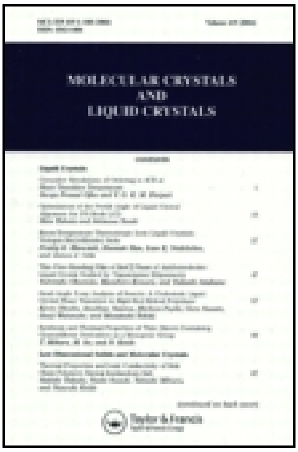

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Photoaddition Reactions in Polycrystalline Mixtures of Diphenylamine and Aromatic Compounds

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To cite this article: Hideko Koshima & Teruo Matsuura (1996): Photoaddition Reactions in Polycrystalline Mixtures of Diphenylamine and Aromatic Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 277:1, 55-62

To link to this article: http://dx.doi.org/10.1080/10587259608046003

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 277, pp. 55–62
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# PHOTOADDITION REACTIONS IN POLYCRYSTALLINE MIXTURES OF DIPHENYLAMINE AND AROMATIC COMPOUNDS

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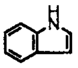
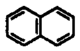
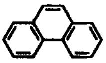
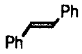
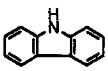
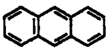
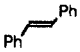
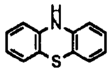
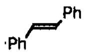
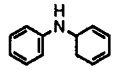
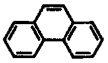
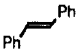
**Abstract** Irradiation of a polycrystalline mixture of diphenylamine (**1**) and *trans*-stilbene (**2**) caused addition reaction to give an adduct (**3**) with C–N bond and two adducts (**4**) and (**5**) with C–C bond. Similar photoaddition reaction of **1** with phenanthrene (**6**) in the solid state produced an adduct (**7**) with C–N bond and another adduct (**8**) with C–C bond. These photoadditon reactions proceed at the interface of the two component crystallites.

## INTRODUCTION

Development of intermolecular reaction between different molecules in the solid state is indispensable for establishing new solid-state chemistry. We have studied solid-state photochemistry between two different organic molecules.[1] Mixed crystals prepared by melting-resolidification or recrystallization from solutions are classified into new two-molecule crystals and simple mixtures of the components. We have already found various photoreactions in the two-molecule crystals[2-7] and in the simple mixtures.[3,8-14] In particular, the reactivities and the selectivities of the two molecule-crystals are quite different from those of the solution photoreactions because the reactions occur in the crystal lattice. On the other hand the reactions of simple polycrystalline mixtures proceed at the crystallite surface.[11]

Photoaddition of the mixed crystals of indole/naphthalene,[2,3] indole/phenanthrene(**6**),[2,3] carbazole/anthracene[4] and NH heteroaromatics/*trans*-stilbene(**2**)[11,12] are caused by photoinduced electron transfer (Table 1). Purposes of the present work are to investigate the photoreactivity of diphenylamine (**1**) with **2** and **6** and subsequently to expand the addition as the reaction forming C–N bond in the solid state.

Table 1 Summary of the mixed crystals undergoing photoaddition reaction

| Component | | Formation of Molecular compound | Literature no. |
|---|---|---|---|
|  |  | Yes | 2, 3 |
| |  | No | 2, 3 |
| |  | No | 12 |
|  |  | Yes | 4 |
| |  | No | 11, 12 |
|  |  | No | 12 |
|  |  | No | This work |
| |  | No | |

## METHODS

$^1$H-NMR spectra were measured on a JEOL PMX-60 spectrometer with tetramethylsilane as an internal standard. IR and UV spectra were measured on a Shimadzu IR-470 spectrophotometer and UV-3100 spectrophotometer, respectively. Powder X-ray diffractograms (PXD) were taken on a Rigaku Geigerflex with RAD-C system. Differential scanning calorimetry (DSC) was performed on a Rigaku Thermoflex TAS-200 DSC-8230D. Static electron spin resonance (ESR) spectra were taken on a JEOL JES-RE2X spectrometer. Polycrystalline mixtures were prepared by melting and resolidification of two components followed by pulverizing in a mortar. All the reagents were commercially available.

Photoreaction of the polycrystalline mixture of diphenylamine **1** and *trans*-stilbene **2**

A 1:1 mixed crystal **1/2** (1.8 g) was placed between two Pyrex glass plates and irradiated with a 400 W high-pressure mercury lamp under argon at 10 °C for 20 h. The irradiated sample was submitted to preparative TLC (silica gel plate and 3:1 hexane-benzene as an eluant) to give **3** in 18 % yield, **4** in 24 % yield and **5** in 9 % yield (Scheme 1). The materials balance was 86 %. **3**; White crystal, mp 110-111 °C (from EtOH), IR (KBr) no NH band, $^1$H-NMR ($CDCl_3$) δ 3.36 (dd, 2H, J=3.0, 7.6 Hz), 5.49 (t, 1H, J=7.6 Hz), 6.75-7.37 (m, 20H, aromatics). Elemental analysis; calcd. for $C_{26}H_{23}N$, C, 89.36 %, H, 6.63 %, N, 4.04 %; analysis, C, 89.54 %, H, 6.93 %, N, 3.90 %. **4**; Not solidified (TLC separation), IR (neat) 3400 cm$^{-1}$ (NH band), $^1$H-NMR ($CDCl_3$) δ 3.36 (d, 2H, J=7.6 Hz), 4.42 (t, 1H, J=7.6 Hz), 4.85 (s, 1H, N<u>H</u>), 6.64-7.44 (m, 19H, aromatics). Elemental analysis; calcd. for $C_{26}H_{23}N$, C, 89.36 %, H, 6.63 %, N, 4.04 %, analysis; C, 89.63 %, H, 6.63 %, N, 3.87 %. This compound was decomposed in air. **5**; Not solidified (TLC separation), IR (neat) 3400 cm$^{-1}$ (NH band), $^1$H-NMR ($CDCl_3$) δ 3.22 (d, 2H, J=7.2 Hz), 4.06 (t, 1H, J=7.2 Hz), 5.37 (s, 1H, broad, N<u>H</u>), 6.56-7.20 (m, 19H, aromatics). Elemental analysis; calcd. for $C_{26}H_{23}N$, C, 89.36 %, H, 6.63 %, N, 4.04 %, analysis; C, 88.11 %, H, 6.67 %, N, 3.51 %. This compound was decomposed in air.

Photoreaction of the polycrystalline mixture of diphenylamine **1** and phenanthrene **6**

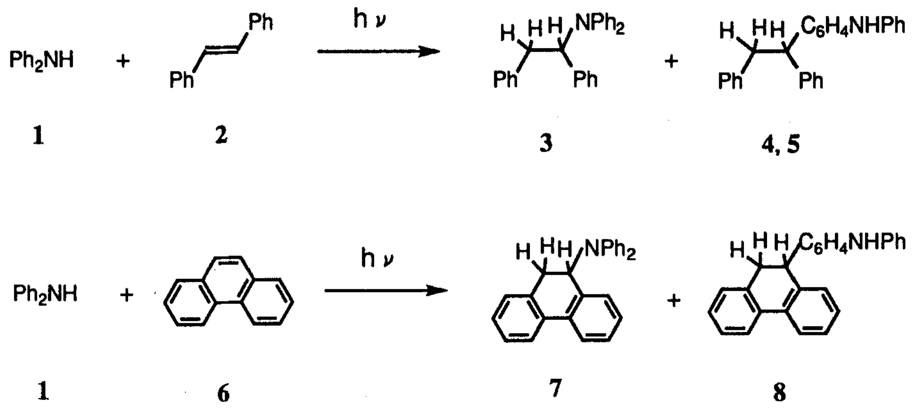
A 1:1 mixed crystal **1/6** (1.6 g) was placed between Pyrex plates and irradiated with a 400 W high-pressure mercury lamp under argon at 10 °C for 20 h. The irradiated mixture was submitted to preparative TLC to give **7** in 10 % yield and **8** in 9 % yield (Scheme 1). The materials balance was 88 %. **7**; Yellow crystal, mp 159-161 °C (from EtOH-$Me_2O$), IR (KBr) no NH band, UV (MeCN) 254 nm (log ε, 4.39), 208 (4.83), $^1$H-NMR ($CDCl_3$) δ 7.10-8.17 (m, 18H, aromatics), 5.77 (dd, 1H, J=6.0, 12.0 Hz), 3.55 (dd, 1H, J=11.6, 16.0 Hz), 3.29 (dd, 1H, J=6.0, 16.0 Hz). Elemental analysis; calcd. for $C_{26}H_{21}N$, C, 89.88 %, H, 6.09 %, N, 4.03 %; analysis, C, 89.95 %, H, 6.16 %, N, 4.02 %. **8**; White crystal, mp 43-46 °C (HPLC separation), IR (KBr) 3395 cm$^{-1}$ (NH band), UV (MeCN) 279 nm (log ε, 4.36), 207 (4.68), $^1$H-NMR {$(CD_3)_2O$} δ 6.65-8.03 (m, 17H, aromatics), 4.16 (t, 1H, J=7.0 Hz), 3.18 (d, 2H, J=7.0 Hz). Elemental analysis; calcd. for $C_{26}H_{21}N$, C, 89.88 %, H, 6.09 %, N, 4.03 %; analysis, C, 89.95 %, H, 6.18 %, N, 4.14 %. This compound was decomposed in air.

### HPLC study of the photoreaction

Details of the photoreaction of **1**/**2** and **1**/**6** were examined by HPLC analysis after irradiating 20 mg of a mixed crystal or 10 ml of a solution in acetonitrile. The results are shown in Tables 2 and 3.

## RESULTS AND DISCUSSION

Irradiation of the mixed crystal of **1** and **2** caused addition reaction to give an adduct **3** with C–N bond and two adducts **4** and **5** with C–C bond (Scheme 1). Table 2 shows the results of the reaction determined by HPLC analysis. The yields are the values based on consumed **1**. The initial 3-h irradiation of 1:1 mixture proceeded fast and further irradiation for 3–20 h was resulted in slight decomposition of the products **3**, **4** and **5**. The yield of **3** increased with an increase of the ratio of **2** in the mixed crystal **1**/**2**. On the other hand, the yield of **4** increased with an increase of the ratio of **1** in **1**/**2**. For a comparison, solution reaction of **1**with **2** in acetonitrile was carried out; the same type reaction occurred to give the three product **3**, **4** and **5**. However the product selectivities were different from those in the solid state photoreaction.



Scheme 1

Table 2 Photoreaction of diphenylamine with *trans*-stilbene in the solid state and in solution

| Molar ratio **1**/**2** | Irrad. time (h) | Conversion (%) **1** | **2** | Yield (%) **3** | **4** | **5** |
|---|---|---|---|---|---|---|
| In the solid state | | | | | | |
| 3:1 | 20 | 29 | 100 | 0 | 55 | 17 |
| 2:1 | 20 | 41 | 100 | 12 | 51 | 17 |
| 1:1 | 3 | 52 | 69 | 37 | 42 | 27 |
| 1:1 | 7 | 59 | 74 | 32 | 41 | 24 |
| 1:1 | 20 | 71 | 91 | 28 | 44 | 17 |
| 1:2 | 20 | 86 | 68 | 30 | 28 | 9 |
| In acetonitrile | | | | | | |
| 0.05M:0.05M | 20 | 21 | 64 | 10 | 19 | 62 |

Photoreaction of the mixed crystal **1**/**6** gave an adduct **7** with C–N bond and another adduct **8** with C–C bond (Scheme 1). Table 3 shows the details of the photoreaction of **1** with **6** by HPLC analysis. The reaction rate of the 1:1 mixed crystal was slow at low temperature; irradiation at –70 °C for 20 h did not produce **7**. Effect of the molar ratio of **1** and **6** in the mixed crystal was not almost observed on the yields of **7** and **8**. Although the same reaction of **1** and **6** in acetonitrile, the efficiency was low at low concentrations of **1** and **6** (0.005M:0.005M).

The mixed crystals **1**/**2** and **1**/**6** prepared by melting and resolidification were characterized by PXD, IR and DSC to be the simple polycrystalline mixtures of the components because of no appearance of new peak in the PXD and IR spectra. The DSC curve of the 1:1 polycrystalline mixture of **1** (mp 54 °C) and **2** (mp 126 °C) shows that the crystallization of **2** begins at 50 °C which is probably the eutectic point and finishes at 108 °C. The phase diagram of **1** and **6** constructed by the DSC measurements of different molar fractions is a typical simple mixture of the two components having an eutectic point at 38 °C (Fig. 1).

Table 3 Photoreaction of diphenylamine with phenanthrene in the solid state and in solution

| Molar ratio **1**/**6** | Irrad. time (h) | Irrad. temp. (°C) | Conversion (%) **1** | Conversion (%) **6** | Yield (%) **7** | Yield (%) **8** |
|---|---|---|---|---|---|---|
| In the solid state | | | | | | |
| 3:1 | 20 | 10 | 22 | 60 | 9 | 25 |
| 2:1 | 20 | 10 | 32 | 49 | 12 | 25 |
| 1:1 | 20 | –70 | 2 | 5 | 0 | 21 |
| 1:1 | 20 | –50 | 9 | 6 | 11 | 15 |
| 1:1 | 20 | –10 | 32 | 18 | 14 | 21 |
| 1:1 | 20 | 10 | 63 | 68 | 9 | 28 |
| 1:1 | 2 | 10 | 46 | 47 | 11 | 8 |
| 1:2 | 20 | 10 | 62 | 16 | 12 | 21 |
| 1:3 | 20 | 10 | 60 | 15 | 12 | 19 |
| In acetonitrile | | | | | | |
| 0.005M:0.005M | 20 | 10 | 86 | 76 | 0 | 5 |
| 0.05M:0.05M | 20 | 10 | 40 | 57 | 5 | 31 |

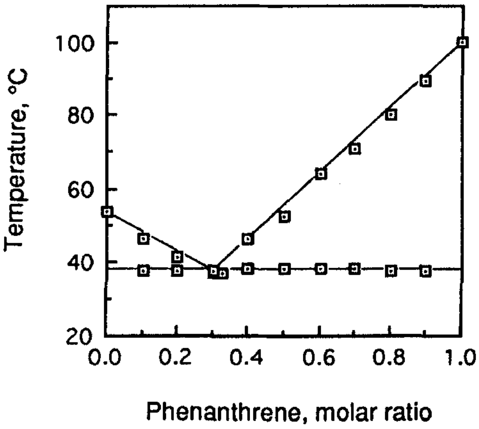


Fig. 1 Phase diagram of diphenylamine and phananthrene

We have already proved that the photoaddition reaction of the polycrystalline mixture of carbazole and **2** proceeds at the interface of the compoonent crystallites.[11] It is reasonable that the simple mixtures **1/2** and **1/6** react at the crystallite surface. The static ESR spectra of **1** and the 1:1 polycrystalline mixture **1/2** in the solid state under UV irradiation at –100 °C were measured to be broad without hyperfine structure. The ESR signal of **1/2** has the G value of 2.0044 with the peak-to-peak width of 1.221 mT. The ESR signal of **1** has the G value of 2.0041 with the peak-to-peak width of 1.412 mT. The signal similarity between the free radicals for **1/2** and **1** and the result of the photoreaction giving the three products **3**, **4** and **5** suggest the formation of a radical intermediate (three canonical forms) derived from diphenylamine (Fig. 2). A possible reaction mechanism in Fig. 2 involves the formation of a radical ion pair followed by NH proton transfer. The mixed crystals which cause the same type of photoaddition are summarized in Table 1. The mixed crystals of indole/**6**, indole/**2**, carbazole/**2**, phenothiazine/**2**, **1/2** and **1/6** are the simple polycrystalline mixtures of the components; these reactions proceed at the interface of the two crystallites. On ther other hand the mixed crystals of indole/naphthalene and carbazole/anthracene forms the molecular compounds betwee the components; in these cases the reactions occur in the crystal

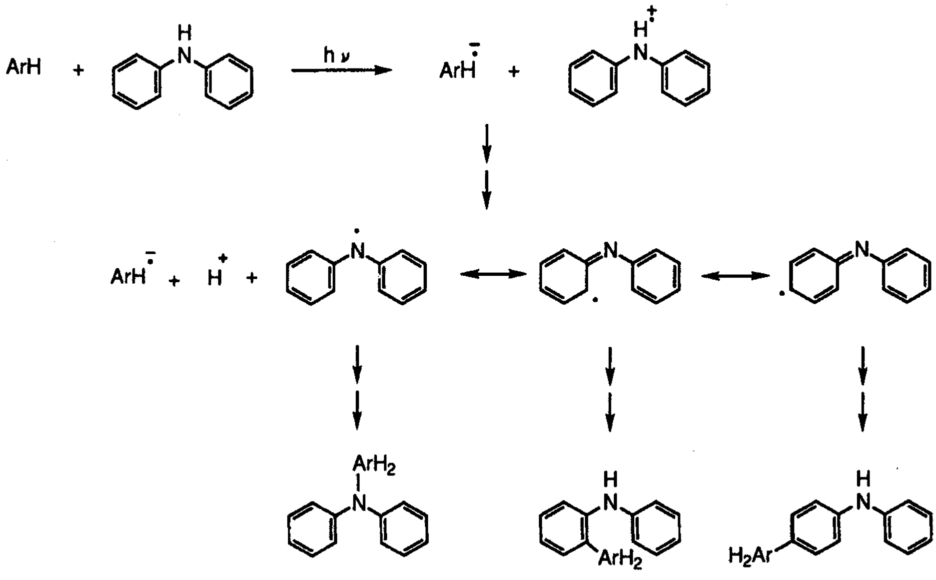


Fig. 2 Possible reaction mechanism of diphenylamine with aromatic compounds

lattice of the molecular compound. However, no difference of the reactivities between the simple polycrystalline mixtures and the molecular crystals was observed. In addition the solid-state photoaddition reactions are essentially the same as those of aliphatic amines with **2** in solution which were comprehensively studied by Lewis and his coworkers.[15-17]

In conclusion these photoaddition reactions are useful for the formation of C–N bond in the solid state.

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