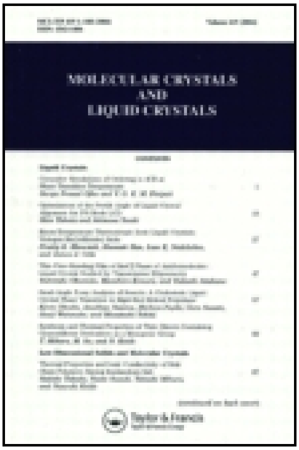

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Photochemistry of Organic Mixed Crystals: Carbazole/Anthracene and Benzimidazole/2,3-Dimethylnaphthalene

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PHOTOCHEMISTRY OF ORGANIC MIXED CRYSTALS: CARBAZOLE/ANTHRACENE AND BENZIMIDAZOLE/ 2,3-DIMETHYLNAPHTHALENE

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Abstract--Among the mixed crystals between carbazole (**1**) or benzimidazole (**2**) and an aromatic hydrocarbon, such as naphthalene, phenanthrene and anthracene, only the carbazole/anthracene mixed crystal was found by powder X-ray diffraction spectroscopy and differential scanning calorimetry to constitute a molecular compound. Irradiation of this molecular compound gave 9-(9-carbazolyl)-9,10-dihydroanthracene (**7**) and 9-(9-carbazolyl)anthracene (**8**) both in the solid state and in an acetonitrile solution. The structure of **7** was established by X-ray crystallographic analysis. Benzimidazole showed no photoreactivity to aromatic hydrocarbons in the solid and solution states, except the irradiation with 2,3-dimethylnaphthalene in acetonitrile leading to the formation of 1-(1-benzimidazolyl)-2,3-dimethylnaphthalene (**9**).

INTRODUCTION

In the course of our studies on the solid-state photoreaction of the mixed crystals between two different organic molecules,[1-6] we found that indole formed a molecular compound with naphthalene in the mixed crystal state, and that the mixed crystal between indole and phenanthrene was a simple mixture of microcrystals of each component.[5] The results suggest that matching of the molecular shapes of the components is important for the formation of a molecular compound. In a continuation of this work, we have characterized the nature of the mixed crystals between polycyclic aromatic hydrocarbons and carbazole (**1**) or benzimidazole (**2**) and have examined the photochemical behaviors of the mixed crystals. As well as the photochemistry, it is of interest to know what kind of combination of two different organic molecules is necessary for the formation of a molecular compound.

MATERIALS AND METHODS

Melting points are uncorrected. ^{1}H-NMR spectra were measured on a JEOL FX-90Q spectrometer using tetramethylsilane as internal standard. IR, UV and mass spectra were recorded on a PYE UNICAM SP3-300 and a Shimadzu UV-240 and a 7070E-HE mass spectrometers, respectively. Powder X-ray diffraction spectra were taken on a Rigaku ROTAFLEX RU-200B. Differential scanning calorimetry (DSC) was done on a Shimadzu differential scanning calorimeter DSC-50. Electron Spin Resonance (ESR) spectra were taken on a JEOL JES-RE2X spectrometer, attaching a UV irradiator ES-UV05X and a variable temperature unit ES-DVTI. Column and thin layer chromatographic separation of the products was carried out on Qing Dao 300 and Merck F_{254} silica gel, respectively. All the reagents were commercially available and were used as received.

Photoreaction of carbazole (**1**) with anthracene (**4**). (i) In solid state. The mixed crystal was prepared by melting a mixture of **1** (0.42 g, 2.5 mmol) and **4** (0.445 g, 2.5 mmol) followed by resolidifying the melt upon cooling. The pulverized mixed crystal was irradiated with a 500 W high-pressure mercury lamp under nitrogen for 25 h at room temperature as described previously.[6] The irradiated mixture was submitted to preparative TLC eluting with 20 : 1 (V/V) petroleum ether-ethyl acetate to give **7** (7 % yield) and **8** (13 % yield). Compound **7**, m.p. 209-211°C; λ_{max} ($CHCl_3$ 265.8 (log ε 4.2), 271.1 nm (4.2); IR (KBr) 3030, 2930, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.30 (m, 2H, 10-CH), 6.50-6.70 (m, 1H, 9-CH), 6.80-8.12 (m, 16 H, Ar-H); mass spectrum, m/z (relative intensity) 345 (M^+, 15), 217 (5), 178 (100), 152 (15). Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.76; H, 5.17; N, 3.88. Compound **8**; m.p. 180-183°C; λ_{max} ($CHCl_3$) 255.8 (log ε 4.7), 290.8 nm (3.8); IR (KBr) 3030, 1600, 1480 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.56-8.5 (m, 16 H, Ar-H), 9.00 (s, 1H, 10-CH); mass spectrum, m/z (relative intensity) 343 (M^+, 100), 189 (50), 140 (20). Anal Calcd for $C_{26}H_{17}N$: C, 90,93; H, 4.99; N, 4.08. Found: C, 90.71; H, 5.26; N, 3.90.

(ii) In solution. A solution of **1** (84 mg, 0.50 mmol) and **4** (89 mg, 0.50 mmol) in acetonitrile (15 ml) was irradiated as above. After the removal of the solvent in reduced pressure, the residue was submitted to preparative TLC eluting 20 : 1 (V/V) petroleum ether-ethyl acetate to give **7** (15 % yield) and **8** (6 % yield).

Photoreaction of benzimidazole (**2**) with 2,3-dimethylnaphthalene (**6**). (i) In the solid state. The mixed crystal prepared from **2** (59 mg, 0.50 mmol) and **6** (78 mg, 0.50 mmol) as above was irradiated in the same manner for 20 h. The starting materials were quantitatively recovered (^{1}H-NMR and TLC).

(ii) In solution. A solution of **2** (0.59 g, 5.0 mmol) and **6** (0.78 g, 5.0 mmol) in acetonitrile (100 ml) was irradiated as above for 20 h. After the removal of the solvent, the residue was submitted to silica gel column chromatography eluting with chloroform to give **9** (22 % yield). Compound **9**; m.p. 169-171°C; λ_{max} ($CHCl_3$) 241.7 (log ε 4.5), 254.2 (4.5), 275.8 (4.0), 283.3 nm (3.7); IR (KBr) 3030, 2910, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.07 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 6.84-7.08 (m, 2H, benzimidazole 2-H, naphthalen 4-CH), 7.08-8.1 (m, 8H, Ar-H); mass spectrum, m/z (relative intensity) 272 (M^+, 100), 257 (10), 245 (15), 128 (20). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.70; H, 5.83; N, 10.07.

Photoreaction of carbazole (**1**) and benzimidazole (**2**) with other aromatic hydrocarbons. Irradiation of a mixture of **1** and naphthalene (**3**) (or phenanthrene (**5**)) was carried out in the solid state and in an acetonitrile solution in the same manner as described above. No photoreaction was observed and all the starting materials were recovered unchanged. No photoreaction was either observed by the irradiation of a mixture of **2** and naphthalene (**3**), anthracene (**4**) or phenanthrene (**5**) in the solid state and in an acetonitrile solution in the same manner.

Attempts to obtain a single crystal of the molecular compound between carbazole (**1**) and anthracene (**4**). The following organic solvents were used for the attempts to crystallize a single crystal of the molecular compound between **1** and **4** from the solutions: hexane, benzene, ethyl acetate, chloroform , diethyl ether and their mixed solvents. In all cases **1** and **4** separately crystallized out.

X-ray crystallographic analysis of compound **7**. A colorless crystal of $C_{26}H_{19}N$ having approximate dimensions of 0.1 x 0.1 x 0.1 mm was mounted on a glass fiber in a random orientation. The determination of unit cell and the data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromator situated in the incident beam. A total of 3729 independent reflections were collected in the range of $2 \leq \theta \leq 25°$ by w - 2θ scan technique at room temperature, in which 976 reflections with $I > 3\sigma$ (I) were considered to be observed and used in the succeeding refinement. The correction for LP factors and empirical absorption were applied to the data.

The crystal is monoclinic, space group Cc, with a = 11.197(2), b = 14.026(5), c = 26.197(7) Å, β = 102.40(2)°, V = 4018(4) $Å^3$, Mr = 345.42, Z = 8, Dx = 1.14 g/cm^3, μ = 0.61 cm^{-1}, F(000) = 1456.

The structure was solved by direct phase determination method (MULTAN 82). The most of non-hydrogen atoms were located from E-map. The other non-hydrogen atoms were determined with successive difference Fourier syntheses. The hydrogen atoms were not included in the refinement and the calculation of structure factors. The final refinement by full matrix least-square method with isotropic thermal parameters for all non-hydrogen atoms was converged with unweighted and weighted agreement factors of 0.096 and 0.089 (unit weights). The highest peak on the final difference Fourier map had a height of 0.74 e/A^3. All calculations were performed on a PDP11/44 computer using SDP-PLUS program package. The moleclar structure of **7** is given in Figure 1 and the parameters are given in Table 1-3.

RESULTS AND DISCUSSION

The mixed crystals between carbazole (**1**) or benzimidazole (**2**) and aromatic hydrocarbons were prepared by melting a 1 : 1 molar mixtures of the components. They were submitted to photoirradiation in the solid state and in the acetonitrile solution and also to the characterization by powder X-ray diffraction (PXD) spectroscopy and differential scanning calorimetry (DSC). The results are summarized

Table 1. Fractional Coordinates and Isotropic Thermal Parameters for Non-hydrogen Atoms with Estimated Standard Deviation in Parentheses.

Atom	*X*	*Y*	*Z*	*Beq.*(A^2)	Atom	*X*	*Y*	*Z*	*Beq.*(A^2)
C11	0.477	0.485(1)	0.626	3.1(4)	C51	0.476(2)	0.750(2)	0.3122(9)	4.8(5)
C12	0.438(2)	0.503(2)	0.5732(9)	5.2(5)	C52	0.359(2)	0.775(2)	0.288(1)	7.8(7)
C13	0.526(2)	0.522(2)	0.543(1)	5.7(6)	C53	0.350(3)	0.811(2)	0.233(1)	8.0(8)
C14	0.647(2)	0.535(2)	0.567(1)	7.2(7)	C54	0.443(2)	0.811(2)	0.209(1)	5.9(6)
C15	0.682(2)	0.512(2)	0.617(1)	6.3(6)	C55	0.555(2)	0.789(2)	0.239(1)	5.6(6)
C16	0.600(2)	0.487(2)	0.6496(9)	5.0(5)	C56	0.569(2)	0.756(2)	0.2887(9)	5.8(6)
C17	0.635(2)	0.470(2)	0.705(1)	5.8(6)	C57	0.695(2)	0.720(2)	0.322(1)	6.1(6)
C18	0.548(2)	0.504(2)	0.7378(8)	4.1(5)	C58	0.710(2)	0741(2)	0.3783(9)	4.9(5)
C19	0.581(2)	0.541(2)	0.788(1)	5.9(6)	C59	0.828(2)	0.761(2)	0.408(1)	5.0(5)
C20	0.500(2)	0.567(2)	0.823(1)	6.8(7)	C60	0.844(2)	0.775(2)	0.458(1)	6.2(6)
C21	0.380(2)	0.562(2)	0.794(1)	7.7(7)	C61	0.751(2)	0.773(2)	0.4845(9)	5.0(5)
C22	0.336(2)	0.527(2)	0.739(1)	6.8(7)	C62	0.628(2)	0.750(2)	0.454(1)	6.2(6)
C23	0.424(2)	0.502(2)	0.717(1)	5.9(6)	C63	0.609(2)	0.734(1)	0.3995(7)	2.9(4)
C24	0.391(2)	0.458(2)	0.6569(9)	5.5(6)	C64	0.493(2)	0.710(2)	0.3678(9)	4.7(5)
N1	0.261(1)	0.484(1)	0.6353(7)	4.1(4)	N2	0.391(1)	0.734(1)	0.3916(7)	4.0(4)
C31	0.167(2)	0.413(1)	0.6111(9)	3.6(4)	C71	0.363(2)	0.825(1)	0.4062(8)	4.2(5)
C32	0.170(2)	0.318(2)	0.613(1)	5.3(5)	C72	0.398(2)	0.909(1)	0.3937(8)	3.3(4)
C33	0.061(2)	0.268(2)	0.5918(9)	4.8(5)	C73	0.351(2)	0.990(2)	0.4073(9)	5.8(6)
C34	-0.033(2)	0.317(2)	0.567(1)	6.8(7)	C74	0.254(2)	0.988(2)	0.435(1)	7.4(7)
C35	-0.036(2)	0.412(2)	0.5635(9)	5.5(6)	C75	0.202(2)	0.894(2)	0.450(1)	6.5(7)
C36	0.061(2)	0.463(1)	0.5875(9)	4.6(5)	C76	0.265(2)	0.819(1)	0.4331(8)	3.8(5)
C37	0.093(2)	0.569(2)	0.5947(9)	4.6(5)	C77	0.242(2)	0.714(1)	0.4398(9)	4.3(5)
C38	0.018(2)	0.649(2)	0.574(1)	6.9(7)	C78	0.165(2)	0.666(2)	0.462(1)	6.0(6)
C39	0.076(2)	0.739(2)	0.591(1)	6.8(7)	C79	0.166(2)	0.565(2)	0.463(1)	6.9(7)
C40	0.204(2)	0743(2)	0.619(1)	6.4(6)	C80	0.236(2)	0.521(1)	0.4334(9)	4.6(5)
C41	0.271(2)	0.662(2)	0.6351(9)	4.6(5)	C81	0.320(2)	0.571(1)	0.4143(9)	4.4(5)
C42	0.221(2)	0.574(2)	0.6234(9)	4.3(5)	C82	0.322(2)	0.677(1)	0.4140(8)	3.5(4)

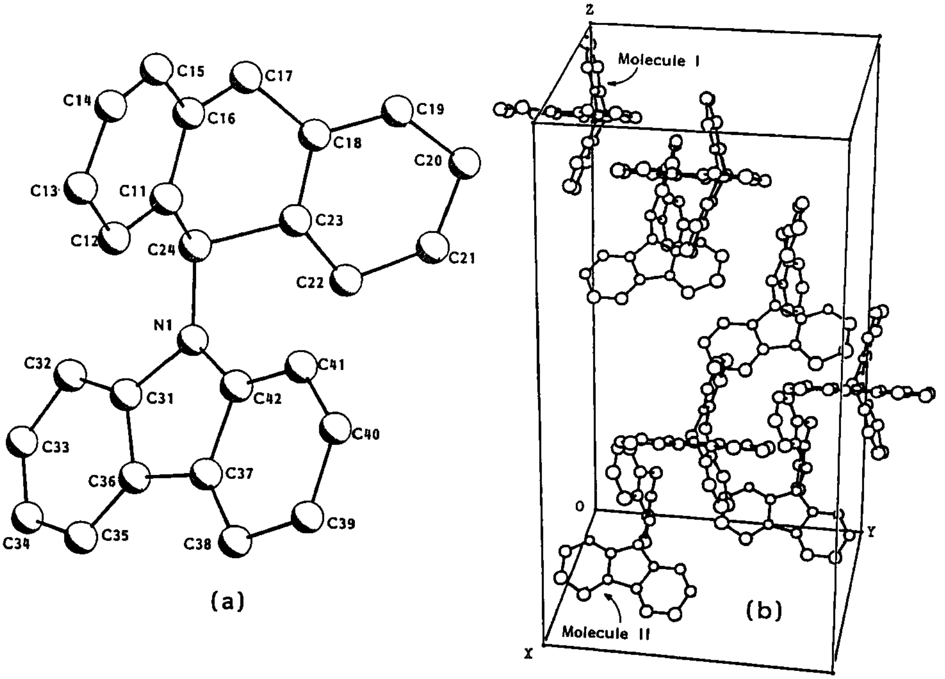
Table 2. Bond Distances (Å) of 7 with Standard Deviation in Parenthesis.

Molecule I				Molecule II			
C11-C12	1.37(2)	C24-N1	1.48(2)	C51-C52	1.37(2)	C64-N2	1.46(2)
C11-C16	1.39(1)	N1-C31	1.49(2)	C51-C56	1.32(2)	N2-C71	1.39(2)
C11-C24	1.45(2)	N1-C42	1.36(2)	C51-C64	1.54(2)	N2-C82	1.42(2)
C12-C13	1.43(2)	C31-C32	1.33(2)	C52-C53	1.49(2)	C71-C72	1.31(3)
C13-C14	1.38(2)	C31-C36	1.40(2)	C53-C54	1.35(2)	C71-C76	1.43(3)
C14-C15	1.32(3)	C32-C33	1.41(3)	C54-C55	1.37(2)	C72-C73	1.32(2)
C15-C16	1.44(2)	C33-C34	1.31(2)	C55-C56	1.36(2)	C73-C74	1.43(2)
C16-C17	1.45(2)	C34-C35	1.35(2)	C56-C57	1.58(2)	C74-C75	1.53(2)
C17-C18	1.51(2)	C35-C36	1.34 (2)	C57-C58	1.48(2)	C75-C76	1.38(2)
C18-C19	1.38(2)	C36-C37	1.53(2)	C58-C59	1.41(2)	C76-C77	1.51(2)
C18-C23	1.38(1)	C37-C38	1.44(2)	C58-C63	1.37(2)	C77-C78	1.33(2)
C19-C20	1.49(2)	C37-C42	1.46(2)	C59-C60	1.30(2)	C77-C82	1.40(1)
C20-C21	1.40(2)	C38-C39	1.44(1)	C60-C61	1.36(2)	C78-C79	1.41(2)
C21-C22	1.49(2)	C39-C40	1.47(2)	C61-C62	1.48(2)	C79-C80	1.35(2)
C22-C23	1.31(2)	C40-C41	1.37(2)	C62-C63	1.42(1)	C80-C81	1.36(2)
C23-C24	1.64(1)	C41-C42	1.35(2)	C63-C64	1.42(2)	C81-C82	1.34(1)

Table 3. Bond Angles (°) with Estimated Standard Deviation in Parentheses.

Molecule I				Molecule II			
C12-C11-C16	121(1)	C24-N1-C31	123(2)	C52-C51-C56	122(1)	C64-N2-C71	126(1)
C12-C11-C24	120(2)	C24-N1-C42	125(1)	C52-C51-C64	117(1)	C64-N2-C82	125(1)
C16-C11-C24	118(1)	C31-N1-C42	111(1)	C56-C51-C64	121(1)	C71-N2-C82	108(2)
C11-C12-C13	119(1)	N1-C31-C32	130(1)	C51-C52-C53	114(1)	N2-C71-C72	131(1)
C12-C13-C14	119(1)	N1-C31-C36	108(2)	C52-C53-C54	124(1)	N2-C71-C76	109(1)
C13-C14-C15	119(2)	C32-C31-C36	122(1)	C53-C54-C55	116(1)	C72-C71-C76	119(1)
C14-C15-C16	124(1)	C31-C32-C33	118(1)	C54-C55-C56	122(1)	C71-C72-C73	123(1)
C11-C16-C15	117(1)	C32-C33-C34	119(2)	C51-C56-C55	122(1)	C72-C73-C74	121(1)
C11-C16-C17	119(1)	C33-C34-C35	125(2)	C51-C56-C57	115(1)	C73-C74-C75	121(1)
C15-C16-C17	125(1)	C34-C35-C36	119(1)	C55-C56-C57	123(1)	C74-C75-C76	109(1)
C16-C17-C18	117(1)	C31-C36-C35	118(1)	C56-C57C58	113(2)	C71-C76-C75	127(1)
C17-C18-C19	126(1)	C31-C36-C37	106(1)	C57-C58-C59	120(1)	C71-C76-C77	107(2)
C17-C18-C23	118(2)	C35-C36-C37	136(1)	C57-C58-C63	117(1)	C75-C76-C77	126(1)
C19-C18-C23	116(2)	C36-C37-C38	128(1)	C59-C58-C63	123(1)	C76-C77-C78	134(2)
C18-C19-C20	128(1)	C36-C37-C42	107(1)	C58-C59-C60	120(1)	C76-C77-C82	105.1(9)
C19-C20-C21	106(1)	C38-C37-C42	125(1)	C59-C60-C61	124(2)	C78-C77-C82	121(1)
C20-C21-C22	129(1)	C37-C38-C39	113(2)	C60-C61-C62	117.5(9)	C77-C78-C79	122(1)
C21-C22-C23	114(2)	C38-C39-C40	121(2)	C61-C62-C63	119.7(8)	C78-C79-C80	118(1)
C18-C23-C22	127(1)	C39-C40-C41	122(1)	C58-C63-C62	117(2)	C79-C80-C81	120(1)
C18-C23-C24	113.5(9)	C40-C41-C42	121(1)	C58-C63-C64	121(2)	C80-C81-C82	122(2)
C22-C23-C24	119.2(8)	N1-C42-C37	108(1)	C62-C63-C64	123(2)	N2-C82-C77	110(1)
C11-C24-C23	113.1(9)	N1-C42-C41	134(2)	C51-C64-C63	112(2)	N2-C82-C81	132(2)
C11-C24-N1	116(2)	C37-C42-C41	118(1)	C51-C64-N2	112(2)	C77-C82-C81	117(2)
C23-C24-N1	106.2(9)			C63-C64-N2	113(2)		

Figure 1. X-ray crystal structures of 7: (a) Molecular structure and (b) crystal packing.



in Table 4. Among the mixed crystals of carbazole (1) with naphthalene (3), anthracene (4) and phenanthrene (5), only the mixed crystal between 1 and 3 was photochemically reactive both in the solid state and in solution. In this case, we confirmed the formation of a molecular compound by PXD and DSC. For the mixed crystal between carbazole (1) and anthracene (4), several new peaks occur in the PDX pattern (Figure 2) and in the DSC curve (Figure 3) a new sharp peak at 223.5°C was observed between the peaks of the components at 216.8°C and 245.6°C corresponding their melting points.

Attempts were made for obtaining a single crystal of the molecular compound between 1 and 4 by crystallization from various solvents, but in all cases 1 and 4 crystallized out separately.

The PXD pattern of the mixed crystal between 1 and phenanthrene (5), which was photochemically unreactive, was approximately the same as the sum of the pattern of each component, suggesting no formation of a molecular compound. However, the DSC measurement (Figure 4) of this mixed crystal showed somewhat broad peaks at 123.4°C and 192.9°C appearing between the peaks of the components at 100.9°C and 245.9°C, indicating that a molecular compound was formed at least partly.

Table 4. Photoreaction and Molecular Compound Formation of the Mixed Crystals.

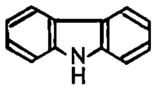
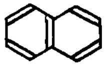
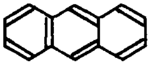
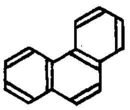
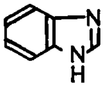
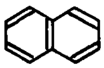
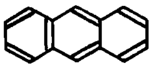
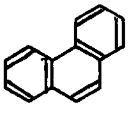
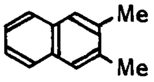
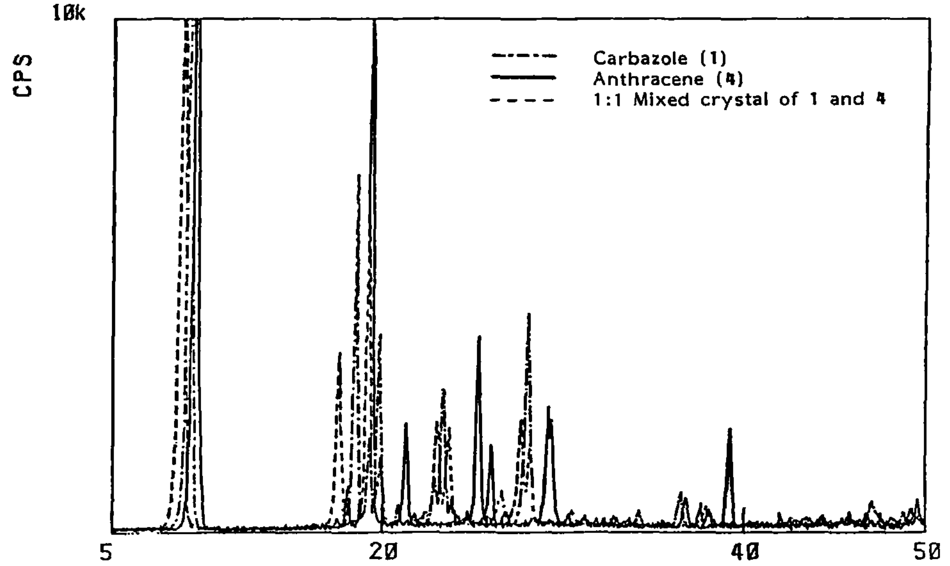
Components of mixed crystal		Photoreaction		Formation of Molecular compound
		Solid	Solution	
 1	 3	No	No	No
	 4	Yes	Yes	Yes (1 : 1)
	 5	No	No	Yes (in part)
 2	 3	No	No	No
	 4	No	No	No
	 5	No	No	No
	 6	No	Yes	No

Figure 2. Powder X-ray diffraction patterns of **1**, **4** and the mixed crystal between **1** and **4**.



The mixed crystals of benzimidazole (**2**) with naphthalene (**3**), anthracene (**4**), phenanthrene (**5**) and 2,3-dimethylnaphthalene (**6**) were found by their PXD and DSC measurements not to be a molecular compound. For this series only a mixture of **2** and **6** was photoreactive in an acetonitrile solution.

Two photoproducts **7** and **8** were obtained from carbazole (**1**) and anthracene either in the solid state or in an acetonitrile solution. Product **7** is the addition product similar to those previously obtained by the solid state photoreaction of indole and naphthalene or phenanthrene.[2,5] Its structure was deduced from the spectral data and confirmed by the X-ray structural analysis of a single crystal (Figure 1). The crystal structure the photoproduct **7** has an interesting feature. There are two different molecular arrangements, molecule I [numbering: C11-C24, C31-C42 and N1] and molecule II [numbering: C51-C64, C71-C82 and N2], constituting the unit cell with four molecules each. The structure of product **8** was assigned from microanalysis and spectral data. Product **8** is considered to be formed by the photochemical dehydrogenation of the initially formed addition product **7**.

The ESR (electron spin resonance) spectrum was taken with an irradiated sample of the mixed crystal beteen **1** and **4** at -100°C in the solid state. We observed a broad singlet signal at g = 2.0036 which was assigned as 1-carbazoyl radical. A radical signal of the same g value was observed with an irradiated sample of **1** in the solid state at -100°C, although its intensity was much smaller than that from the mixed crystal. This result suggests that 1-carbazoyl radical is involved as the intermediate for the formation of the photoaddition product **7** as the mechanism previously proposed for the solid-state photoaddition of indole to naphthalene.[5]

Figure 3. Differential scanning calorimetry (DSC) curves of 1, 4 and the mixed crystal between 1 and 4.

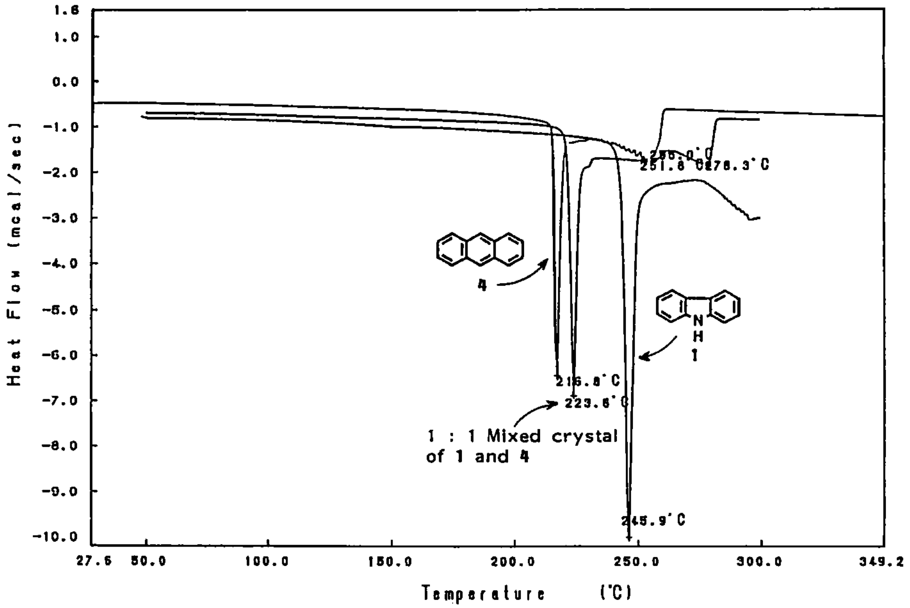
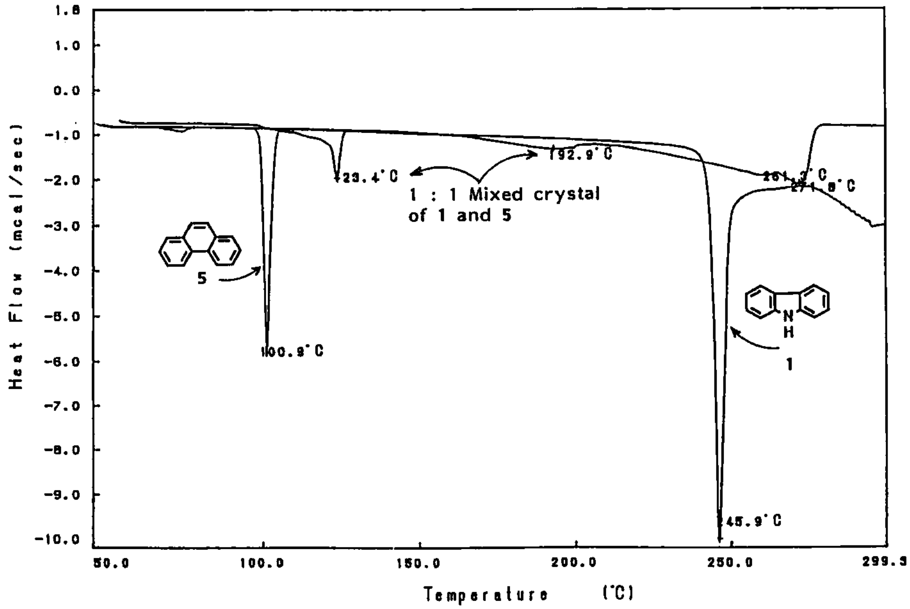
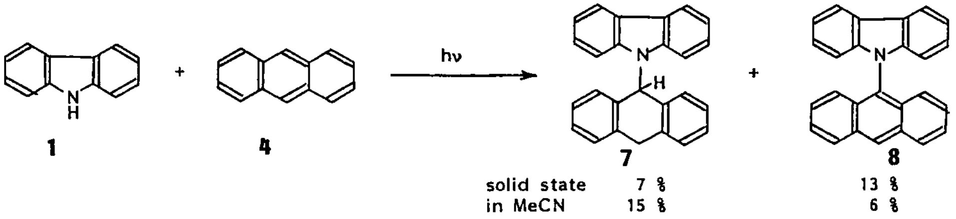


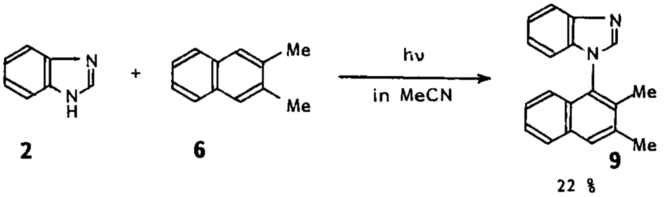
Figure 4. DSC curves of 1, 5 and the mixed crystal between 1 and 5.



The structure of photoproduct **9** from benzimidazole (**2**) and 2,3-dimethylnaphthalene (**6**) was assigned from microanalysis and spectral data. In this case no formation of a photoaddition product like **7** was observed, possibly due to its feasibility to dehydrogenation into **8**.

In summary, for the present series of mixed crystals the formation of a molecular compound appears to be essential for the occurrence of the bimolecular photoreaction in the solid state.





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