

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

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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,¹⁾ little
attention has been drawn to bimolecular photoreactions between two different organic
molecules.²⁾ 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**)³⁾ 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).⁴⁾ 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**⁵⁾ 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**⁶⁾ 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**)³⁾ and phenan-
threne (**4**) (1 : 1) in the solid state gave no photoproduct, while the photo-
reaction of the same mixture in methanol proceeded slowly to give a mixture of

the cis adduct **5b** (10%) and the trans adduct **7b** (7%).⁶⁾ Irradiation of the mixed crystal of the 1 : 1 mixture of 6-cyano-1,3-diethyluracil (**1c**)⁷⁾ 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.

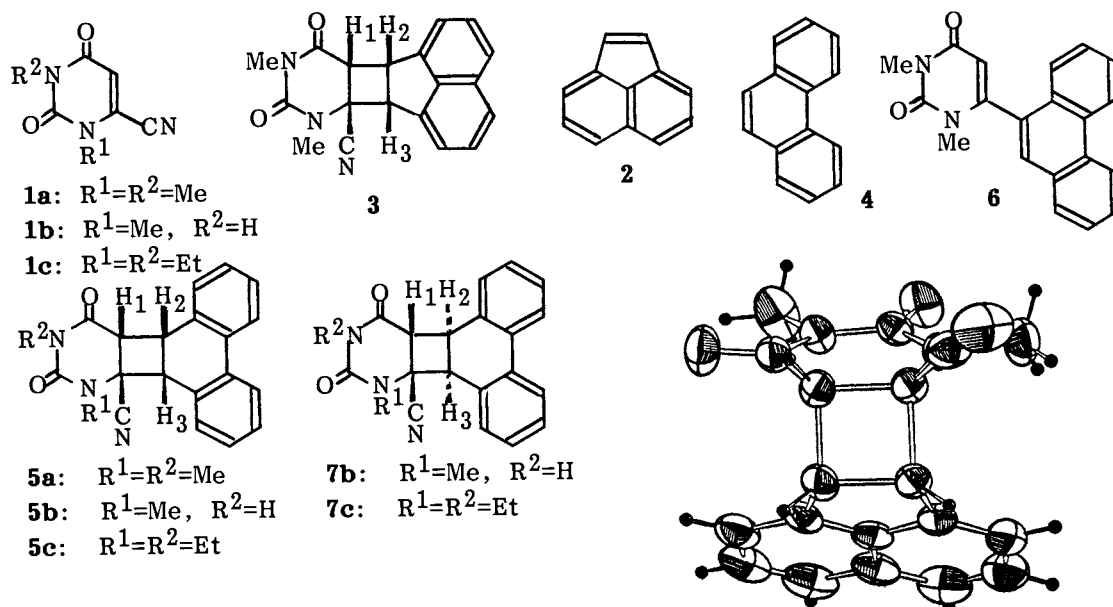


Fig. 1. Stereoview of **3a**.

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 P1, $a = 8.735(1)$, $b = 15.315(2)$, $c = 18.094(4)$ Å, $\alpha = 94.96(2)$, $\beta = 93.89(1)$, $\gamma = 103.79(1)^\circ$, $v = 2332.5$ Å³, $z = 6$, $D_c = 1.36$ g/cm³. $R = 0.040$. 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 ¹H NMR data for H₁, H₂, and H₃. For example, (CDCl₃); **5a**, 4.39 (H₁), 4.48 (H₂), 4.49 (H₃), $J_{12}=9.5$, $J_{23}=9.5$, $J_{13}=0.5$ Hz; **5b**, 4.35 (H₁), 4.51 (H₂), 4.54 (H₃), $J_{12}=9.5$, $J_{23}=10.0$, $J_{13}=0.5$ Hz; **7b**, 3.77 (H₁), 4.23 (H₂), 4.21 (H₃), $J_{12}=7.2$, $J_{23}=10.0$, $J_{13}=-1.2$ Hz. The J values were obtained by a computer-aided simulation.
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