

Selectivity in the Solid-State Photoreaction of 6-Cyanouracils  
with Aromatic Hydrocarbons

Ji-ben MENG, Zuo-lin ZHU, Ru-ji WANG,<sup>†</sup> Xin-kan YAO,<sup>†</sup>  
Yoshikatsu ITO,<sup>††</sup> Hiroyasu IHARA,<sup>††</sup> and Teruo MATSUURA<sup>†† \*</sup>

Department of Chemistry, Nankai University, Tianjin, China

<sup>†</sup>Central Laboratory, Nankai University, Tianjin, China

<sup>††</sup>Department of Synthetic Chemistry, Faculty of Engineering,  
Kyoto University, Yoshida, Kyoto 606

The photoreactions of 6-cyanouracils with aromatic hydrocarbons  
in the solid state proceed with a selectivity different from that  
in solution.

Among increasing interests in the solid-state organic photochemistry,<sup>1)</sup> little attention has been drawn to bimolecular photoreactions between two different organic molecules.<sup>2)</sup> We report here on differences in selectivity of the photoreactions of 6-cyanouracils with aromatic hydrocarbons between solid and solution phases.

The mixed crystal, prepared by melting the 1 : 2 mixture of 6-cyano-1,3-dimethyluracil (**1a**)<sup>3)</sup> and acenaphthylene (**2**) crystals followed by resolidifying the melt, was irradiated with a high-pressure mercury lamp (Pyrex housing) in the solid state to give a cis [2 + 2] adduct **3** as the sole product in 50% yield. Its structure was determined by X-ray crystallographic analysis (Fig. 1).<sup>4)</sup> When a solution of the 1 : 2 mixture of **1a** and **2** in benzene, acetonitrile, or methanol was irradiated, the adduct **3** was obtained in 55, 45, and 70% yield, respectively, together with a mixture of the known trans and cis photodimers of **2**<sup>5)</sup> in 15, 18, and 12% yield, respectively.

Similar irradiation of the mixed crystal of **1a** and phenanthrene (**4**) (1 : 2) in the solid state gave a cis adduct **5a**<sup>6)</sup> in 98% yield. The product yield was depending upon the molar ratio of **1a** to **4**; yield of **5a**, 44 (1 : 1), 98 (1 : 2), 88 (1 : 3), 87 (1 : 4), 79% (1 : 5). Irradiation of the 1 : 2 mixture of **1a** and **2** in solution gave **5a** in 23 (benzene), 18 (acetonitrile), and 19% (methanol) yield, and 6-(9-phenanthryl)-1,3-dimethyluracil (**6**) was obtained in 8% yield as a byproduct only in case that benzene was used as a solvent.

Irradiation of the mixed crystal of 6-cyano-1-methyluracil (**1b**)<sup>3)</sup> and phenanthrene (**4**) (1 : 1) in the solid state gave no photoproduct, while the photoreaction of the same mixture in methanol proceeded slowly to give a mixture of

the cis adduct **5b** (10%) and the trans adduct **7b** (7%).<sup>6</sup> Irradiation of the mixed crystal of the 1 : 1 mixture of 6-cyano-1,3-diethyluracil (**1c**)<sup>7</sup> and **4** in acetonitrile gave a mixture of the cis adduct (**5c**) (6%) and the trans adduct **5c** (17%), while **5c** (8%) was the sole product from the irradiation of the mixed crystal.

As seen in the cases of **1a** and **1c**, these solid-state photoreactions proceed with a high selectivity to give a single product providing a useful tool for the synthesis of this type of photoadduct.

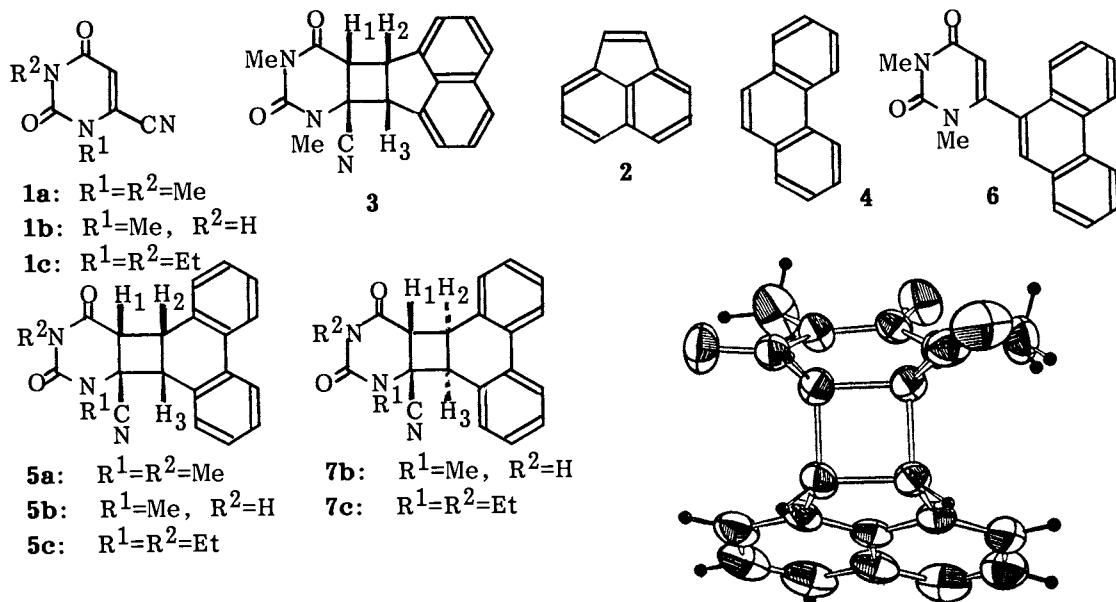


Fig. 1. Stereoview of **3a**.

#### References

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- 4) The crystal data were as follows:  $C_{19}H_{15}N_3O_2$ ,  $M = 317.1$ , triclinic, space group  $P\bar{1}$ ,  $a = 8.735(1)$ ,  $b = 15.315(2)$ ,  $c = 18.094(4)$  Å,  $\alpha = 94.96(2)$ ,  $\beta = 93.89(1)$ ,  $\gamma = 103.79(1)$ °,  $v = 2332.5$  Å<sup>3</sup>,  $z = 6$ ,  $D_C = 1.36$  g/cm<sup>3</sup>,  $R = 0.040$ . The details will be published elsewhere.
- 5) D. O. Cowan and R. L. Drisko, *J. Am. Chem. Soc.*, **89**, 3068 (1967); *Tetrahedron Lett.*, **1967**, 1255.
- 6) The stereochemistry of the photoadducts between 6-cyanouracils (**1**) and phenanthrene (**4**) were assigned by comparisons of the 400 MHz <sup>1</sup>H NMR data for H<sub>1</sub>, H<sub>2</sub>, and H<sub>3</sub>. For example, (*CDCl*<sub>3</sub>): **5a**, 4.39 (H<sub>1</sub>), 4.48 (H<sub>2</sub>), 4.49 (H<sub>3</sub>),  $J_{12}=9.5$ ,  $J_{23}=9.5$ ,  $J_{13}=0.5$  Hz; **5b**, 4.35 (H<sub>1</sub>), 4.51 (H<sub>2</sub>), 4.54 (H<sub>3</sub>),  $J_{12}=9.5$ ,  $J_{23}=10.0$ ,  $J_{13}=0.5$  Hz; **7b**, 3.77 (H<sub>1</sub>), 4.23 (H<sub>2</sub>), 4.21 (H<sub>3</sub>),  $J_{12}=7.2$ ,  $J_{23}=10.0$ ,  $J_{13}=-1.2$  Hz. The *J* values were obtained by a computer-aided simulation.
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