1}H NMR (Me_2SO-d_6/Me_4Si) δ 3.81 ($CH_3OSO_2^-$, s), 4.25 (CH_3^+, s), 8.78 ($H_{6'}$, d), others 7.40–8.70 (9 H).

(f) *t*-2,2′-DPyE·2CH_3I: fast decomposition above 285 °C; ^{1}H NMR (Me_2SO-d_6/Me_4Si) δ 9.15 (H_6, d), 8.75 (H_3, H_4, d), 8.20 (H_5, dt), 8.10 (H_7, s), 4.47 (CH_3, s).

Infrared spectra were obtained on pressed KBr pellets with Perkin-Elmer 267 and 367 spectrometers and UV spectra were obtained with a PE-Hitachi 200 spectrometer. Mass spectrometry data were determined on an AEI MS 9025 spectrometer. NMR spectra were determined on Jeol 100 MHz and Varian XL-100. Purifications by high-performance LC were carried out on a Waters Associate ALC/GPC 244 with Microsorb SI 60, 4 mL/min with methanol/acetonitrile (10/90 up to 30/70) as solvent, and Waters Associate detector R 403.

X-ray Structure of Azastilbenes

trans-1,2-Diarylethylenes dimerize in the solid state as long as the molecules are properly oriented within the crystal lattice and the distances between neighboring olefinic bonds are between 3.8 and 4.2 Å. According to Schmidt, "topochemical" dimerization will occur when these requirements are met.[32,33] In view of the photodimerization experiments (see following paper) it was highly desirable to determine, with X-ray diffraction, the crystalline and molecular structure of the azastilbenes described in the present paper. In this part of the work, a synoptic presentation of the data is used which affords

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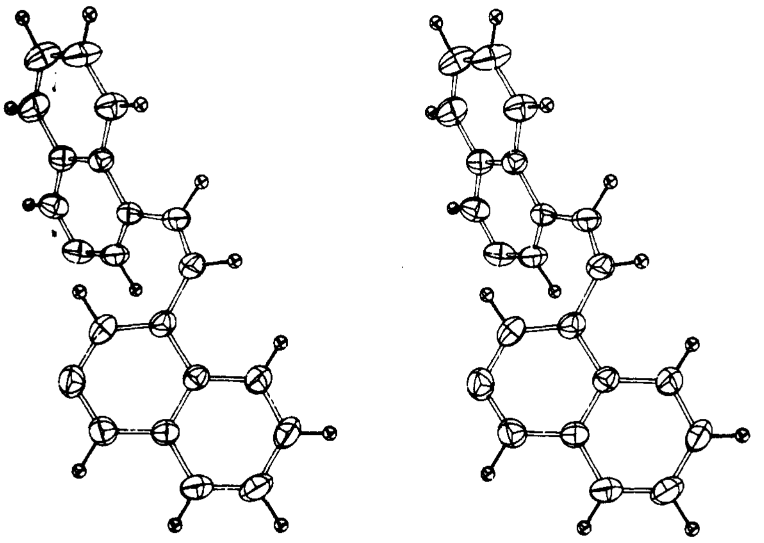

Figure 3. Molecular structure of V, (*Z*)-dibenzo[*e*,*e*′]-3,3′-diazastilbene.

Table II. Nomenclature of Azastilbenes

I	*t*-2,2′-DPyE	(*E*)-2,2′-diazastilbene
II	*t*-4,4′-DPyE	(*E*)-4,4′-diazastilbene
III	*t*-3,2′-PyPaE	(*E*)-2′,5,5′-triazastilbene
IV	*t*-2,2′-DPaE	(*E*)-2,2′,5,5′-tetraazastilbene
V	*c*-4,4′-DiQE	(*Z*)-dibenzo[*e*,*e*′]-3,3′-diazastilbene
VI	*t*-4,4′-DiQE	(*E*)-dibenzo[*e*,*e*′]-3,3′-diazastilbene
VII	*t*-2,2′-DPyE·2CH$_3$I	(*E*)-6,6′-dimethyl-6,6′-diazoniastilbene diiodide
VIII	*t*-2,2′-DPyE·CH$_3$I	(*E*)-6-methyl-6-azonia-2′-azastilbene iodide
IX	*t*-4,4′-DPyE·2CH$_3$I	(*E*)-4,4′-dimethyl-4,4′-diazoniastilbene diiodide

the advantage of a uniform numbering of atoms of all nine compounds based on that of stilbene (Figure 2). Table II gives the corresponding nomenclature of the analyzed products; it agrees with the numbering rule mentioned above and takes account of the conformations observed in the crystals resulting from rotations around C(1)–C(α) and C(β)–C(1′) bonds.

Table III gives the crystallographic data while Table IV indicates the procedure used in measuring diffraction spectra, and in the resolution and refinement of structures for the nine products. Final atomic parameters, temperature factors, and bond lengths and angles are given as supplementary material in the microfilm edition.

It should be pointed out that IV has been obtained in two different crystalline modifications, a monoclinic one from benzene and a triclinic form from cyclohexane. It was, however, not possible to obtain triclinic crystals of sufficient quality to permit a complete structural analysis; nevertheless a small number of Bragg reflections were observed and the symmetry and cell parameters were

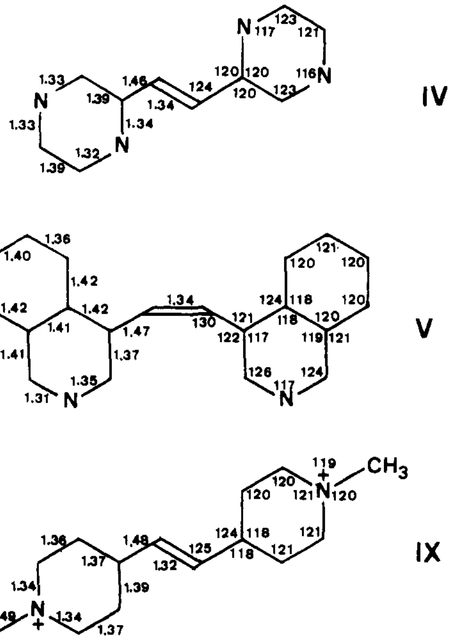

Figure 4. Bond lengths and angles of azastilbenes: (IV) (*E*)-2,2′,5,5′-tetraazastilbene, (V) (*Z*)-dibenzo[*e*,*e*′]-3,3′-diazastilbene, (IX) (*E*)-4,4′-dimethyl-4,4′-diazoniastilbene diiodide.

determined (see Table III). Considering that the triclinic unit contains only one molecule, a very interesting observation can be made; namely, the shortest distance between two neighboring molecule centers is equal to 3.85 Å and should therefore allow a topochemical dimerization.

Discussion

For eight of the nine molecules analyzed by X-ray methods, the asymmetric unit contains half a molecule; only VIII is an exception. In seven of these eight molecules, the two half-molecules are related by a crystallographic inversion center; these trans isomers thus have strictly centrosymmetric conformations. In the eighth (V) the symmetry operation that relates the two half-molecules is a twofold rotation axis, which is often found for a cis isomer; its molecular structure is given in Figure 3. It should be noticed that III (for which the molecular structure is asymmetric) presents an apparent centrosymmetry due to disorder at the positions 2 and 2′. These positions are occupied 50% of the time, alternatively by

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Table III. Crystallographic Data

	I	II	III	IV		V	VI	VII	VIII	IX
formula unit	$C_{12}H_{10}N_2$	$C_{12}H_{10}N_2$	$C_{11}H_9N_3$	$C_{10}H_8N_4$		$C_{20}H_{14}N_2$	$C_{20}H_{14}N_2$	$C_{14}H_{16}N_2I_2$	$C_{13}H_{13}N_2I$	$C_{14}H_{16}N_2I_2$
system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	*Pbca*	*P*2$_1$/*a*	*P*2$_1$/*n*	*P*2$_1$/*a*	*P*1 or *P*$\bar{1}$	*C*2/*c*	*Pcab*	*P*$\bar{1}$	*P*$\bar{2}_1$/*a*	*P*2$_1$/*n*
unit cell										
a, Å	9.810 (4)	7.822 (2)	11.740 (4)	9.190 (4)	11.52 (2)	16.079 (5)	12.722 (4)	8.119 (3)	13.644 (4)	11.901 (3)
b, Å	7.206 (2)	10.562 (4)	5.385 (2)	5.894 (2)	5.26 (1)	6.399 (2)	14.843 (5)	7.017 (2)	10.489 (3)	11.275 (3)
c, Å	13.693 (4)	5.772 (2)	7.474 (2)	9.080 (4)	3.85 (1)	15.688 (5)	7.556 (2)	7.743 (2)	9.713 (3)	6.271 (1)
α, deg					101.2 (1)			84.19 (2)		
β, deg		92.68 (2)	100.13 (2)	114.77 (2)	92.4 (1)	117.73 (2)		61.56 (2)	110.67 (2)	100.83 (2)
γ, deg					95.1 (1)			80.26 (2)		
V, Å^3	968.0 (6)	476.3 (2)	465.1 (3)	446.6 (3)	227.6 (8)	1428.7 (8)	1426.8 (8)	382.2 (2)	1300.6 (7)	826.5 (3)
M	182.22	182.22	183.21	184.20	184.2	282.34	282.34	466.10	324.16	466.10
Z	4	2	2	2	1	4	4	1	4	2
D_x, g cm^{-3}	1.25	1.27	1.31	1.37	1.34	1.31	1.31	2.03	1.66	1.87
F^- (000)	384	192	192	192	96	592	592	220	632	440

Table IV. X-ray Data, Resolution, and Refinement

	I	II	III	IV (mono)	V	VI	VII	VIII	IX
instrument	Syntex P2	Syntex P2$_1$	Syntex P2$_1$	Picker	Picker	Picker	Picker	Picker	Syntex P2$_1$
radiation	Mo Kα	Cu Kα	Mo Kα	Cu Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα	Mo Kα
filter (f) or graphite monochromator (m)	m	m	m	f Ni	f Zr	f Zr	f Ni	f Ni	m
2Θ$_{max}$, deg	47	114	47	135	47	47	120	100	47
independent reflections									
measured	715	647	688	795	1051	1060	1103	1334	1222
observed	419	423	618	737	793	643	1042	1175	1077
resolution[34, 35]	MULTAN 77	MULTAN 77	MULTAN 77	MULTAN 78	MULTAN 77	MULTAN 77	Patterson	MULTAN 77	MULTAN 77
refinement[36, 37]	XRAY 72	XRAY 72	XRAY 72	SHELX 76	XRAY 72	XRAY 72	XRAY 72	XRAY 72	XRAY 72
hydrogen observation	+	+	8/9	+	+	–	–	–	+
final *R*	0.044	0.049	0.053	0.074	0.041	0.104	0.095	0.058	0.018

Table V. Molecular Dimensions of Azastilbenes

	A					B		C		
	I	II	III	IV	M(I to IV)	V	VI	VII	VIII	IX
Lengths, Å										
⟨σ⟩	0.005	0.005	0.003	0.003	0.002	0.004	0.015	0.025	0.017	0.005
central bonds										
C(α)-C(β)	1.335	1.329	1.331	1.335	1.333	1.337	1.331	1.350	1.358	1.321
C(α)-C(1)	1.461	1.463	1.464	1.459	1.462	1.468	1.454	1.472	⟨1.449⟩	1.447
cycles										
⟨C-C⟩	1.384	1.382	1.380	1.388	1.384	1.396	1.404	1.366	1.403	1.375
⟨C-N⟩	1.346	1.330	1.333	1.330	1.335	1.333	1.325		1.355	
⟨C-N$^+$⟩								1.353	1.344	1.338
⟨N$^+$-C(Me)⟩								1.490	1.486	1.489
Angles, deg										
⟨σ⟩	0.3	0.3	0.2	0.2	0.2	0.2	0.9	1.7	1.1	0.3
between central bonds										
C(β)-C(α)-C(1)	124.7	126.1	125.6	124.3	125.2	130.0	124.0	120.8	⟨122.2⟩	124.6
C(α)-C(1)-C(2)		123.6	120.1		121.8	122.3	120.3	123.3	123.1	123.8
C(α)-C(1)-N(2)	118.0			119.6	118.8				118.9	
C(α)-C(1)-C(6)	120.3	120.3		120.2	120.3	120.5	123.0		117.1	118.4
C(α)-C(1)-N$^+$								117.0	120.1	
endocyclic										
⟨C-C-C⟩	118.8	118.5			118.7	119.3	119.2	119.6	118.8	119.4
⟨C-N-C⟩	117.1	115.4	116.0	116.2	116.2	116.5	118.1		116.8	
⟨N-C-C⟩	123.2	124.6	123.3	121.9	123.3	125.0	124.7		124.4	
⟨C-N$^+$-C⟩								120.6	123.6	120.7
⟨C-C-N$^+$⟩								120.3	119.0	120.6
⟨C-N$^+$-C(Me)⟩								119.7	118.2	119.5
Torsion Angles, deg										
⟨σ⟩	1	1	1	1		1	2	2	2	1
C(1)-C(α)-C(β)-C(1′)	180	180	180	180	-	−5	180	180	+179	180
C(β)-C(α)-C(1)-(2)	+7	−8	−1	0	-	−39	−38	−32	+13; −5[a]	+8
C(β)-C(α)-C(1)-C(6)	−172	+172	+178	180	-	+145	+143	+150	−169; +174[a]	−172
Shortest Distance, *d*, Å, between C(α) = C(β) Double Bond Centers[b]										
d	6.09	5.77	5.39	5.46[b]	-	6.40	7.40	7.02	3.76	6.27

[a] C(β)-C(α)-C(1)-(2′) and C(β)-C(α)-C(1)-(6′). [b] In the triclinic variety, of which the cell parameters are given in Table III, this distance is much shorter and is equal to 3.85 Å.

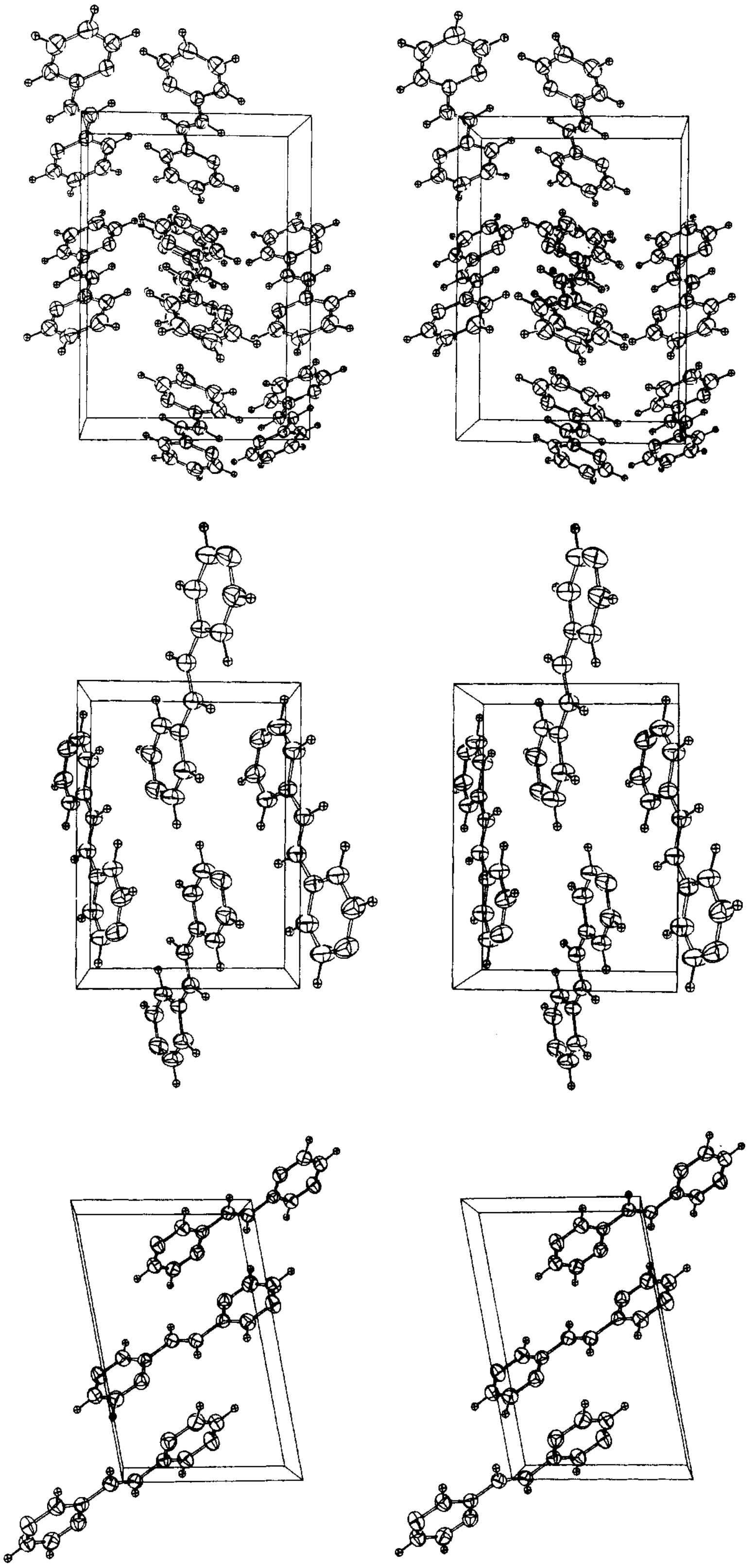

Figure 5. Molecular stacking of (I, top) (*E*)-2,2′-diazastilbene, view down *b* with *a* horizontal and *c* vertical; (II, middle) (*E*)-4,4′-diazastilbene, view down *c* with *a* horizontal and *b* vertical; (III, bottom) (*E*)-2′,5,5′-triazastilbene, view down *b* with *c* horizontal and *a* vertical.

a carbon or a nitrogen atom.

The nine substances may be grouped in three classes:

(A) I–IV (di-, tri-, or tetraazastilbenes): These compounds were analyzed with a similar precision; it is therefore possible to obtain meaningful mean values of some molecular parameters.

(B) V and VI are cis/trans isomers, directly comparable to each other though the structure determination of V is much more precise than that of VI.

(C) VII–IX are iodides of organic cations derived from molecules of class A. Analysis of IX had a precision similar to that for I–V; VII and VIII are less accurate and rather similar to VI as far as precision is concerned.

Table V gives the central bond lengths and angles and the mean values of the ring dimensions for each molecule. Column M presents the mean values as calculated for the

Table VI. Distances (Å) and Angles (deg) in Pyridine and Pyrazine Rings

	pyridine MW[39]	pyridine RX[40]	pyrazine RX[41]	present data
⟨C-C⟩	1.394 (1)	1.367 (3)	1.378 (3)	1.384 (1)
⟨C-N⟩	1.340 (1)	1.330 (4)	1.334 (3)	1.335 (2)
⟨C-C-C⟩	118.5 (1)	118.9 (2)		118.7 (2)
⟨C-N-C⟩	116.8 (1)	116.5 (4)	115.1 (3)	116.2 (2)
⟨N-C-C⟩	123.9 (1)	123.5 (3)	122.4 (3)	123.3 (2)

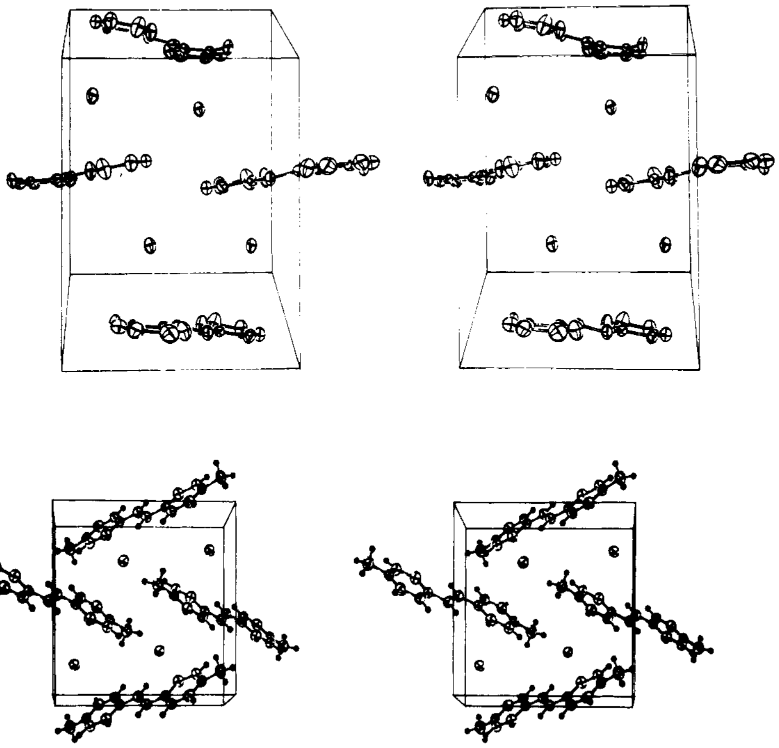

Figure 6. Molecular stacking of (VIII, upper) (*E*)-6-methyl-6-azonia-2′-azastilbene iodide, view down *c* with *b* horizontal and *a* vertical; (IX, lower) (*E*)-4,4′-dimethyl-4,4′-diazoniastilbene diiodide, view down *c* with *b* horizontal and *a* vertical.

observation for I–IV. As examples, all bond lengths and valence angles are given for compounds IV, V, and IX (Figure 4). It can be seen that the individual values do not differ significantly from the mean values of Table V. The situation is identical for the other compounds analyzed with the same precision. However, as would be expected, the C–C or C–N lengths are not equivalent in the isoquinoline rings; for V the experimental values agree well with other determinations on isoquinoline derivatives, e.g., the structure of 6-cyano-7-(2-aminophenyl)isoquinoline.[38] From the data of Table V the following statements can be made: (1) excellent agreement of bond lengths and angles for compounds I–IV; the differences could be rather more significant for the angles than for the distances, taking account that angles are more easily deformed than interatomic distances; (2) similarity of the values in columns M and V, and of those for V and VI, if account is taken of the higher standard deviations for VI; the only one significative disagreement is for the angle C(β)–C(α)–C(1) which, probably for steric reasons, is 6° larger for the cis isomer than for the trans one; (3) good agreement between the values of column IX (class C) and those of columns M and V (class A and B).

In the pyridinium groups, the endocyclic angles have a tendency to become equal, while the ⟨C–C–C⟩, ⟨C–N–C⟩, ⟨N–C–C⟩ are significantly different in the pyridyl and pyrazinyl rings. This last observation agrees with those in the literature (Table VI).

Table VII. Closest Interionic Contacts (Å) in Azoniastilbene Iodides

	VII	VIII	IX
$I^- \cdots I^-$	4.95	5.97	5.26
$I^- \cdots N^+$	3.90	4.41	3.70

III, which shows disorder N/C in the occupancy of sites 2 and 2′, exhibits distances (C–(N/C) = 1.360 Å) and angles (C–(N/C)–C = 117.5°, (N/C)–C–C = 119.9°) intermediate between those observed when N/C is replaced either by nitrogen or by carbon. Molecular conformations are described by the torsion angles indicated in Table V. The rings as well as their methyl/carbon substituents are planar in all cases within the limits of experimental error, regardless of whether the nitrogen carries a positive charge or not.

Examples of the positions of the molecules in the unit cell can be seen in Figures 5 and 6.

Table V also gives the values of the shortest distances between the centers of two double bonds C(α) = C(β) in the several examples examined. Only VIII and the triclinic variety of IV present a distance sufficiently short for cyclodimerization.[42] In the iodides VII–IX the anion is located at distances of about 4 Å from the positively charged nitrogen cation. Contacts between ions are

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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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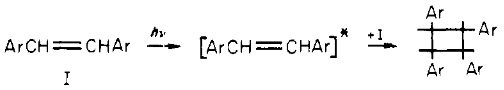
The photochemical behavior of several azastilbenes has been followed in concentrated solution and in the solid state. In acetonitrile and benzene isomerization and dimerization occur, the reactions being generally faster in acetonitrile. In methanol, however, photoreduction as well as photoaddition of 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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