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Selective Topochemical Photodimerization of Styryldicyanopyrazines in the Solid State†

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Selective topochemical photodimerization of styryldicyanopyrazines proceeded in the solid state, and their differences in molecular stacking evaluated by X-ray analysis controlled the reactivity and stereochemistry.

Solid state chemistry of organic functional materials is of current interest to correlate their functionality with the molecular stacking behaviour in the solid state. Functional materials useful as organic non-linear optical materials,[1] organic photoconductors[2] and emitters for electroluminescence devices have been studied from the viewpoint of intermolecular π–π interactions of the molecules in the solid state.

In recent years, solid state reactions have been demonstrated to be a suitable method for completely crystalline polymerization[3] and absolute asymmetric syntheses with quantitative enantiomeric yield.[4] Topochemical photoreactions in the solid state give highly regioselective and stereoselective products because the mobility of each molecule is restricted compared with that in solution.[5] One of the attractive photoreactions is $[2\pi + 2\pi]$-cycloaddition in which topochemical dimerization and polymerization proceed.[6,7]

In this work, photocycloadditions of 2-phenylethenyldicyanopyrazine **1a** and 2-(4-*tert*-butylphenylethenyl)-3-ethyldicyanopyrazine **1b**[8] are studied in solution and in a single crystal. It is seen that the crystal structures, evaluated by X-ray crystal analysis of **1a** and **1b**, strongly influence reactivity for photodimerization.

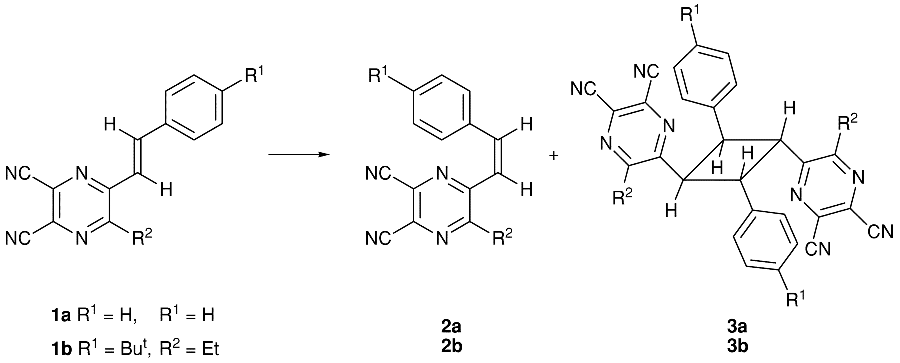
A benzene solution of **1a** was irradiated by 366 nm UV light for 20 h, and **2a** (*cis* isomer of **1a**) and photodimer **3a** were isolated in a ratio of 82 and 18%, respectively, with an overall conversion of 78% (Scheme 1). Similar results were also obtained for **1b** in benzene solution (**2b** and **3b**, 85 and 15%, conv. 81%).

On the other hand, photoreactions of **1a** and **1b** in the solid state gave different results from those in solution. Upon photoirradiation of single crystals of **1a** and **1b** with 366 nm UV light for 15 h a photodimer of **1a** having an *anti* head-to-tail form, **3a**, was obtained in excellent yield (90%), whereas **1b** gave **3b** in poor yield (17%) together with unreacted **1b** (83%). Neither of **2a** and **2b** were obtained in the solid state. For solid state photocycloaddition, it is well known that the crystal structure and the distance between the reactive centers determine the stereoselectivity and the reactivity because of the limited motion of the molecules. The crystal structures of **1a** and **1b** were determined by X-ray crystallography and results are summarized in Table 1.

Table 1 Crystal data for **1a** and **1b**

	1a	**1b**
Chemical formula	$C_{14}H_8N_4$	$C_{20}H_{20}N_4$
M	232.24	316.40
Crystal system	Monoclinic	Orthorhombic
Lattice parameters		
a/Å	7.317(2)	27.772(7)
b/Å	14.155(8)	9.441(2)
c/Å	11.061(3)	7.012(9)
β/°	94.54(3)	—
V/Å^3	1140.3(7)	1838.4(5)
Goodness of fit indicator	1.48	1.89
Space group	$P2_1/c$	$Pna2_1$
Z	4	4
μ/cm^{-1}	0.86	5.45
No. of reflections observed	2278	1669
R	0.056	0.046
R_w	0.072	0.071
Distance between interlayer/Å	3.33	3.54
Distance between double bonds/Å	3.65, 3.66	4.64, 4.65

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research* (*S*), 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/14.



Scheme 1

X-Ray crystal analysis of **1a** reveals a planar layered structure with interlayer distances of 3.33 Å (Fig. 1). Each

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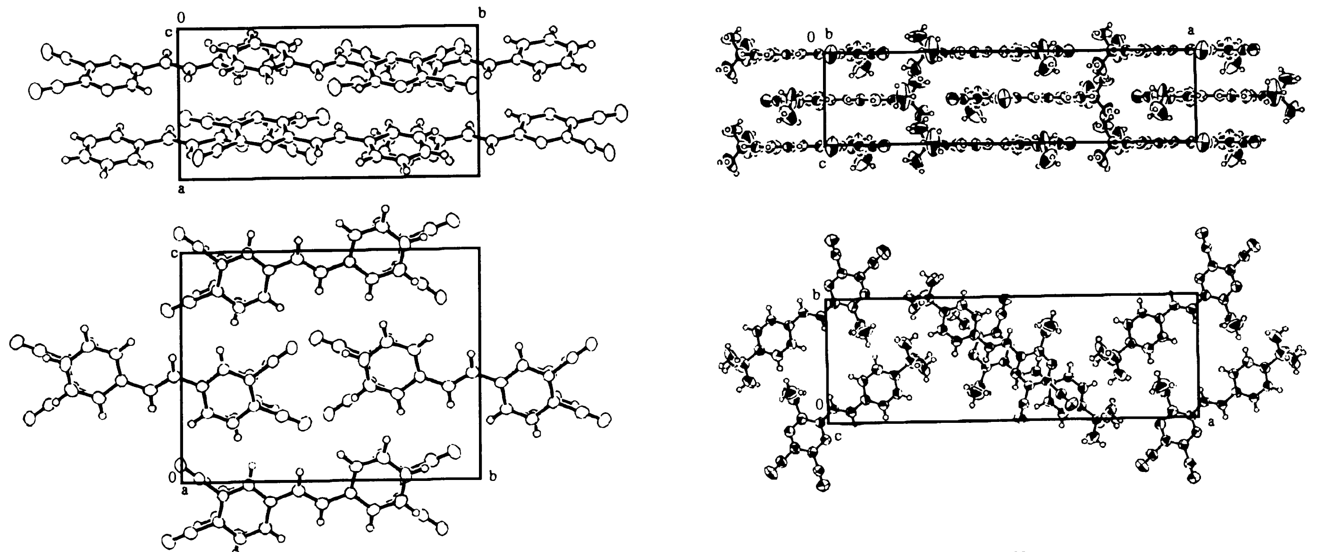

1a **1b**

Fig. 1 The molecular packing arrangements of **1a** and **1b**; interlayer structure (up) and the overlapped pair (down)

molecule is oriented in the same direction, and the nearest neighbours are oriented in the reverse direction. Alternative orientations of each row are observed in the same plane. Molecular pairing is observed between the interlayered structures and two molecules are overlapped completely in the reverse direction to cancel the dipole moment in each of the paired molecules. The reactive double bonds lie parallel to each other and the separation of the corresponding carbon atoms around the double bonds are 3.65 and 3.66 Å (Table 1). There is no doubt that the photoreaction product **3a** in the solid state is the *anti* head-to-tail dimer.

On the other hand, **1b** shows a different crystal structure from that of **1a**, each molecule of **1b** is oriented in a zigzag fashion along the *a*-axis and in the diverse direction to the *b*-axis in a plane to avoid steric repulsion between *tert*-butyl groups. Molecular pairing occurs with the reverse direction between the layered structures and the average distance between the planes is found to be 3.54 Å. However, the steric repulsion of the *tert*-butyl and 5-cyano groups is expected to bring about a slant of overlap in the molecular pairing. The interlayer distances between the two carbon atoms of the reactive double bonds in a pair are 4.64 and 4.65 Å. Similar solid state photodimerization of 4-formyl cinnamic acid has been reported to proceed in spite of remote double bond distances of 4.8 Å.[9] This suggests that topochemical photoreaction occurs with molecular movement in the crystal lattices. For **1b**, it is likely that the repulsion of the *tert*-butyl group and the 5-cyano group may make it difficult for the molecules to undergo motion in the paired structure to facilitate cycloaddition. Reduced photoreactivity of single crystals of **1b** is attributed to reduced overlap of the double bond relative to **1a**.

Differences in molecular stacking of **1a** and **1b** also influence their fluorescence properties. Both **1a** and **1b** shows strong fluorescence in solution at 439 and 452 nm, respectively. While single crystals of **1a** show very weak fluorescence, **1b** showed intense fluorescence at 500 mm reflecting differences in the intermolecular interactions between **1a** and **1b** in the paired structure.

In conclusion, the molecular stacking of styryldicyanopyrazines in their self-assembled structures controlled their topochemical photoreactions. The reactivity of **1a** and **1b**, and the stereochemical structure of their products are well explained from X-ray crystal analysis.

Experimental

Stereochemical Assignment of Photodimers **3a** *and* **3b**.—The stereochemical assignment of **3a** was performed by mass spectroscopy, which shows *m*/*z* 464 (M^+) and 232 ($M^+/2$), while the peak corresponding to asymmetric cleavage of the cyclobutane, usually observed in similar non-centrosymmetric 1,2- or 1,3-diaryldisubstituted cyclobutane, was completely absent. The NMR spectrum showed a singlet for two protons of the pyrazine ring at δ 8.51 and two multiplets for 10 aromatic protons on the cyclobutane ring (centered at δ 7.22 and 7.10). Two sets of doublets for the two paired protons on the cyclobutane ring were observed at δ 5.05 and 4.85 ($J_1 = 10.2$ Hz, $J_2 = 7.2$ Hz) that were typical for a symmetrical *trans,trans*-AA′BB′ pattern. From these results, **3a** consists of *anti* head-to-tail form, which is in accordance with the expectation from the crystal structure of paired **1a**.

3b; *m*/*z* 632 (M^+), 316 ($M^+/2$); δ_H ($CDCl_3$) 7.19(4H, d, $J = 8.1$ Hz), 6.97(4H, d, $J = 8.1$ Hz), 5.23(2H, dd, $J_1 = 10.1$, $J_2 = 7.2$ Hz), 4.66(2H, dd, $J_1 = 10.2$, $J_2 = 7.2$ Hz), 2.95–2.82(2H, m), 2.76–2.65(2H, m), 1.13(6H, t, $J = 7.5$ Hz).

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