Controlled Photocycloaddition of Stilbazolium Ions Intercalated in Saponite Clay Layers

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The photochemical cycloaddition of stilbazolium ions intercalated in clay layers has been studied. *syn* Head-to-tail dimers were predominantly formed at the expense of *E–Z* isomerization which is a major path in homogeneous solution. The selective formation of head-to-tail dimers suggests that the intercalation occurs in an antiparallel fashion. The dimerization efficiencies were not affected even when the degree of adsorption of alkene molecules on the anionic-exchange site of the clay was decreased from 100 to 1%. The intercalated stilbazolium ions exhibited a strong excimer emission at 490–520 nm in addition to the monomer fluorescence at 380–450 nm. The strong excimer emission was not decreased even at 0.1% adsorption. These facts suggest that the intercalation starts *via* formation of small aggregates of adsorbate molecules, caused by their hydrophobic attraction. Details of the intercalation and photocycloaddition are discussed.

Surface photochemistry concerning the spacially controlled alignment of adsorbed organic substrates is an intriguing subject. Although such studies have extensively been concerned with micelles of organic surfactants,[1] only a limited number of reports on the photochemical behaviour of substrates adsorbed on inorganic surfaces such as zeolites and clay minerals have appeared.[2,3] Silicate or ZSM-zeolite with relatively narrow cavities (*ca.* 6 Å diameter) is known to adsorb organic molecules selectively, depending on their molecular size, causing a substantial conformational restriction of the adsorbates. Hence, their photochemical behaviour has been found to be unusual and in sharp contrast to that in solutions.[4]

On the other hand, clay minerals possess interlayers with anionic-exchange sites and can adsorb, by their cation-exchange abilities, cationic materials to form a molecular aggregate.[5] Here cationic molecules are fixed electrostatically on anionic-exchange sites regularly scattered throughout the layers. A number of examples have been reported in which cationic surfactant molecules are oriented perpendicularly to their layer surfaces and which can sometimes arrange to form a monolayer of alternately oppositely oriented molecules.[6,7]

In relation to studies on the effect of electrostatic fields, *e.g.*, micelles, on photochemical reactions,[8] we are interested in the charged inorganic surfaces of clay minerals, and have published our results as a communication.[9] Independently, Backer and Whitten[10] have recently reported on the photochemical cyclodimerization of 2- and 4-stilbazolium ions on Montmorillonite clay. The present paper deals with our results on the molecular packing of stilbazolium ions in clay layers and their photochemical behaviour.

Results and Discussion

Irradiation of Stilbazolium Ions Adsorbed on Clay.—(*E*)-Stilbazolium ion [(*E*)-(1a)] was easily adsorbed on Saponite clay simply by mixing both components in water, resulting in the precipitation of the clay-intercalated (*E*)-(1). The Saponite clay had 80% transmittance at 300 nm and 95% transmittance at >500 nm, and its cation-exchange capacity (CEC) was 99.7 mequiv./100 g.† The intercalation of compound (1a) was almost quantitative on the basis of the CEC of the clay.

Irradiation of the clay-intercalated (*E*)-(1a) suspended in water with UV light (>300 nm) afforded predominantly *syn*

Py⁺ = HN⁺⟨ ⟩-§

a; Ar = Ph
b; Ar = *p*-MeC$_6$H$_4$
c; Ar = *p*-ClC$_6$H$_4$
d; Ar = *p*-NCC$_6$H$_4$
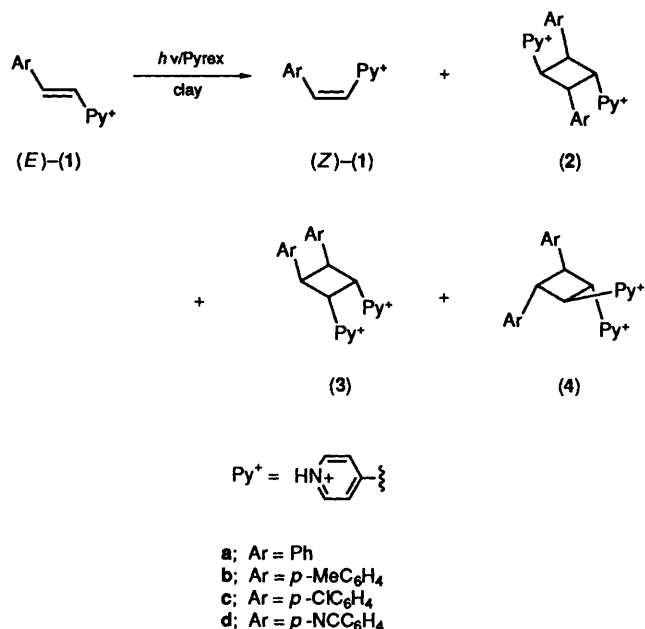
head-to-tail cyclodimer (2a) in addition to small amounts of *syn* head-to-head dimer (3a) and some *E–Z* isomerization of compound (1a) as shown in Table 1. The results of experiments in the absence of clay are shown in parenthesis in Table 1; irradiation of (*E*)-(1a) without clay in 10% aq. methanol resulted mostly in *E–Z* isomerization, the photocyclodimerization being a minor process, affording only trace amounts of compound (2a) and *anti* head-to-head dimer (4a). Similarly, *syn* head-to-tail dimers (2) were formed selectively from the substituted substrates (1b) (*p*-Me) and (1c) (*p*-Cl) in the presence of clay.

Isolation and characterization of products were as follows. The reaction mixture, after irradiation, was treated with excess

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† The amounts of adsorbed (1) were estimated from those of the remaining alkene in the filtrate after work-up of the reaction mixture.

Table 1. Products from the irradiation of stilabazolium ions (1) intercalated on Saponite clay.[a]

Ar in (1)		Conversion (%)	Products (%)				(2)/(3)	pK_a of (1)
			(Z)-(1)	(2)	(3)	(4)		
Ph	(1a)	87	15	79	6	0	13	5.17[b]
		(68)	(97)	(2)	(0)	(1)		
p-MeC$_6$H$_4$	(1b)	76	24	76	0	0	>100	5.02[b]
		(54)	(92)	(8)	(0)	(0)		
p-ClC$_6$H$_4$	(1c)	96	7	93	0	0	>100	4.88[b]
		(76)	(>99)	(0)	(0)	(0)		
p-NCC$_6$H$_4$	(1d)	88	33	35	32	0	1.1	4.5[c]
		91[d]	42	34	24	0	1.4	
		(97)	(96)	(4)	(0)	(0)		

[a] A suspended mixture of stilbazolium ions (1 mmol dm^{-3}) and an equivalent amount of Saponite clay was irradiated through a Pyrex filter (>300 nm) for 30 min. See Experimental section for details. The figures in parentheses are those of homogeneous reactions without clay in 10% aq. methanol. [b] Cited from the literature; J. C. Doty, J. L. R. Williams, and P. J. Grisdale, Can. J. Chem., 1969, 47, 2355. [c] Determined according to the literature; shown in footnote b. [d] Reaction in the presence of 2.1 mol dm^{-3} HCl.

Table 2. Interlayer space distance of stilbazolium ion-intercalated clay.[a]

Additive	Clearance space/Å
None[b]	6.2
(1a)	9.2
(1b)	9.5
(1d)	9.4

[a] An equivalent amount of compound (1) was intercalated. [b] Saponite clay without any additives.
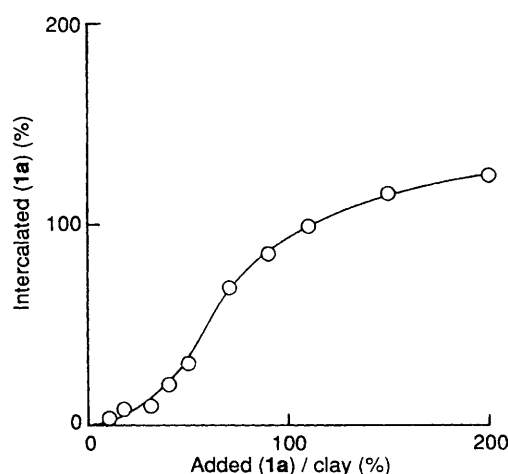

Figure 1. An intercalation curve of stilbazolium ion (1a) on Saponite clay in water; [clay] 0.898 mmol dm^{-3} (vs. CEC) and [(1a)] 0.09–1.8 mmol dm^{-3}. The amount of intercalated (1a) was determined by filtering out the (1a)-adsorbed clay.

of conc. hydrochloric acid overnight at room temperature to decompose the layer structure of clay,* and was then neutralized with aq. sodium hydroxide and extracted with

* The layer structure of Sumecton SA has been confirmed (X-ray diffraction analysis) to be decomposed under the conditions used here.
† The proportions among dimers (2a), (3a), and (4a) were coincident within experimental error (±10%) before and after the work-up described in the text.

dichloromethane.† Dimers were purified by silica gel chromatography, isolated as white solids, and their NMR spectra exhibited typical cyclobutane ring protons at $\delta_H \sim 4.4$, which were identical with those of authentic samples synthesized independently (see Experimental section for details).

Interesting points in Table 1 are the dramatic reduction in the E–Z photoisomerization of compounds (1) and the selective formation of syn head-to-tail cyclodimer (2). This observation is suggestive of antiparallel adsorption of the ionic alkene molecules on the clay interlayers, leading to efficient photodimerization to afford head-to-tail dimer (2), without any product arising from E–Z isomerization being formed.

p-Cyano alkene [(E)-(1d)], however, gave a considerable amount of syn head-to-head dimer (3d) in addition to the expected dimer (2d) (Table 1). The lower regioselectivity of the dimerization implies a considerable disordering of the alkene packing in the clay layers. A possible explanation for the disordering may be co-ordination of the cyano group to sodium ions on the layer surface in addition to the adsorption of the pyridinium cation, which would cause a disordered orientation and hence non-regioselective dimerization. Cyano groups are known to co-ordinate easily to metallic or non-metallic cations in clay layers.[11] Another explanation for the disordering might be an involvement of the non-protonated cyano alkene, but the difference in pK_a values in Table 1 is too small for this to be a definite possibility.

Intercalation of Stilbazolium Ions on Clay.—Saponite clay minerals used in the present study have anionically charged layers in which cations are intercalated. The intercalation of stilbazolium ion was performed by mixing of compound (1) and the clay, resulting in the precipitation of clay-intercalated compound (1). Intercalation was increased with increasing amounts of compound (1a) up to the equivalent of the CEC of clay. As shown in Figure 1, the addition of an excess of compound (1a) produced a plateau in the intercalation at ca. 150% adsorption based on the CEC. In the present study experiments were performed mostly at equivalent amounts of compound (1) and CEC, i.e., 100% adsorption, unless otherwise noted in the text.

A colloidal suspension of the clay minerals or the alkene-intercalated clays in water was filtered and air-dried at room temperature. The resulting powdered clay was analysed by X-ray powder diffraction spectroscopy. Table 2 shows the resulting
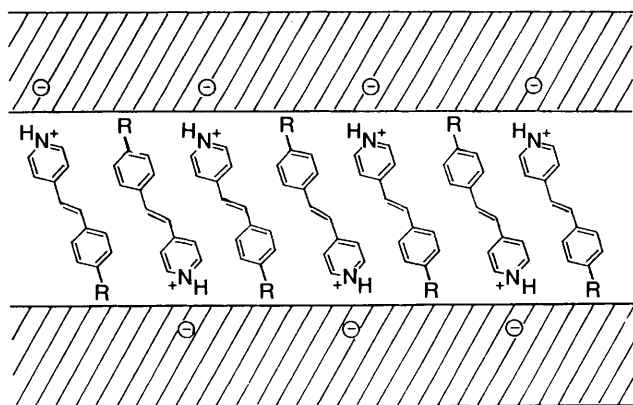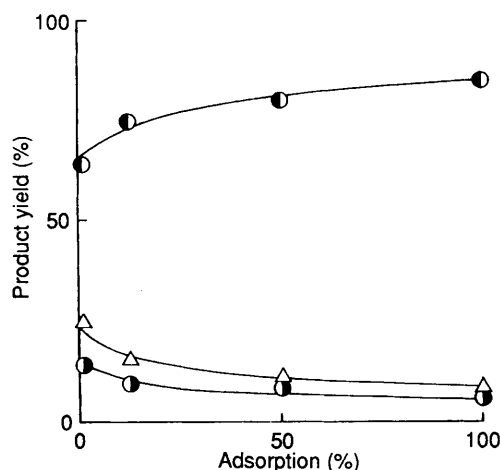
Figure 2.

Figure 3. Effect of degree of adsorption of substrate (1a) on the efficiency of photodimerization; –◐–, yield of (2a); –◑–, yield of (3a); –△–, yield of (Z)-(1a). A suspended solution of compound (1a) (1 mmol dm⁻³) and clay (1–80 mmol dm⁻³) was irradiated at >300 nm for 30 min under argon. The degree of adsorption was calculated from the ratios of (1a) vs. the CEC of clay.

clearance spaces, which were calculated by subtracting the layer thickness from the 001 basal spacings obtained. The space value of clay itself was 6.2 Å and the intercalation of equivalent amounts of (1a–1d) elongated the interlayer distance up to 9.2–9.5 Å. Note that these distances are comparable with the molecular lengths of compounds (1); *e.g.* 10.4 Å for (*E*)-(1a).

The cation-adsorbing sites of the clay are scattered on both sides of the interlayers, with average intervals of *ca.* 11 Å as estimated by the lattice constant and the molecular composition.[12,]* Thus, (*E*)-(1)-adsorbed clay interlayers can be depicted as in Figure 2.† A similar orientation of adsorbates has been suggested in the case of n-alkylammonium cations.[7]

* Calculated from the values of the Technical Bulletin of Sumecton SA by Kunimine Ind.
† Alternative possibility is a planar adsorption, *i.e.* parallel to the layer surface, of stilbazolium ions. This type of adsorption, however, is not likely since one alkene molecule would cover some neighbouring adsorption sites. In other words, this model cannot explain the 100% adsorption of alkene molecules.
‡ The small increase of absorbance at >380 nm as observed for the clay-intercalated substrate (1a) seems to indicate a charge-transfer-type interaction between adsorbed stilbazolium ions. We hope to clarify the nature of the intercalation by choosing more appropriate systems for study.
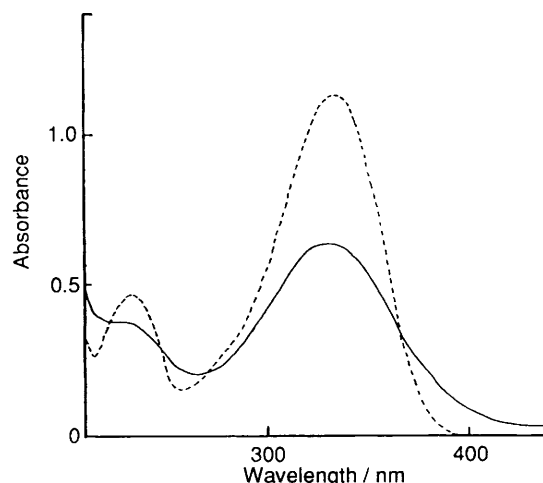

Figure 4. Absorption spectrum of compound (1a) adsorbed on Saponite clay (——) in water; 50 μmol dm⁻³ (1a), 50 μmol dm⁻³ equivalent clay, and 60 μmol dm⁻³ HCl. The dotted line (– – –) is the absorption of compound (1a) in homogeneous aq. solution; 50 μmol dm⁻³ (1a) and 60 μmol dm⁻³ HCl.
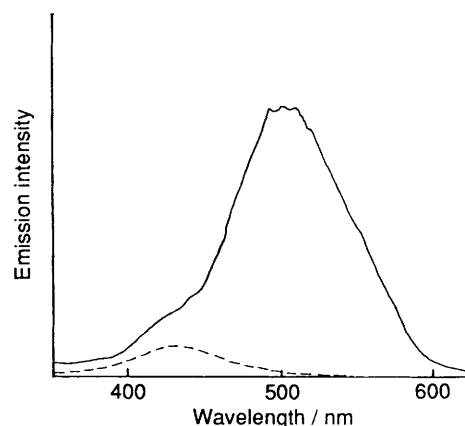

Figure 5. Emission spectrum of compound (1a) adsorbed on clay (——) and without clay (– – –). Excited at 330 nm for 10 μmol dm⁻³ each of compound (1a) and clay in water containing 0.02% methanol. The emission maxima of substituted stilbazolium ions are shown in Table 3.

Here it is notable that the percentage adsorption of compounds (1) on clay exhibited no significant effect on the relative efficiencies of photodimerization. Figure 3 shows the effect of percentage adsorption on the relative efficiency of photodimerization. No significant difference was observed between 1% and 100% adsorption efficiencies. Moreover, the regioisomer ratios of dimers (2) and (3) were practically independent of the degree of adsorption. These facts suggest that alkene molecules are not dispersed but are adsorbed as aggregates in the clay layers.

Absorption and Fluorescence Spectra of Intercalated Compounds (1).—The clay-adsorbed substrate (1a) as colloidal suspension showed a UV spectrum with absorption maxima at 235 and 334 nm which were practically the same as those in homogeneous aq. solution as shown in Figure 4.‡ However, the fluorescence spectrum of clay-adsorbed (1a) was quite different from that in the absence of clay (Figure 5). Absorption and fluorescence spectra of a series of substituted stilbazolium ions (1a–d) exhibited a similar trend, as summarized in Table 3. Excimer fluorescence maxima of intercalated compounds (1) were observed at 490–515 nm at the expense of their monomer fluorescences at *ca.* 385–450 nm.

Table 3. Absorption and emission maxima of compounds (1) adsorbed on clay.

	Stilbazolium ion	Maximum wavelength/nm	
		Clay	Without clay
Absorption[a]	(1a)	334	334
	(1b)	348	349
	(1c)	330	325
	(1d)	328	329
Emission[b]	(1a)	500	430
	(1b)	516	448
	(1c)	498	438
	(1d)	488, 385	385

[a] Absorption spectra were determined with 20 $\mu mol\ dm^{-3}$ (1), an equivalent amount of Saponite clay, and 24 $\mu mol\ dm^{-3}$ HCl in water. [b] Emission spectra were obtained by 330 nm excitation of an aq. solution of 10 $\mu mol\ dm^{-3}$ (1), 10 $\mu mol\ dm^{-3}$ clay, and 12 $\mu mol\ dm^{-3}$ HCl at room temperature.

Figure 7. Dependence of the excimer fluorescence intensity (I) of compound (1a) upon its degree of adsorption; see Figure 6 for conditions. I_{max} is the maximum intensity of excimer fluorescence at 10% adsorption.
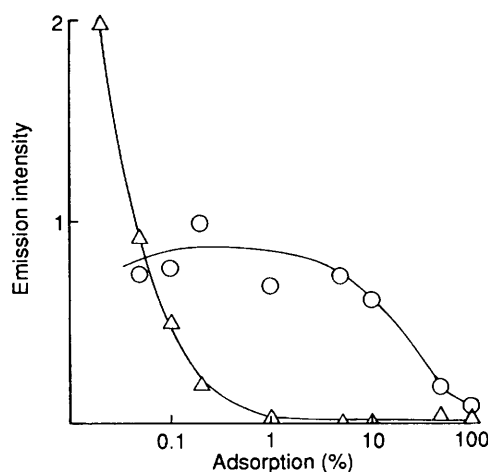

Figure 6. Dependence of emission intensity upon the degree of adsorption of compound (1a) on clay interlayer: 1 $\mu mol\ dm^{-3}$ (1a), 1–5 000 $\mu mol\ dm^{-3}$ clay, and 1.2 $\mu mol\ dm^{-3}$ HCl. Excitation at 335 nm; emission of monomer (-△-) and excimer (-○-). Degree of adsorption was calculated from the ratio of (1a) vs. CEC of clay.

The dependence of the emission intensities of compound (1a) on the degree of adsorption is shown in Figure 6. The monomer fluorescence disappeared at *ca.* 1% adsorption based on the CEC of the clay. It is interesting to note that the intensity of excimer fluorescence remained constant over a range of adsorption of 0.2–10%. Excimer fluorescence disappeared only at below *ca.* 0.02% adsorption. These facts indicate that the alkene molecules are adsorbed inhomogeneously and probably as aggregates. This correlates nicely with the observed constant efficiency of cyclodimerization, as mentioned previously, regardless of the degree of adsorption over the range 1–100%.

The decrease in excimer fluorescence at >10% adsorption may be due to self-quenching by adjacent molecules. This could be verified in a Stern–Volmer-type plot, as shown in Figure 7; the static quenching is shown as the linearity of the plot in the range of 10–100% adsorption.

Aggregation and Packing of Intercalated Molecules.—All of the results mentioned above indicate that alkene molecules are adsorbed inhomogeneously on the layer surfaces of clay, forming aggregates even at very low adsorption (*e.g.* 1%). Hence, the
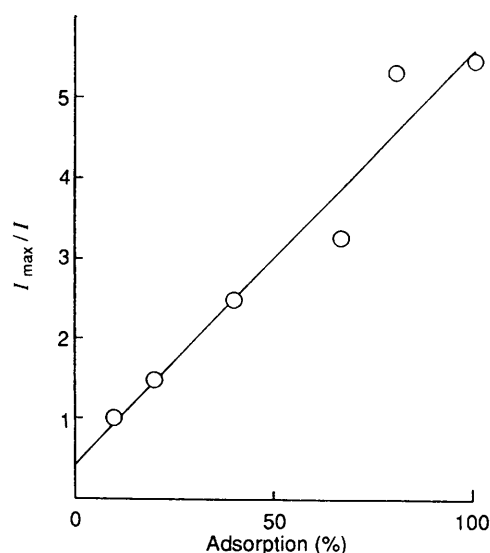
photodimerization proceeds smoothly under conditions of very low adsorption.

The average distance between anionic-exchange sites on the interlayers has been estimated to be *ca.* 11 Å from the lattice constant and the chemical formula of Saponite clay. Then the cationic alkene molecules are adsorbed as chequers of 11 Å side-length, and incorporation of each side of the layer reasonably results in the antiparallel packing of alkene molecules as shown in Figure 2. This is exactly in line with the predominant formation of head-to-tail cyclodimers as observed. The combination or packing of two chequers of 11 Å side-length results in the distance between the adsorbed molecules being in the range of 5.5–7.8 Å. This distance between alkene molecules seems to aid cyclodimerization because the alkenes can easily interact with each other, needing only a minimum movement over a very small distance for orbital overlap to occur. In other words, the alkene molecules can easily attain the close intermolecular distance of ~ 4.2 Å, which is reported to be the best distance for [2 + 2] photodimerization in the solid state.[13]

Conclusions.—It is shown that clay interlayers serve as a stable and characteristic reaction field suitable for photodimerizations. Thus, the stilbazolium ions intercalated in clay layers readily undergo regioselective [2 + 2] photocyclodimerization. The selective formation of *syn* head-to-tail dimers indicates that the intercalation is of antiparallel fashion. It is shown that the intercalation starts by the formation of small aggregates owing to hydrophobic interaction between the adsorbate molecules.

Experimental

Materials.—A synthesized Saponite clay was used: Sumecton SA, >110 mesh (Kunimine Ind. Co., Japan); chemical formula $[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]^{0.77-}$ $(Na_{0.49}Mg_{0.14})^{0.77+}$. Its reflection spectrum showed *ca.* 80% transmittance at 300 nm and complete transmittance at >500 nm. Cation-exchange capacity (CEC) of the clay was estimated to be 99.68 mequiv./100 g. Substituted stilbazolium ions (1b–d) were synthesized by the condensation of γ-picoline and corresponding benzaldehydes according to the literature method;[14,15] *p*-H, m.p. 132–133 °C (lit.,[15] 131–133 °C); *p*-Me,

Table 4. Analytical data of the cyclodimers.

Dimer	Ar	$t_R{}^a$/min	Chemical shift of cyclobutane protons (δ_H)[b]		Fragment ions in mass spectrum $(M^+/z)^c$
(2a)	Ph	8.4	4.37	4.41	180[d]
(2b)	p-MeC$_6$H$_4$	7.0	4.39	4.42	208 (1), 196 (21), 195 (100)
(2c)	p-ClC$_6$H$_4$	10	4.38	4.41	217 (34), 215 (100), 180 (36)
(2d)	p-NCC$_6$H$_4$	36	e		207 (14), 206 (100)
(3a)	Ph	9.8	4.39	4.40	180[d]
(3b)	p-MeC$_6$H$_4$	9.1	4.40	4.41	208 (4), 196 (19), 195 (100)
(3c)	p-ClC$_6$H$_4$	14	4.40		250 (2), 248 (4), 217 (56) 215 (100), 180 (64)
(3d)	p-NCC$_6$H$_4$	44	4.51	4.55	230 (16), 207 (16), 206 (100)

[a] Retention times in HPLC analysis with a Sil-NH$_2$ column with hexane–ethanol–aq. ammonium hydroxide as eluant. [b] Analysed with a 200 MHz FT-NMR spectrometer. [c] Mass spectral data were obtained by 20 eV electron bombardment. The values in parentheses are the relative intensities. [d] Fragments from the cyclodimers (3a) were stilbene, dipyridylethylene, and compound (1a) moieties, which show m/z 180. The data were thus not appropriate for the identification of dimers (2a) and (3a). [e] Dimer (2d) was sparingly soluble in any ordinary solvent used for NMR analysis.

m.p. 147–152 °C (lit.,[15] 147–150 °C); p-Cl, m.p. 111–113 °C (lit.,[15] 112–113 °C); p-CN, m.p. 139–140 °C (lit.,[15] 139–140 °C).

Irradiation of Stilbazolium Ions Adsorbed on Clay.—A 10% aq. methanol solution of stilbazolium ions (1 mmol dm^{-3}) containing 1.2 mmol dm^{-3} HCl was treated with Saponite clay colloid (20–25 mg) in water to give yellow or pale yellow precipitates. The stirred mixture was irradiated at >300 nm through a Pyrex filter using a medium-pressure Hg lamp under argon for 30 min. The reaction mixture was concentrated by evaporation of solvent, treated with conc. HCl (20 cm^3), and kept overnight at room temperature to decompose the clay layer structure. After neutralization with 7.5 mol dm^{-3} NaOH the products were extracted with CH$_2$Cl$_2$ and analysed by


(2c)

(3c)

HPLC in comparison with authentic samples prepared independently. HPLC analysis was carried out using a Jasco UVIDEC-100-III HPLC instrument with a UV detector (250 nm) and a Sil-NH$_2$ column; a mixed eluant of hexane–ethanol–25% aq. ammonium hydroxide (400:100:1 in v/v) was used. The authentic samples of *syn* head-to-tail dimers (2) and *anti* head-to-head dimers (4) were prepared by UV irradiation of concentrated solution of compounds (1) (*ca.* 1 mol dm^{-3}) in aq. hydrochloric acid.[14,16] *syn* Head-to-head dimers (3) were obtained by UV irradiation of compounds (1) in AOT (Aerosol OT) reversed micelles.[14,17]

The structures of these dimers were characterized by their mass and NMR spectra, using a JEOL JMSD-300 mass spectrometer and a Varian Gemini 200 NMR spectrometer, respectively. Fragment ions in the mass spectra involve monomer units from dimers (2), and furthermore disubstituted stilbene and dipyridylethylene moieties from dimers (3). For example, while fragment ions from compound (2c) involve only m/z 217 and 215, those from compound (3c) were m/z 217, 215, 250, 248, and 180. In NMR spectra the characteristic cyclobutane methine protons show a symmetric multiplet, and the splitting in compounds (2) was wider than that in compounds (3). These analytical data are compiled in Table 4.

X-Ray Powder Diffraction of Intercalated Clay.—The powdered sample was prepared as follows. An aq. solution of stilbazolium ions (1 mmol dm^{-3}) containing 36 mmol dm^{-3} HCl was treated with an equivalent amount of Saponite clay (*vs.* CEC) in 10% aq. methanol to give a yellow precipitate. After filtration through a membrane filter (Toyo Roshi, Ltd., 0.45 μm), the sample was dried *in vacuo* at room temperature for 1 day and was then ground in a mortar. The intercalated clay samples were measured by X-ray powder diffraction analysis with an X-ray diffractometer (Riken Ind. Ltd.) with Ni-filtered Cu-K_α radiation. The 001 basal spacings of the layers were measured by the Debye–Scherrer method. The values for the clearance space were obtained by subtraction of silicate layer thickness, 6.6 Å, from the basal spacings, and are summarized in Table 2.

Measurement of Monomer and Excimer Fluorescence of Intercalated Compound (1).—The fluorescence spectra were recorded on an Hitachi 650-10S Fluorescence Spectrometer. Samples ($\sim 10^{-5}$ mol dm^{-3}) were dissolved in 10% aq. methanol in the presence of clay, and the emission spectra were taken under Ar-purged conditions.

The fluorescence intensity dependence on the degree of
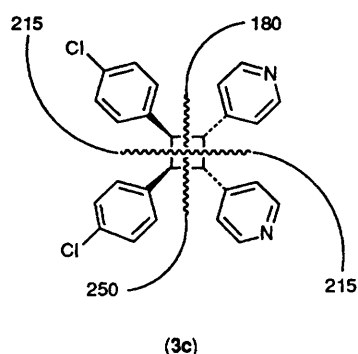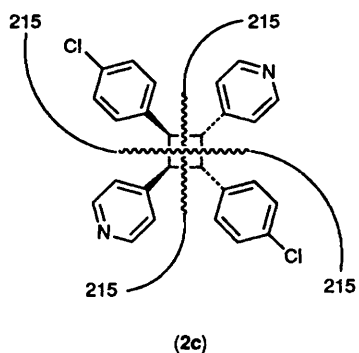
adsorption was measured by changing the amount of clay while keeping the concentration and hence the excitation efficiency of compounds (1) constant.

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