# The Photochemical Reaction of Benzo[*c*]cinnoline. III. Mechanism of Carbazole Formation

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5,6-Dihydrobenzo[*c*]cinnoline is an intermediate in the photochemical formation of carbazole from benzo[*c*]cinnoline. The mechanism of the photo-induced carbazole formation from 5,6-dihydrobenzo[*c*]cinnoline has been studied in acidic aqueous 2-propanol of the reactant previously produced by the photo-reduction of benzo[*c*]cinnoline. It has been established that only the protonated species of the reactant undergoes photoreaction. The results of quenching experiments on quantum yields for the reaction and on the fluorescence of the reactant have shown that the reactive state is the first excited singlet state of protonated 5,6-dihydrobenzo[*c*]cinnoline. The initial step in the reaction is the hydrogen atom abstraction followed by elimination of the amino radical.

It has been reported that benzo[*c*]cinnoline in acidic alcohol solutions gives rise to carbazole under ultraviolet light irradiation.[1] 5,6-Dihydrobenzo[*c*]cinnoline has been found to be an intermediate in the carbazole formation. This intermediate is obtained in acidic 2-propanol with visible light irradiation. No subsequent reaction occurs,[2] hence the photo-induced carbazole formation from 5,6-dihydrobenzo[*c*]cinnoline can be studied using the solution thus obtained. In strongly acidic solution such as 4 M HCl aqueous 2-propanol, 5,6-dihydrobenzo[*c*]cinnoline exists in the monoprotonated form and has absorption bands at 240, 270, and 315 nm.

The purpose of this paper is to clarify the mechanism regarding the photochemical reaction of 5,6-dihydrobenzo[*c*]cinnoline to carbazole. The reactive excited state of the reactant and the mode of elimination of fragments from the reactant are of particular interest.

## Experimental

*Materials.* Benzo[*c*]cinnoline, naphthalene, anthracene, pyrene, and 2-propanol were the same as those used previously.[2] Phenanthrene and fluorene were recrystallized from ethanol. Acetophenone was purified by distillation. *trans*-1,3-Pentadiene was used without further purification.

*Irradiation.* To convert benzo[*c*]cinnoline into 5,6-dihydrobenzo[*c*]cinnoline, an acidic aqueous 2-propanol solution of the former was irradiated with light of a wavelength in excess of 400 nm, obtained from a 500 W high pressure mercury arc lamp and a Corning glass filter (CS 3-73). The solution of the reactant thus prepared was irradiated with 315 nm light from a Shimadzu excitation apparatus GF-16E, equipped with a 500 W Xe lamp and a grating monochromator. All irradiations were conducted at room temperature under nitrogen to prevent oxidation of the reactant.

*Measurements and Analysis.* Ultraviolet spectra were measured with a Shimadzu UV-200 spectrophotometer using 1 cm cells. Fluorescence and phosphorescence spectra were recorded on a Shimadzu RF-500 spectrofluorimeter at room temperature and 77 K, respectively. The quantum yield for the carbazole formation was determined as follows. Acidic aqueous 2-propanol solution (4 M HCl) of benzo[*c*]cinnoline ($1.0 \times 10^{-4}$ M) was irradiated, first with light of a wavelength in excess of 400 nm for 3 h to give 5,6-dihydrobenzo[*c*]cinnoline quantitatively, and then the resulting solution was irradiated with light of wavelength 315 nm for 15 min. The actionmetry was performed together with the spectrophotometric determination of the amount of carbazole produced, a potassium ferrioxalate solution being employed as the actinometer.[3]

## Results and Discussion

The quantum yield for the carbazole formation was determined to be 0.15 and this did not change with variation in the initial concentration of reactant in the range $7.5 \times 10^{-5}$—$2.0 \times 10^{-4}$ M. In order to estimate the energies of the lowest excited singlet and triplet states of the reactant, the fluorescence and phosphorescence spectra were measured. From the observed emission spectra presented in Fig. 1 the energies of the lowest excited singlet and triplet states were evaluated to be 82.7 and 63.4 kcal/mol, respectively. These values were determined from the wavelengths of the emission band shoulders indicated by the arrows in Fig. 1, since the emission bands have no distinct fine structures.

To identify the reactive state of the photoreaction, quenching experiments were conducted using several compounds, *e.g.* fluorene, naphthalene, acetophenone

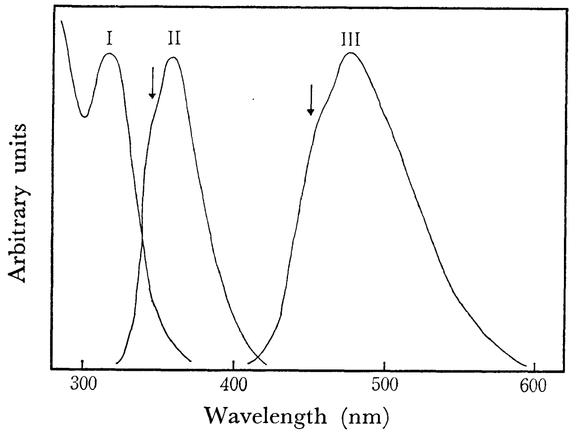


Fig. 1. Absorption and emission spectra of 5,6-dihydrobenzo[*c*]cinnoline in 4 M HCl aqueous 2-propanol. Excitation wavelength: 315 nm. I: Absorption, II: fluorescence, III: phosphorescence.

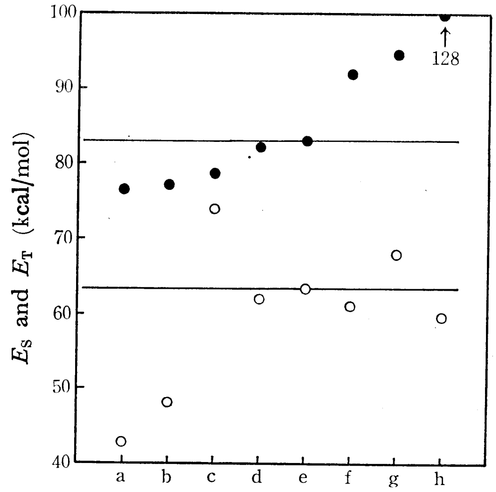


Fig. 2. Energies of the lowest excited singlet (●) and triplet (○) states for 5,6-dihydrobenzo[*c*]cinnoline and the quenchers. a: Anthracene, b: pyrene, c: acetophenone, d : phenanthrene, e : 5,6-dihydrobenzo[*c*]cinnoline, f : naphthalene, g : fluorene, h : *trans*-1,3-pentadiene (The singlet energy was estimated from the absorption band at 223 nm).

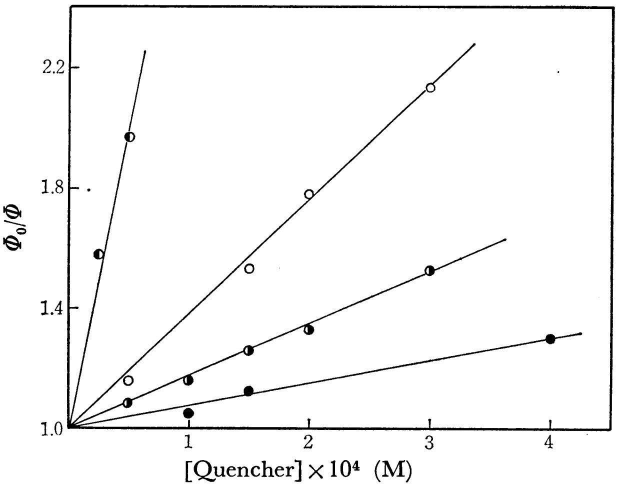


Fig. 3. Stern-Volmer plots for the carbazole formation. [5,6-dihydrobenzo[*c*]cinnoline] = $1.0 \times 10^{-4}$ M.
◐: Pyrene, ○: anthracene, ◑: phenanthrene, ●: acetophenone.

pyrene, phenanthrene, anthracene, and *trans*-1,3-pentadiene. The energies of the lowest excited singlet and triplet states for these compounds in polar solvents[4] and the estimated values for 5,6-dihydrobenzo[*c*]cinnoline are presented in Fig. 2. Fluorene, naphthalene and *trans*-1,3-pentadiene have no quenching effect, whereas phenanthrene, acetophenone, pyrene, and anthracene were found to reduce the quantum yield of the reaction. The quenching data is presented in Fig. 3 for each quencher, and the Stern-Volmer plots give straight lines.

The results can be interpreted in terms of the energy levels illustrated in Fig. 2. All effective quenchers studied have singlet energies lower than that of the reactant, whereas fluorene, naphthalene, and *trans*-1,3-pentadiene have higher singlet energies. Naphthalene and *trans*-1,3-pentadiene have triplet energies lower than that of the reactant and do not quench the reaction, indicating the unsuitability of the triplet-triplet energy transfer as a mechanism for the quenching effect. This is also indicated in the case of acetophenone as a quencher, since this molecule has a triplet energy higher than the reactant. Consequently, the observed quenching may be ascribed to an energy transfer from the lowest excited singlet 5,6-dihydrobenzo[*c*]cinnoline to the quenchers. Further evidence for this mechanism can be given from the fluorescence quenching study using acetophenone as a quencher, the results of which are shown in Fig. 4, where the quantities $I$ and $I_0$ are fluorescence intensities at 356 nm with and without acetophenone, respectively. From this figure it is evident that the fluorescent state of the reactant is deactivated with acetophenone through singlet-singlet energy transfer.

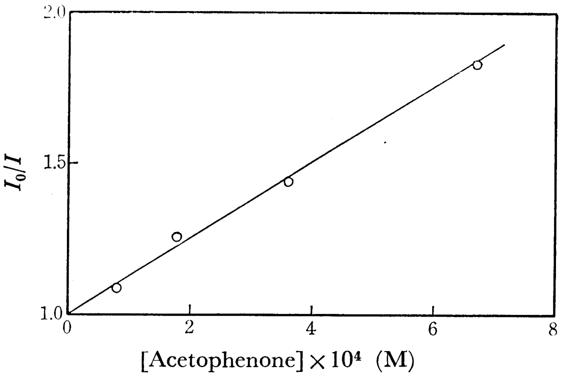
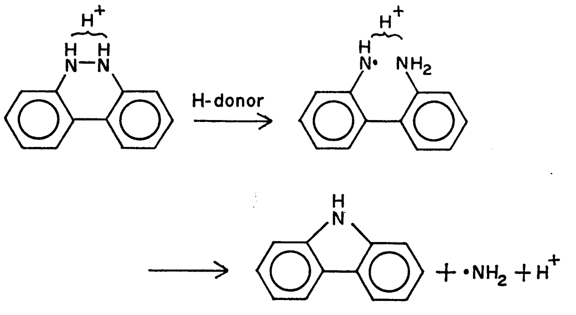


Fig. 4. Fluorescence quenching plot of 5,6-dihydrobenzo[*c*]cinnoline by acetophenone. [5,6-Dihydrobenzo[*c*]cinnoline] = $1.0 \times 10^{-4}$ M.

The indication is that the photoreaction proceeds through the lowest excited singlet state of the reactant and that the triplet state does not participate in the reaction.

Although benzo[*c*]cinnoline is reduced photochemically to 5,6-dihydrobenzo[*c*]cinnoline in neutral ethylene glycol[5] and poly(vinyl alcohol) film,[6] the subsequent reaction to lead carbazole does not occur in these media with the light of wavelength 315 nm. Consequently only the protonated species of the reactant undergoes the photochemical formation of carbazole.

Ammonia ($NH_4Cl$ in acidic solution) has been found to be generated in carbazole formation. Trace amounts of ammonia in the irradiated solution have been detected using a thymol indicator,[7] but hydrazine was not detected. Subsequently the mode of the photo-elimination was examined through the determination of the fragment which participated in the ammonia formation. The amino radical ($\cdot NH_2$) is known to react with alcohol or hydrochloric acid to yield ammonia.[8] Therefore, the fragment produce in the photo-elimination is presumed to be the amino radical. If this is the case, the initial step in the reaction may be abstraction of the hydrogen atom from the solvent molecule by the reactant as illustrated below. The necessity of hydrogen atom donors in the initial step of the carbazole formation has been examined as follows. Benzo[*c*]cinnoline has been photo-reduced in poly(vinyl alcohol) film as earlier



reported,[6] and the 5,6-dihydrobenzo[*c*]cinnoline thus produced has been extracted with acidic aqueous acetonitrile (4 M HCl) under nitrogen.[9] The resulting solution of 5,6-dihydrobenzo[*c*]cinnoline was irradiated with light of wavelength 315 nm, the carbazole formation was not observed at all. This supports the above assertion and consequently the direct elimination of the imino radical ($\dot{N}H$) from the reactant can be ruled out as the mechanism of the photo-elimination to yield carbazole.

## References

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9) The absorption spectrum of the acetonitrile solution showed that 5,6-dihydrobenzo[*c*]cinnoline was present in $10^{-4}$ M concentration.