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Solid state photoreactions occurring at the interface between crystallites of two different organic compounds

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Abstract

This paper deals with the solid state bimolecular photoreactions occurring at the interface between crystallites of two different organic compounds prepared as a polycrystalline mixture by melting–resolidification. The photoreactions include the photoaddition of NH compounds to aromatic and olefinic double bonds, hydrogen abstraction, condensation reaction via photoelectron transfer and [2+2] photoaddition. Particular attention is focused on the characterization of the polycrystalline mixture, the selectivity of the photoreactions in the solid state compared with those in the solution phase and the factors controlling the photoreactions.

Keywords: Crystallite interface; Mixed crystals; Solid state bimolecular photoreactions

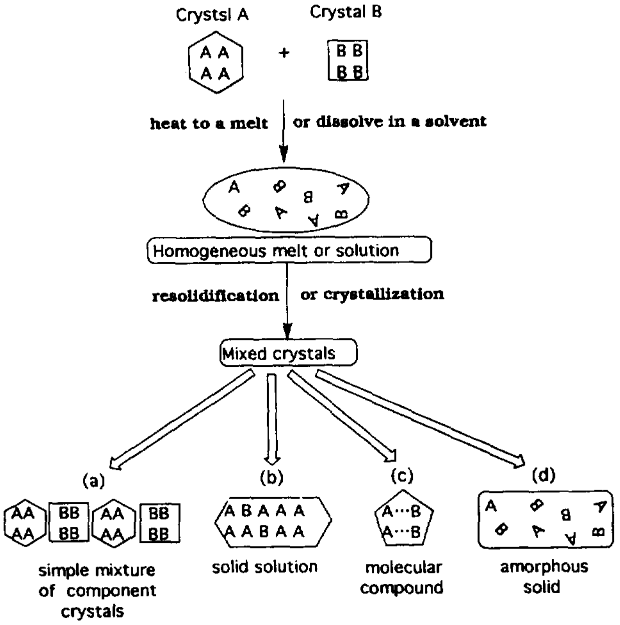
1. Introduction

In order to carry out bimolecular photoreactions between two different organic molecules in the solid state, we must prepare mixed crystals consisting of two components. Such mixed crystals can be prepared by the following two methods as illustrated in Scheme 1:

1. melting–resolidification, which involves the heating of a mixture, often equimolar, of two crystalline compounds to a homogeneous melt, followed by resolidification on cooling to give mixed crystals as a polycrystalline solid;
2. crystallization from a solution of a mixture of two compounds involving evaporation or recrystallization.

The mixed crystals thus prepared are obtained in various forms: (a) a simple mixture of the component crystallites; (b) a solid solution; (c) a molecular compound which we designate as a "two-molecule crystal" [1]; (d) an amorphous solid.

In this paper, the photoreactions of mixed crystals of type (a), occurring at the interface of the component crystallites, are particularly discussed. According to our experience, when two organic compounds are selected for the preparation of mixed crystals, mixed crystals of type (a) are most frequently obtained, although type (c) crystals ("two-molecule crystals") are obtained in certain cases [1].



Scheme 1. Preparation of mixed crystals from two different organic compounds.

2. Characterization of polycrystalline mixtures

The four forms of mixed crystal shown in Scheme 1 can be distinguished by characterization in the solid state using several physical methods, such as powder X-ray diffracto-

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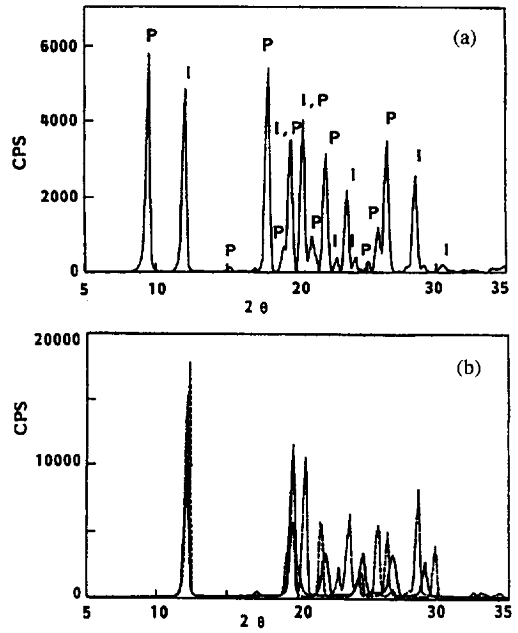


Fig. 1. PXD patterns of mixed crystals of (a) indole and phenanthrene (I and P denote the peaks of indole and phenanthrene respectively) and (b) indole and naphthalene (– · –, indole; - - -, naphthalene; ———, mixed crystal).

metry (PXD), differential scanning calorimetry (DSC), infrared (IR) spectroscopy, cross polarisation magic angle spinning (CP-MAS), ^{13}C nuclear magnetic resonance (NMR) spectroscopy, the construction of a phase diagram, etc.

The PXD method may be the simplest. Fig. 1 shows a comparison between the PXD patterns of mixed crystals of indole–phenanthrene (Fig. 1(a)) and indole–naphthalene (Fig. 1(b)), indicating that the former is the sum of the patterns of the two components and the latter contains many new peaks which do not appear in the patterns of the two components [2]. Fig. 1 suggests that the similarity between the molecular shapes of the two components is an important factor controlling whether the mixed crystal involves a molecular compound or a simple mixture of the crystallites of the components. The molecular shapes of indole and naphthalene are more similar than those of indole and phenanthrene.

The phase diagram may be the best method of characterization, although it requires DSC measurements at numerous ratios of the two components. Fig. 2 shows representative phase diagrams for two-component mixed crystals. The mixed crystals can be categorized into the following major groups [3]: in Fig. 2(a), the diagram has a eutectic point, indicating that the mixed crystal is a simple mixture of the component crystallites; in Fig. 2(b), the diagram shows a solid solution with unlimited solubility; in Fig. 2(c), the diagram is representative of a binary system forming a molecular compound; this diagram is the sum of two simpler diagrams (Fig. 2(a)). The diagrams correspond to forms (a), (b) and (c) respectively of Scheme 1. Typical examples are shown in Fig. 3. In Fig. 3, we compare the phase diagram of duroquinone-pentamethylbenzene (Fig. 3(a)) with that of duroquinone–1,2,4,5-tetramethylbenzene (durene) (Fig. 3(b)). The former has a eutectic point showing the formation of a mixture of component crystallites, whereas the latter shows the formation of a molecular compound from duroquinone and durene [4]. Again, the result indicates that the similarity between the molecular shapes of the components is an important factor in the formation of a molecular compound.

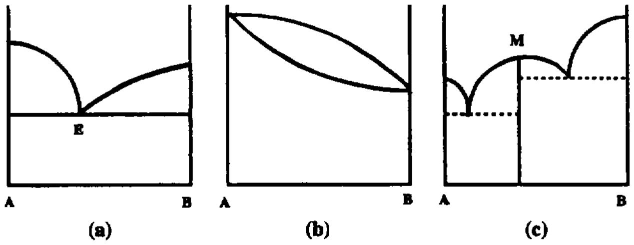


Fig. 2. Typical phase diagrams of two-component (A and B) mixed crystals: (a) simple mixture of component crystallites showing a eutectic point (E); (b) solid solution with unlimited solubility; (c) molecular compound (M).

3. Examples of photoreactions occurring at crystal interfaces

3.1. Photoadditions of NH compounds to aromatic and olefinic double bonds

Solid state photoadditions have been shown to occur between NH compounds, such as indole, carbazole and diphenylamine, and aromatic and olefinic compounds, such as phenanthrene and *trans*-stilbene [4–10]. Typical examples are given in Scheme 2. The yields of the addition products **3**, **7** and **8**–**12** are not always satisfactory. However, as shown for the formation of **7** from carbazole (**4**) and *trans*-stilbene (**6**) and from phenothiazine (**5**) and *trans*-stilbene (**6**), reasonably good yields of **7** can be obtained when an excess of *trans*-stilbene is used for the preparation of the mixed crystals. The yields of the products depend on the ratio of the two substrates in the mixed crystals in the photoaddition reactions of diphenylamine to phenanthrene (**2**) and *trans*-stilbene (**6**).

The solid state photoreactions between these substrates are very different from the solution photoreactions. Thus indole (**1**) and phenanthrene (**2**) do not undergo photoreaction in benzene, acetonitrile or methanol solution, but are recovered unchanged [2]. In contrast, the mixed crystal between benzimidazole and 2,3-dimethylnaphthalene shows no photoreactivity in the solid state, whereas a photoproduct is obtained in 22% yield in acetonitrile solution [9]. We have compared the solid state and solution reactions in other cases. For example, in the photoreaction of indole (**1**) and *trans*-stilbene (**6**), the photoproduct **7** is the major product in the solid state, whereas in acetonitrile solution **7** is only a minor product and *cis*-stilbene and phenanthrene (a cyclization product of *cis*-stilbene) are the major products.

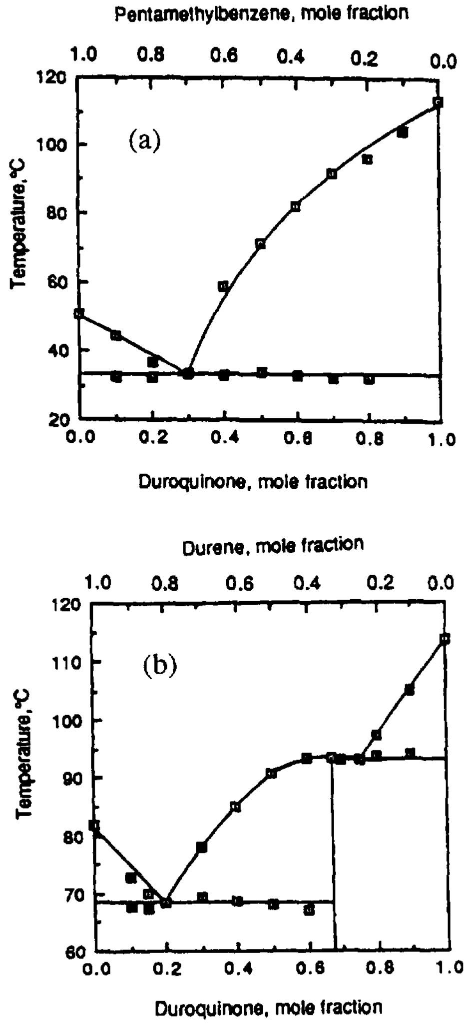
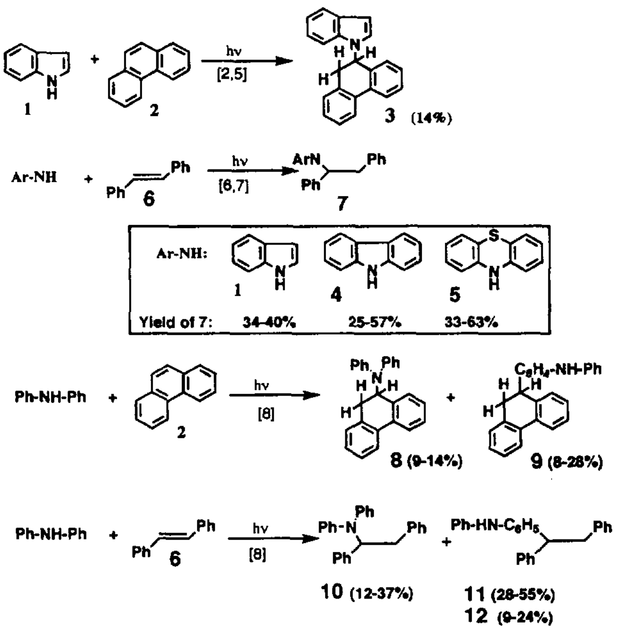
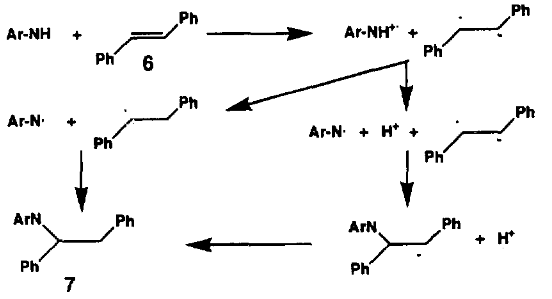


Fig. 3. Phase diagrams of mixed crystals of (a) duroquinone–pentamethylbenzene and (b) duroquinone–durene.



Scheme 2. Photoaddition reactions.



Scheme 3. Mechanism of photoaddition of Ar-NH to *trans*-stilbene.

These photoaddition reactions have been interpreted to occur via initial electron transfer, followed by coupling of the intermediate free radicals, as illustrated in Scheme 3 for NH heteroaromatics (Ar-NH) and *trans*-stilbene (**6**) [7].

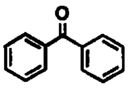
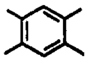
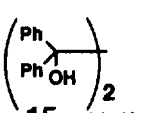
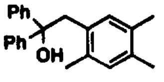
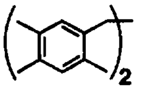
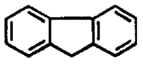
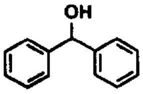
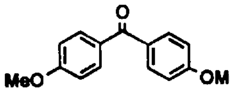
3.2. Hydrogen abstraction

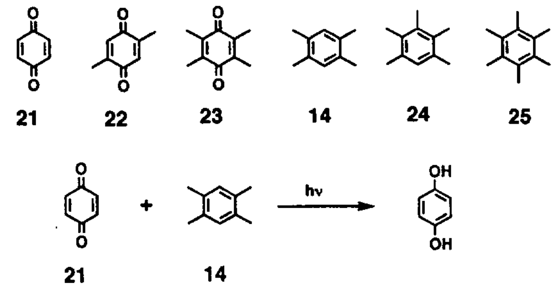
Hydrogen abstraction reactions are observed at the interface of certain mixed crystals on irradiation in the solid state. The most typical example is the photochemical hydrogen abstraction by excited benzophenones **13** and **20** from various hydrogen donors [10]. Selected results are listed in Table 1. For all mixed crystals, we did not observe the formation of a molecular compound, but a mixture of the crystallites of the two components. The product distribution in the photoreaction of **13** and **14** in acetonitrile solution is much the same as that in the solid state, indicating that the molecular arrangement of the substrates in the polycrystalline state of **13** and **14** may be random and similar to that in solution. The lack of reactivity observed for mixed crystals **13–18** and **20–19** is due to an unsuitable molecular arrangement near the surface of the component crystallites.

Mixed crystals of 1,4-benzoquinone (**21**), 2,5-xyloquinone (**22**) and duroquinone (**23**) with durene (**14**), pentamethylbenzene (**24**) and hexamethylbenzene (**25**) (Scheme 4) were prepared by the melting–resolidification process, and characterized by PXD, DSC, IR spectroscopy and the construction of phase diagrams. Only the mixed crystal of **23–14** was found to form a 2 : 1 two-molecule crystal; the other eight mixed crystals were simple polycrystalline mixtures of the component crystallites [4].

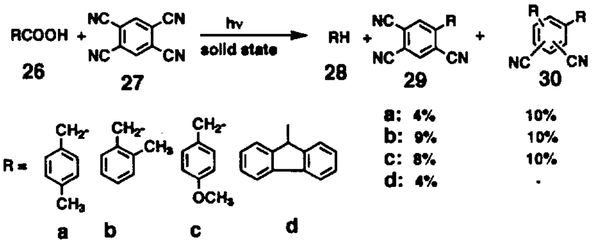
Irradiation of the two-molecule crystal **23–14** and mixed crystals **21–14**, **21–24** and **23–24** caused intermolecular hydrogen abstraction to give the corresponding hydroquinones in 20%, 29%, 36% and 23% yield respectively. In the case of the mixed crystals containing **22**, photodimers of **22** were the major product and the corresponding hydroquinone was formed in a minute amount. Product selectivities in the solid state were different from those in acetonitrile solution: for example, the mixed crystal **22–14** gave the corresponding hydroquinone in 43% yield in acetonitrile solution, but photodimers of **22** in the solid state.

Table 1
Hydrogen abstraction reactions

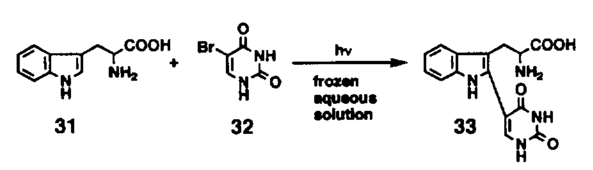
Mixed crystal		Photoproducts: percentage yield in the solid state (percentage yield in solution)
Benzophenone	Hydrogen donor	
 **13**	 **14**	 **15** 22(20)  **16** 20(17)  **17** 2(3) **Polymer** 30-35(30-35)
13	 **18**	No reaction in the solid state
13	 **19**	15, 35. Recovery: 13, 74; 19, 59
 **20**	19	No reaction in the solid state



Scheme 4. Hydrogen abstraction between benzoquinones and methylbenzenes.



Scheme 5. Photocondensation between arylacetic acids and 1,2,4,5-tetracyanobenzene.

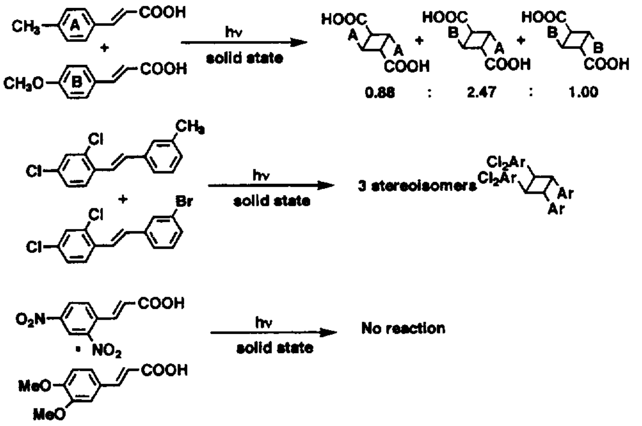


Scheme 6. Photocondensation between tryptophan and 5-bromouracil.

3.3. Condensation reactions

Irradiation of simple polycrystalline mixtures of arylacetic acids **26a–26d** and 1,2,4,5-tetracyanobenzene (**27**, TCNB) caused decarboxylation of the acids, followed by dehydrocyanating condensation to give the corresponding arylmethanes **28** (Scheme 5), monoarylmethyltricyanobenzenes **29** and bisarylmethyldicyanobenzenes **30**. In the case of **26d–27**, 9-fluorenone (80%) and 9-fluorene (**28d**, 18%) were the major products [11]. For **26a–27**, **26b–27** and **26c–27**, the corresponding arylmethanes **28** were not detected due to their volatile properties. In these solid state photoreactions, the conversions of the starting acids **26** and TCNB were 87%–100% and 13%–44% respectively.

A freeze-dried mixed crystal was prepared from a frozen aqueous solution of a mixture of L-tryptophan (**31**) and 5-bromouracil (**32**), and the spectral and photochemical properties were compared with those of a mixed crystal obtained by evaporation of an aqueous solution at room temperature [12]. This type of comparison is interesting, since it is known that the photocoupling between **31** and **32** to form **33** (Scheme 6) occurs only in aqueous frozen solution, but not in aqueous solution at room temperature [13]. The mixed crystals obtained by the two evaporation methods were found to be identical and gave the same products, i.e. **33** and uracil (about 5% each). The results show that the formation of **33** can occur at the interface of the component crystallites.



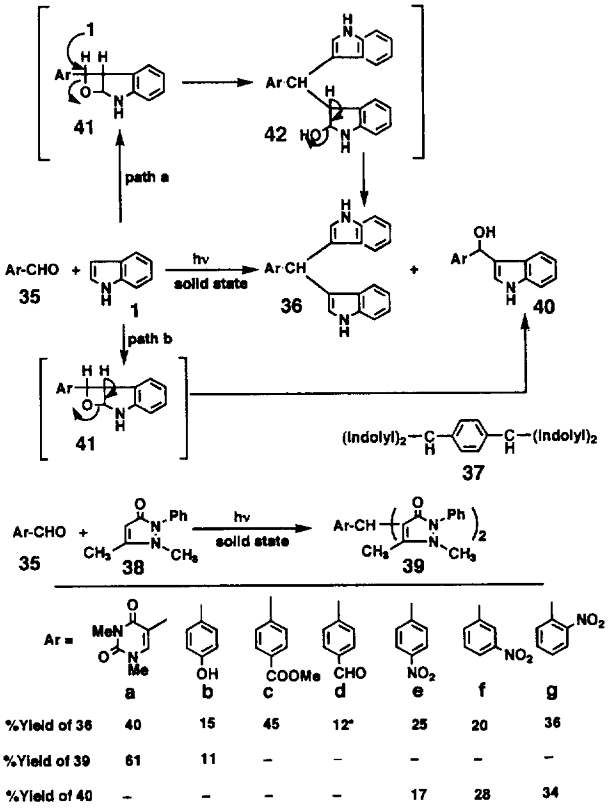
Scheme 7. [2+2] Photoaddition of mixed crystals of two different organic compounds.

3.4. [2+2] Photocycloaddition

[2+2] Photocycloaddition reactions between two different, but structurally similar, cinnamic acids and stilbene derivatives have been reported [14–16]. Examples of these photoreactions are shown in Scheme 7. The first two cases give a mixture of three dimeric stereoisomers. In these cases, the mixed crystals prepared by melting–resolidification consist of random solid solutions [14,15]. On the other hand, in the last case (2,4-dinitro- and 3,4-dimethoxy-cinnamic acids), a 1 : 1 molecular complex is formed as demonstrated by X-ray crystallographic analysis, but it shows no reaction on irradiation in the solid state [16].

Mixed crystals obtained by melting–resolidification from various heterocyclic and aromatic aldehydes **35a–35d** and excess indole (**1**) undergo a solid state photoreaction to give condensation products **36a–36d**, whose structures were confirmed by X-ray crystallographic analyses of **36a**, **36c** and **36d** (Scheme 8) [17,18]. The major product from the mixed crystal of **35d–1** is a tetraindolyl compound **37** (25%), in addition to **36d** (12%) and an unstable unknown product (8%). In the case of the mixed crystal **35c–1**, indole can be substituted by antipyrine (**38**) and irradiation of the mixed crystal **35c–38** gives **39c** (11%) and *p*-hydroxybenzoic acid (38%) [18]. The mixed crystal between 5-formyl-1,3-dimethyluracil (**35a**) and antipyrine (**38**), which on irradiation gives **39a** (61% yield), is a molecular compound (PXD analysis), while the mixed crystal **35b–1** is a simple mixture of the component crystallites.

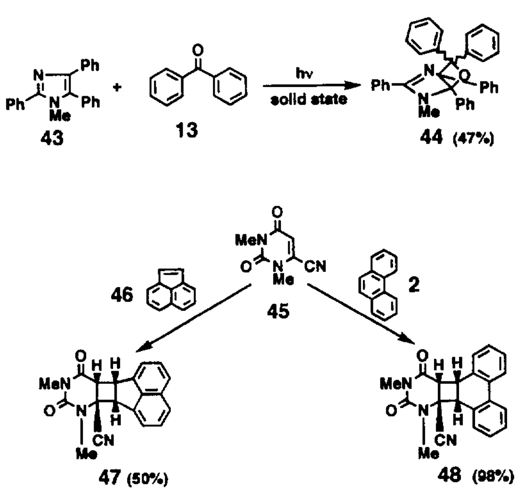
This type of solid state photoreaction has been found to show a substituent effect. Mixed crystals between nitrobenzaldehydes **35e–35g** and indole (**1**) give nitrophenyl-(3-indolyl)-methanols **40e–40g** in addition to **36e–36g**. A dual pathway from an oxetane intermediate **41** (a [2+2] cycloaddition product between the C=O group of **35** and the double bond of **1**) has been proposed for the formation of **36** and **40** [19]. In path (a), **41** undergoes ring cleavage to react with another molecule of indole (**1**) to eventually give **36**, whereas in path (b), **41** undergoes ring cleavage to give directly **40**.



	a	b	c	d	e	f	g
%Yield of 36	40	15	45	12*	25	20	36
%Yield of 39	61	11	–	–	–	–	–
%Yield of 40	–	–	–	–	17	28	34

* + 25% of 37

Scheme 8. Photocondensation via [2+2] cycloaddition.



Scheme 9. Other [2+2] cycloaddition reactions.

In the latter case, the process from **41** to **42** may be destabilized by the nitro group.

Scheme 9 shows additional examples of the [2+2] cycloaddition occurring on solid state irradiation of mixed crystals **43–13** (1 : 6 molar ratio), **45–46** (1 : 2) and **45–2** (1 : 2) to form **44**, **47** and **48** respectively [20,21]. The mixed crystal **45–46** gives **47** as the sole major product in the solid state; two stereoisomeric photodimers of **46** are also obtained as minor products. The nature of these mixed crystals is unknown.

4. Factors controlling the photoreactions occurring at the polycrystalline interface

4.1. Proximity effect

In the solid state photoreactions of mixed crystals, the close contact of the crystal surfaces at the interface of the component crystallites is one of the important conditions for reaction. In order to determine the proximity effect in the solid state photoreaction between aromatic aldehydes **35** and indole (**1**) (Scheme 8), solution phase irradiation was carried out. Irradiation of an acetonitrile solution of 5–19 mM of aromatic aldehydes **35a–35d** and 38–51 mM of indole gives no condensation products **36a–36d** [17,18]. However, when a liquid mixture of indole and excess benzaldehyde is irradiated, **36** (Ar ≡ Ph) is obtained in 75%–85% yield [18]. D'Auria [22] also reported that irradiation of an acetonitrile solution of 6.7 mM of benzaldehyde and 83 mM of indole gives **36** (Ar ≡ Ph) in 48% yield.

The proximity effect does not always play an important role in the photoreactions at the interface. The surface structure of the component crystallites, namely the geometrical arrangement of the functional groups participating in the photoreaction, is an important factor for the occurrence of the photoreaction. Thus the lack of photoreactivity between benzophenone (**13**) and fluorene (**18**) and between 4,4′-dimethoxybenzophenone (**20**) and benzhydrol (**19**) in the mixed crystalline state (Table 1) is assumed to be due to this factor. However, further experimental and theoretical approaches are required to solve this problem.

4.2. Effect of the size of the component crystallites

It is essential for the occurrence of bimolecular photoreactions at the polycrystalline interface of two components that mixed crystals having as large a surface area as possible are prepared. A larger surface area will also increase the conversion of the starting materials. For the photoaddition of Scheme 2, mixed crystals of carbazole (**4**) and *trans*-stilbene (**6**) were prepared under various conditions [6]. Their PXD patterns show that they consist of a simple mixture of the crystallites of **4** and **6**, since the PXD patterns are the sum of those of the component crystals (Fig. 4). The crystallite sizes were determined by the Scherrer method. Independent peaks of $2\theta = 9.16°$ and $2\theta = 12.06°$ were obtained for **4** and **6** respectively in Fig. 4. Table 2 shows the effect of the cooling temperature of the 1 : 1 melt of **4** and **6** on the formation rate of the photoadduct **7**. Faster cooling of the melt gave smaller sized crystallites of **4** and **6** and higher rates of adduct formation [1,6].

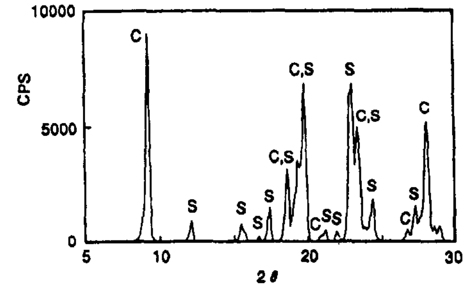


Fig. 4. PXD pattern of the mixed crystal of carbazole and *trans*-stilbene. C and S denote the peaks due to carbazole and *trans*-stilbene respectively.

Table 2
Crystallite size in a 1 : 1 mixed crystal of carbazole (**4**) and *trans*-stilbene (**6**) and its photoreactivity

Cooling temperature (°C)	Crystallite size (Å)		Yield of **7** after 3 h of irradiation (%)
	Carbazole	*trans*-Stilbene	
−78	294	342	5.1
20	364	381	3.9
100	412	415	3.1

4.3. Energy transfer in mixed crystals

The exciton migration theory explains the fast energy transfer in the crystalline state [23]. Thus irradiation of anthracene crystals doped with a trace (10^{-4} mol) of naphthacene leads to the emission of naphthacene fluorescence only. The polycrystalline mixed crystal prepared from indole (**1**) and phenanthrene (**2**) by melting–resolidification emits only phenanthrene fluorescence, showing that a facile energy transfer occurs through the crystallite interface to form the fluorescent state of phenanthrene having a lower singlet level. This indicates that the photochemical formation of adduct **3** in the solid state (Scheme 2) occurs from the singlet state of phenanthrene. On the other hand, the mixed crystal of indole–naphthalene, which consists of a molecular compound and forms a photoadduct of type **3** in the solid state, emits only indole fluorescence, showing a facile energy transfer in the crystal lattice of the molecular compound to the component having a lower singlet level [2].

The luminescence spectra of the mixed crystals between NH heteroaromatics (**1**, **4** and **5**) and *trans*-stilbene (**6**) (Scheme 2) were measured [7]. The mixed crystal **1–6** emits only *trans*-stilbene fluorescence, while mixed crystals **4–6** and **5–6** emit carbazole (**4**) and phenothiazine (**5**) phosphorescence respectively. The results indicate that the excitation energy migrates smoothly through the interfaces of the mixed crystals to result in the formation of the fluorescent or phosphorescent state of the component having a lower singlet or triplet level [7].

The fluorescence spectra of polycrystalline mixtures of arylacetic acids **26a–26d** and 1,2,4,5-tetracyanobenzene (**27**) (Scheme 5) were measured with a front face arrangement [11]. In all cases, the fluorescence spectra of the mixed crystals were approximately the same as the sum of those of the two components, showing lower emission intensities. Only in the case of the mixed crystals **26a–27** and **26b–27** did new peaks, ascribed to excimer fluorescence at 457 and

428 nm respectively, appear. This fluorescence behaviour is different from facile energy transfer through the interface of the mixed crystals of the above two cases.

4.4. *Other factors*

Distinct selectivities were observed for the solid state photoreactions of most of the mixed crystals in comparison with the solution phase photoreactions of the two components. These have been described in Sections 3.1, 3.2, 3.3 and 3.4. However, in certain cases, a similar product ratio was observed for the solid state and solution phase photoreactions. Due to the experimental difficulties in elucidating the exact molecular arrangement at the interface of polycrystalline mixed crystals, we await further experimental developments for details.

The other important problem is whether the solid state photoreactions at the interface continue until total conversion of the substrates. In order to throw light on this problem, the quantum yield of the solid state photoreaction of the mixed crystal between *p*-tolylacetic acid (**26a**) and 1,2,4,5-tetracyanobenzene (**27**) was measured [11] using a thin film of the mixed crystal, according to the reported method [24]. The quantum yields were 0.04 and 0.20 in the solid state and acetonitrile solution respectively. The actual conversions of **26a** and **27** were 100% and 99% respectively after 4 h of irradiation of the mixed crystal, showing that solid state photoreactions at the interface proceed effectively in certain cases in spite of the low mobility of the molecules.

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