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Solid state photoaddition reactions in polycrystalline mixtures of NH heteroaromatic compounds and *trans*-stilbene[☆]

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Abstract

Photoaddition reactions of indole (**1a**), carbazole (**1b**) and phenothiazine (**1c**) to *trans*-stilbene (**2**) occurred in the mixed crystal state to give the corresponding adducts **3a**, **3b** and **3c** with an N–C bond. Photoadduct **4a** with a C–C bond was also obtained by the solid state photoreaction of **1a** with **2**. The mixed crystals prepared by the melting and resolidifying method were simple polycrystalline mixtures of the two components, and the photoreactions proceeded at the interface of the two crystallites. The selectivity of the photoaddition reaction was higher in the solid state than in solution.

Keywords: Solid state photoaddition; NH heteroaromatic compounds; *Trans*-stilbene

1. Introduction

A key step in the investigation of intermolecular photoreactions between two different organic molecules in the crystalline state is to find photoreactive molecular compounds. We have attempted to obtain new molecular compounds by preparing various mixed crystals of two components by the melting–resolidifying method. Although new molecular compounds were sometimes formed in the mixed crystal preparation, in many cases they were simple mixtures of component crystallites. Some of the simple mixtures exhibited photoreactivity in the solid state [1,2]. Although photoreactive molecular compounds are important substrates for obtaining correlation between the reaction and the geometrical molecular arrangement in the crystal lattice, the photoreaction of simple polycrystalline mixtures is also valuable from a synthetic aspect. We have reported previously [3] that the photoaddition reaction in the simple polycrystalline mixture of carbazole (**1b**) and *trans*-stilbene (**2**) proceeds at the interface of the two crystallites on the basis of the experimental data which indicate that the reaction rate increases with an increase in the crystallite surface area. Several simple polycrystalline mixtures, such as indole (**1a**) and phenanthrene [1] and **1a** and 4-hydroxybenzaldehyde [2], also undergo photoreaction at the interface of the crystallites. A similar type of solid state photoaddition reaction occurs with mixed crystals of **1a** and naphthalene [1] and **1b** and anthracene [4]. In this paper, we describe the details of the preliminary work [3], the extension to photoreactions of other NH heteroaromatic compounds with **2** and a comparison between the solid state and solution reactions.

2. Experimental details

2.1. Materials and methods

Melting points (m.p.) are uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured on a JEOL PMX-60 spectrometer with tetramethylsilane as an internal standard. IR spectra were measured on a Shimadzu IR-470 spectrophotometer. UV and luminescence spectra were recorded on a Shimadzu UV-3100 spectrophotometer and RF-5000 spectrofluorophotometer respectively. Powder X-ray diffraction spectra were taken on a Rigaku Geigerflex with RAD-C

[☆] Supplementary data deposited at the Cambridge Crystallographic Data Centre.

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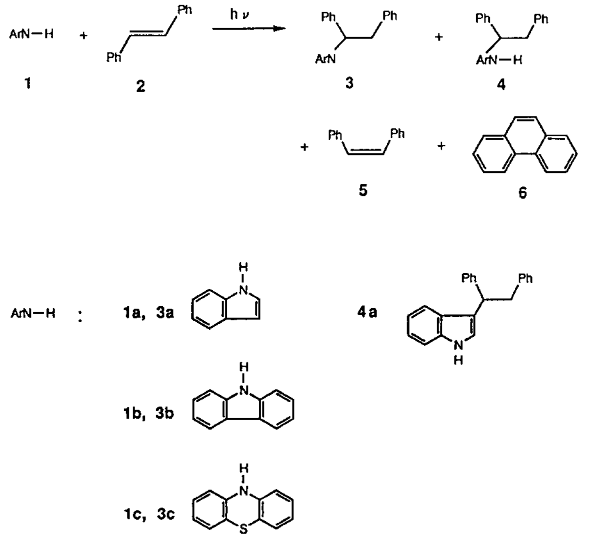
system. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermoflex TAS-200 DSC-8230D. Static electron spin resonance (ESR) spectra were measured on a JEOL JES-RE2X spectrometer. A 400 W high-pressure mercury lamp was used for the irradiation of solid and solution samples. Preparative thin layer chromatography (TLC) was carried out on Merck silica gel, No. 13793. High performance liquid chromatography (HPLC) was performed on a Waters LCM-1 using a silica gel column and hexane–ethyl acetate as eluent. Mixed crystals were prepared by melting a mixture of a given molar ratio of two components, followed by resolidification of the melt at room temperature and pulverization in a mortar. All the reagents were commercially available.

2.2. Preparative photoreactions in the solid state (see Scheme 1)

*2.2.1. The mixed crystal between **1a** and **2***

The mixed crystal of 1:1 molar ratio between **1a** and **2** (1.19 g) was placed between two Pyrex glass plates and irradiated for 20 h under argon at 5 °C. The UV light strength at 360 nm during irradiation was measured as about 40 mW cm^{-2} with a UV radiometer. The irradiated sample was submitted to preparative TLC using hexane–benzene as an eluent to give **3a** in 20% yield and **4a** in 6% yield and a small amount of a mixture of other products. 1,2-Diphenyl-(*N*-indolyl)ethane (**3a**) had an m.p. of 88–89 °C (from ethanol). IR (KBr): no protic H, 2920, 1455, 1375, 735 cm^{-1}. UV (cyclohexane): $\lambda_{max}=293$ nm ($\log \epsilon=3.73$), 281 (3.96), 270 (3.88), 217 (4.37). ^{1}H-NMR ($CDCl_3$): δ 3.63 (d, 2H, $J=8.0$ Hz), 5.73 (t, 1H, $J=8.0$ Hz), 6.54 (d, 1H, $J=3.3$ Hz, indole 3-H), 6.99–7.63 (m, 15H, aromatics). Analysis: calculated for $C_{22}H_{19}N$: C, 88.86; H, 6.44; N, 4.71. Found: C, 89.09; H, 6.70; N, 4.56. 1,2-Diphenyl-(3-indolyl)ethane (**4a**) had an m.p. of 105–109 °C. IR (KBr): 3410 (indole NH), 2920, 1460, 1380, 725 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.50 (d, 2H, $J=8.0$ Hz), 4.80 (t, 1H, $J=8.0$ Hz), 6.95–7.41 (m, 15H, aromatics), 7.92 (s, 1H, broad, NH). Analysis: calculated for $C_{22}H_{19}N$: C, 88.86; H, 6.44; N, 4.71. Found: C, 89.06; H, 6.62; N, 4.67. Compound **4a** was somewhat unstable and gradually decomposed in air.



Scheme 1.

*2.2.2. The mixed crystal between **1b** and **2***

The mixed crystal of 1:1 molar ratio between **1b** and **2** (797 mg) was placed between two Pyrex glass plates and irradiated for 20 h under argon at about 20 °C. Product isolation by preparative TLC gave 1,2-diphenyl-(*N*-cabazolyl)ethane (**3b**) in 18% yield, for which the spectral data and elemental analysis have already been described [3].

*2.2.3. The mixed crystal between **1c** and **2***

The mixed crystal of 1 : 1 molar ratio between **1c** and **2** (1.14 g) was placed between two Pyrex glass plates and irradiated for 20 h under argon at 20 °C. 1,2-Diphenyl-(9-phenothyazinyl)ethane (**3c**) (m.p., 135–136 °C, from ethanol) was obtained in 25% yield after preparative TLC separation. IR (KBr): no protic H, 3030, 1590, 1465, 1240, 750 cm^{-1}. UV (ethanol): $\lambda_{max}=316$ nm ($\log \epsilon=3.78$), 256 (4.63). ^{1}H-NMR ($CDCl_3$): δ 3.44–3.84 (m, 2H, CH_2), 5.31–5.57 (m, 1H, CH), 6.56–7.02 (m, 18H, aromatic). Analysis: calculated for $C_{26}H_{21}NS$: C, 82.28; H, 5.58; N, 3.69. Found: C, 82.38; H, 5.78; N, 3.35.

2.3. HPLC study of the photoreactions

2.3.1. In the solid state

The effects of the molar ratio of **1a**, **1b** or **1c** and **2** in the mixed crystal on the photoreaction were investigated by HPLC analysis using a 20 mg sample irradiated for 20 h. The results are given in Tables 1–3 (see Section 3).

2.3.2. In solution

A mixed solution of **1a**, **1b** or **1c** and **2** in acetonitrile (10 ml) was irradiated in a Pyrex glass tube for 20 h under argon at 20 °C. The effect of the concentration on the photoreaction was examined. The results are given in Tables 1–3 (see Section 3).

3. Results and discussion

A mixed crystal of indole (**1a**) and *trans*-stilbene (**2**) prepared by the melting–resolidifying method was irradiated with a high-pressure mercury lamp through Pyrex glass under argon for 20 h. The solid state

Table 1
Photoreaction of indole (**1a**) with *trans*-stilbene (**2**)

Molar ratio **1a**:**2**	Yield (%)				Conversion (%)	
	3a	**4a**	**5**	**6**	**1a**	**2**
Solid state						
1:1	34	12	<1	1	88	100
1:2	40	4	<1	2	100	100
1:3	39	1	<1	3	100	100
1:4	37	1	<1	3	100	100
Acetonitrile solution						
0.005 M:0.005 M	0	0	14	46	100	93
0.05 M:0.05 M	2	2	35	12	82	82
0:0.05 M	–	–	49	6	–	81

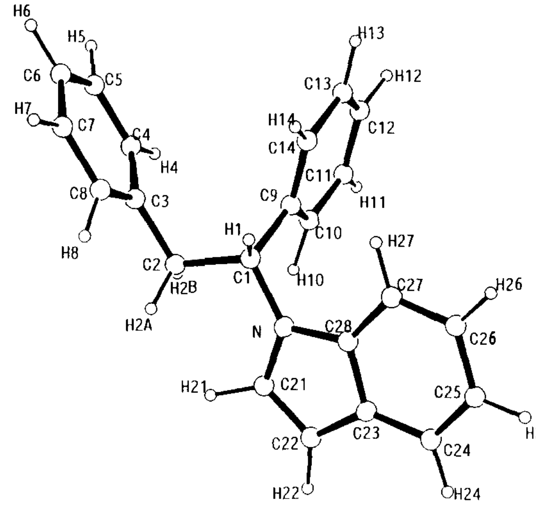


Fig. 1. X-Ray crystal structure of **3a**.

photoreaction gave two adducts **3a** and **4a** connected via a C–N and C–C bond respectively (Scheme 1). The influence of the molar ratio of **1a** and **2** on the yield of **3a** was small (Table 1); almost a constant yield of about 40% was obtained at the complete conversion of the starting materials. However, the yield of **4a** decreased with increasing amount of **2** in the mixed crystal. One of the products (**3a**) was analysed by X-ray crystallography[2] and the structure was confirmed as shown in Fig. 1 [6]. Although several other photoadducts were produced in 6% total yield, they could not be separated because the R_f values for preparative TLC separation were nearly the same as that of **1a**. In addition, small amounts of *cis*-stilbene (**5**), phenanthrene (**6**), some stilbene dimers and insoluble polymers were detected by HPLC as minor peaks. On the other hand, irradiation of a mixed solution of **1a** and **2** in acetonitrile at low concentrations (0.005 M:0.005 M) gave no photoadducts; the photoaddition reaction occurred more effectively in the solid state than in solution. Another feature of the solution reaction was the low selectivity; the production of **5** and **6** was caused by the well-known photoisomerization of **2** to **5** followed by the cyclization of **5** to **6**.

The same type of photoaddition reaction of the mixed crystal between carbazole (**1b**) and **2** to give an adduct **3b** has been described previously [3]. The effect of the irradiation time on the photoreaction of the 1:1 mixed crystal was investigated; irradiation for 7 and 35 h gave **3b** in 23% and 28% yields at 25% and 35% conversions of **1b** and 87% and 100% conversions of **2** respectively. It seems reasonable to assume that the formation rate of **3b** is faster at the initial stage, because the photoaddition reaction of the simple polycrystalline mixture of **1b** and **2** proceeds at the crystallite interface and is not so disturbed by covering with the products [3]. Irradiation for 3 h with a 400 W high-pressure mercury lamp gave **3b** in 17% yield. On the other hand, irradiation with a 500 W super-high-pressure mercury lamp gave only a 4% yield of **3b** [3], probably because the light intensity of the lamp was weak at wavelengths shorter than 300 nm. The yield of **3b** on the basis of consumed **1b** was virtually constant (about 80%) at the molar ratios of 1:1 to 1:4 of **1b** and **2** (Table 2). The high conversion of **2** is due to the occurrence of side reactions such as isomerization, dimerization and polymerization. Although the same type of photoaddition reaction occurred in an acetonitrile solution of **1b** and **2**, the yields based on consumed **1b** were less than that in the solid state.

Table 2
Photoreaction of carbazole (**1b**) and *trans*-stilbene (**2**)

Molar ratio **1b**:**2**	Yield (%)			Conversion (%)	
	3b	**5**	**6**	**1b**	**2**
Solid state					
1:1	25	1	4	30	87
1:2	41	3	5	51	83
1:3	49	2	6	61	71
1:4	57	2	6	68	57
Acetonitrile solution					
0.005 M:0.005 M	3	<1	14	100	100
0.05 M:0.05 M	23	5	14	66	98

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[2] Crystallographic data of **3a**: triclinic, $a=12.445(4)$, $b=10.738(4)$, $c=6.496(2)$ Å, $\alpha=86.29(3)°$, $\beta=84.99(3)°$, $\gamma=106.12(3)°$; $\rho_{calc}=1.189$ g cm^{-3}; $Z=2$ in space group $P\bar{1}$. 2374 reflections with $2\theta \leq 110.0°$ were recorded on a four-circle diffractometer using graphite-monochromated Cu Kα radiation. Of these, 2089 with $I>3\sigma(I)$ were judged as observed. The structure was solved using SHELX-86 [5]. Full-matrix least-squares refinement with anisotropic temperature factors for hydrogen atoms and isotropic hydrogens converged to $R=0.059$ and $R_w=0.104$. The details of the crystallographic data are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW.

Table 3
Photoreaction of phenothiazine (**1c**) and *trans*-stilbene (**2**)

Molar ratio **1c**:**2**	Yield (%)			Conversion (%)	
	3c	**5**	**6**	**1c**	**2**
Solid state					
1:1	33	1	7	58	80
1:2	59	1	10	80	78
1:3	57	2	5	93	82
1:4	63	0	1	97	96
Acetonitrile solution					
0.005 M:0.005 M	0	4	17	100	93
0.05 M:0.05 M	39	18	4	86	87

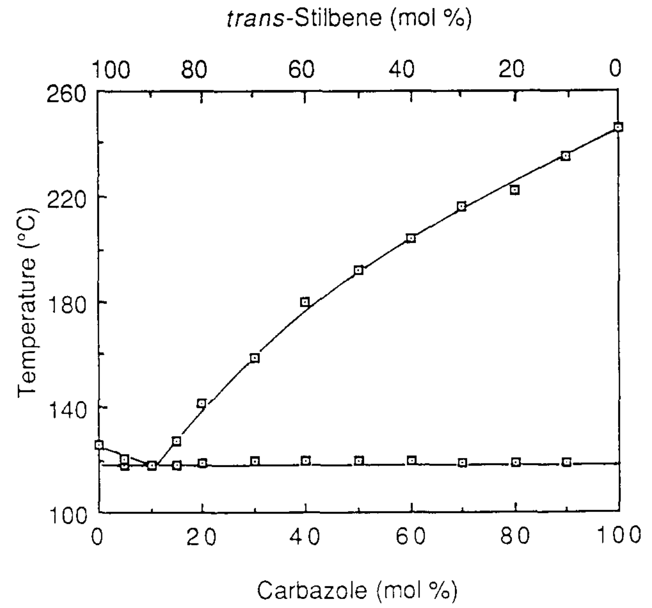

Fig. 2. Phase diagram of carbazole and *trans*-stilbene.

The results of the photoreaction between **1c** and **2** in the solid state and solution were analogous to those for **1b** and **2** as shown in Table 3.

The three mixed crystals composed of **1a**, **1b** or **1c** and **2** were simple mixtures of each crystallite, because the powder X-ray diffraction spectra of the mixed crystals are the same as the sum of the spectra of each component. The phase diagram of **1b** and **2** was constructed from DSC measurements at different molar ratios and from powder X-ray diffractometry of the solid phase (Fig. 2). It is a typical phase diagram for a simple polycrystalline mixture of two components which has a eutectic point at 119 °C. When the 1:1 melt of **1b** and **2** is cooled, the crystallization of **1b** begins at 192 °C and all the **1b** and **2** are solidified simultaneously at 119 °C. We have already reported the crystallite sizes of **1b** and **2** in the mixed crystals prepared by resolidifying the melt in a cooling bath at different temperatures [3]. The melting ranges of the 1:1 mixtures of **1a** (m.p., 55 °C) and **2** (m.p., 126 °C) and of **1c** (m.p., 185 °C) and **2** are 48–107 °C and 114–155 °C respectively; the lower-limit temperatures are probably the eutectic points.

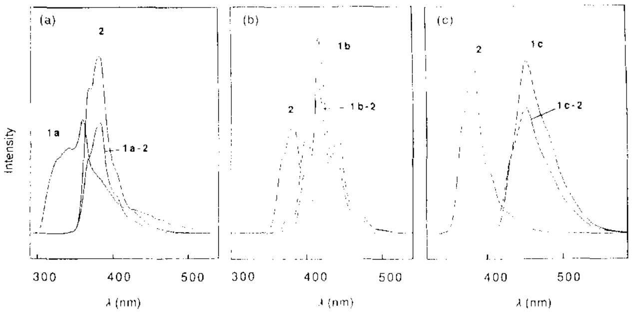

Fig. 3. Luminescence spectra for the mixed crystals and their components in the solid state (excitation at 275 nm): (a) 1:1 mixed crystal (**1a–2**) of indole (**1a**) and *trans*-stilbene (**2**); (b) 1:1 mixed crystal (**1b–2**) of carbazole (**1b**) and (**2**); (c) 1:1 mixed crystal (**1c–2**) of phenothiazine (**1c**) and **2**.

Table 4
ESR spectra of the mixed crystals and their components in the solid state on UV irradiation at −100 °C

Compound	*G* value	ΔH_{pp} (mT)
Indole	2.0044	2.06
Carbazole	2.0038	2.24
Phenothiazine	2.0057	1.16
Indole–*trans*-stilbene (1:1)	2.0044	2.18
Carbazole–*trans*-stilbene (1:1)	2.0041	2.16
Phenothiazine–*trans*-stilbene (1:1)	2.0059	1.16

The luminescence spectra of the three mixed crystals are shown in Fig. 3. The mixed crystal **1a–2** emits only *trans*-stilbene fluorescence, while the mixed crystals **1b–2** and **1c–2** emit carbazole and phenothiazine phosphorescence respectively. These results indicate that, in the mixed crystals, the excitation energy migrates smoothly to result in the fluorescent or phosphorescent state of the component with the lower singlet or triplet energy. The static ESR spectral data of the mixed crystals and their components in the solid state on UV irradiation at −100 °C are summarized in Table 4. The ESR signals in the solid state are broad and have no hyperfine structure. The *G* values and the peak-to-peak widths of the free radical signals of the mixed crystals are nearly in accordance with those of the free radical signals obtained by irradiation of the corresponding NH heteroaromatic compounds, suggesting the involvement of the free radicals ($R–N^{\cdot}$ in Fig. 4) of the heteroaromatic compounds in the solid state photoreaction. The photoaddition reactions forming N–C bonds are similar to those of **1a** with naphthalene, **1a** with phenanthrene [1] and **1b** with anthracene [4]. Lewis and coworkers [7–9] and Pienta [10] studied comprehensively the photoaddition reactions of aliphatic amines with *trans*-stilbene in organic media and proposed an electron transfer mechanism. We also formulate a similar mechanism, involving the formation

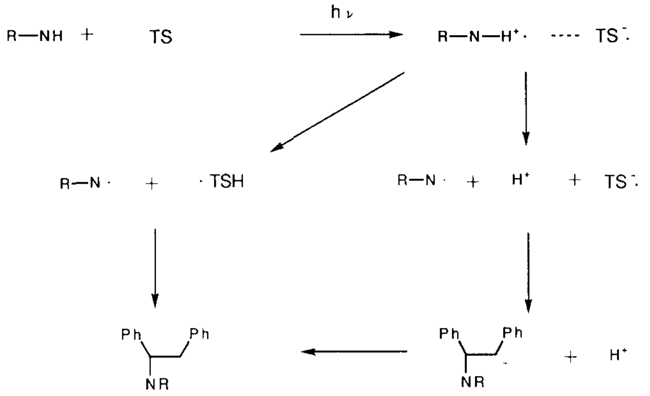

Fig. 4. Possible mechanism of the photoreaction of the NH heteroaromatic compounds with *trans*-stilbene.

of a radical ion pair followed by NH proton transfer, in Fig. 4.

4. Conclusions

We have shown that the mixed crystals of the NH heteroaromatic compounds **1a**, **1b** and **1c** with *trans*-stilbene are simple polycrystalline mixtures of the two components and the photoaddition reactions occur more selectively in the solid state than in solution.

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