

# Cycloaddition Reaction of 1,4,5,8-Tetraazaphenanthrene Photoexcited Triplet State to Some Olefins

Seung Ki Park and Sang Chul Shim\*

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received October 14, 1986

Photocycloaddition of 1,4,5,8-tetraazaphenanthrene to olefins proceeds through a biradical triplet-state intermediate as proven by the photoproduct stereochemistry, quantum yield measurements, sensitization, quenching, and fluorescence and phosphorescence quenching studies.

## Introduction

Photochemical reactions proceeding through the triplet states of organic molecules frequently involve triplet biradicals or biradicaloids as the ultimate triplet-state intermediate. Product structures and yields may reflect the structure of triplet biradicals and the conformations in which they undergo intersystem crossing<sup>1</sup>. The properties of triplet biradicals and the structural and environmental factors which influence their intersystem crossing are thus important determinants for the reactivity, quantum yields of products, and product stereochemistry and regiochemistry in a wide variety of photochemical reactions.

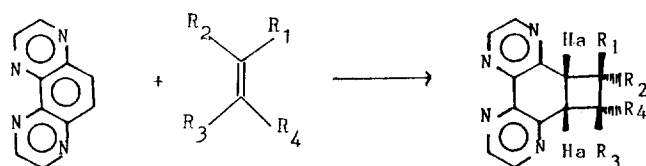
Despite their central importance in a variety of photochemical reactions and their interest in both experimental and

theoretical photophysical studies<sup>2</sup>, it has been difficult to detect these species until the relatively recent advent of nanosecond laser flash photolysis techniques by which the triplet biradicals and related species could be studied systematically<sup>3-6</sup> and these studies paved the way for future advances in understanding of their properties.

Our concern has been concentrated on the photochemical and photophysical behavior of 1,4,5,8-tetraazaphenanthrene (TAP). The photophysical properties of TAP is revealed that it has both ( $n, \pi^*$ ) and ( $\pi, \pi^*$ ) excited states in contrast to phenanthrene which has only ( $\pi, \pi^*$ ) excited states<sup>7</sup>. The preliminary results on photocycloaddition reaction of TAP with some olefins are reported to undergo through a triplet excited state<sup>8</sup> and we now report that the triplet-state reaction of TAP proceeds through a triplet biradical intermediate.

## Results and Discussion

Table 1. Photocycloaddition Reaction of TAP with Halogenated Olefins



TAP

entry	olefin				cycloadduct				% yield
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	
1	1a: Cl	H	Cl	H	1b: Cl	H	Cl	H	100
2	2a: Cl	Cl	H	H	2b: Cl	Cl	H	H	45
3	3a: Cl	Cl	Cl	H	3b: Cl	Cl	Cl	H	32
4	4a: Cl	Cl	Cl	Cl	4b: Cl	Cl	Cl	Cl	17
5	5a: Br	H	H	H	5b: Br	H	H	H	100
6	6a: Br	CH <sub>3</sub>	H	H	6b: Br	CH <sub>3</sub>	H	H	7
7	7a: Cl	CN	H	H	7b: Cl	CN	H	H	100
8	8a: CN	H	H	H	8b: CN	H	H	H	34
					8c: H	CN	H	H	66
9	9a: CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	—	—	—	—	0
10	10a: CO <sub>2</sub> Me	H	CH <sub>3</sub>	H	—	—	—	—	0
11	11a: CO <sub>2</sub> Me	H	CO <sub>2</sub> Me	H	—	—	—	—	0
12	12a: CN	H	p-Cl-C <sub>6</sub> H <sub>4</sub>	H	—	—	—	—	0
13	13a: CN	H	CN	H	—	—	—	—	0
14	14a: CN	CN	CN	CN	—	—	—	—	0

**Photoproduct Studies.** The cycloaddition reaction of TAP with various olefins are summarized in Table 1.

Direct photolysis of TAP with *trans*-1,2-dichloroethylene (1a) leads to formation of (1b) in quantitative yields. The stereochemistry of the cycloadduct, (1b), is readily determined on the basis of <sup>1</sup>H NMR and two-dimensional NMR spectra. The <sup>1</sup>H NMR spectra of (1b) exhibits a symmetrical AA'XX' splitting pattern for the cyclobutane ring protons indicating the *cis* stereochemistry for the two carbon-chlorine bonds. In the two-dimensional NMR spectra (COSY method) of (1b), diagonal peaks are centered at the coordinates ( $\delta$  4.5,  $\delta$  4.5) and ( $\delta$  4.9,  $\delta$  4.9) while cross peaks are centered at ( $\delta$  4.5,  $\delta$  4.9) and ( $\delta$  4.9,  $\delta$  4.5). Cross peaks indicate spin coupling between the protons (R<sub>2</sub>, R<sub>4</sub>) and H<sub>a</sub> protons (Figure 1). This is the direct evidence for the *cis* stereochemistry of the two carbon-chlorine bonds. No cycloadduct, however, was obtained even on the prolonged irradiation of TAP with *cis*-1,2-dichloroethylene.

Direct photolysis with other halogenated olefins such as vinylidene chloride(2a), trichloroethylene(3a), and tetrachloroethylene(4a) leads to formation of (2b), (3b), and (4b), respectively in low yields (not quantitative yields). As the number of chlorine atom in olefin moiety increases, the yield of cycloadduct formation decreases due to the steric effect as observed in other triplet state reactions<sup>9</sup>.

In the photoreaction of TAP with vinyl bromide(5a) and 2-bromopropene(6a), the steric effect plays also important role.

Irradiation of TAP in the presence of 2-chloroacrylonitrile (7a) led to the formation of single cycloadduct, (7b), in quantitative yields, while the two isomeric cycloadducts (8b) and

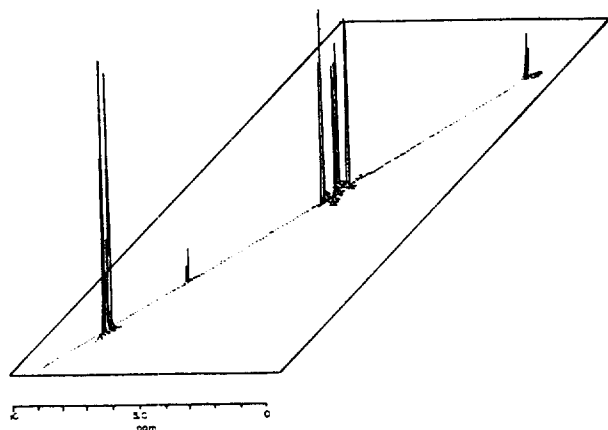


Figure 1. Two-dimensional NMR spectrum(COSY method) of TAP-*trans*-1,2-dichloroethylene photoproducts.

(8c) in 1:3 ratio were obtained with acrylonitrile (8a). The stereochemical assignments of (8b) and (8c) were based on the chemical shift of the proton ( $R_2$ ) in (8b) which is located in the shielding zone of anisotropic pyrazine ring. The photocycloaddition to acrylonitrile favors the formation of the endo adduct, (8c), which is stabilized by the overlap interaction of  $\pi$ -orbitals of CN triple bond and pyrazine ring in TAP. The optical rotations,  $[\alpha]_D^{20}$ , deg(molar concentration, solvent), of (8b) and (8c) were determined to be  $[\alpha]_D^{20} = -1.02$  (0.98,  $\text{CHCl}_3$ ) and  $[\alpha]_D^{20} = +0.96$  (1.04,  $\text{CHCl}_3$ ), respectively.

In order to study the dimerization of TAP, a concentrated chloroform solution of TAP was irradiated but no dimer was obtained and TAP was recovered quantitatively.

Irradiation of TAP in the presence of some olefins such as 2,3-dimethyl-2-butene(9a), methyl crotonate(10a), dimethyl fumarate(11a), *p*-chlorocinnamionitrile(12a), fumaronitrile (13a), tetracyanoethylene(14a), 3-chloro-1-propene, and 2,3-dichloro-1-propene gave no product other than starting material in contrast to phenanthrene which forms a photo-

Table 3. Fluorescence quenching of TAP by Dimethyl Fumarate and Fumaronitrile

Olefin	Solvent	$k_q\tau$ , $\text{M}^{-1}$
Dimethyl Fumarate	<i>n</i> -hexane	63.6
	benzene	13.05
	$\text{CH}_2\text{Cl}_2$	16.18
Fumaronitrile	$\text{CH}_2\text{Cl}_2$	7.19

\*Stern-Volmer equation.  $\frac{\Phi^0}{\Phi} = 1 + k_q\tau [Q]$ .

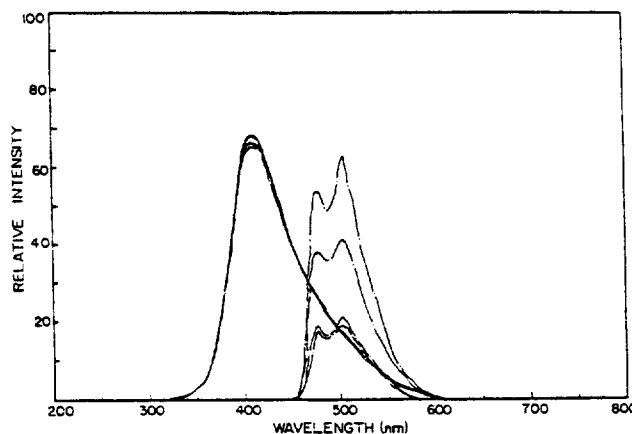


Figure 2. The Fluorescence (—) (room temperature) and phosphorescence (---) (77K) quenching of TAP.  $\lambda_{ex}$  280 nm. Concentration of TAP:  $1 \times 10^{-5}$  M.

cycloadduct with most of these olefins.

The spectral data of the photocycloadducts are summarized in Table 2.

**Fluorescence and Phosphorescence Studies.** In the phenanthrene-dimethyl fumarate reaction, phenanthrene

Table 2.  $^1\text{H}$  NMR, IR, UV, MS Spectral Data of the Photocycloadducts

compd.	$^1\text{H}$ NMR( $\text{CDCl}_3$ , $\delta$ )	IR( $\text{CM}^{-1}$ )	UV ( $\lambda_{max}$ , nm)	MS(m/e)
1b	4.5(2H, d, $J=4\text{Hz}$ ), 4.9(2H, d, $J=4\text{Hz}$ )	3040,2960	270,322	278( $\text{M}^*$ )
	8.7(4H, q)	1400,1250		280( $\text{M}+2$ )
2b	3.3-4.05(2H, m), 4.1-5.1(2H, m)	3060,2960	274,322	278( $\text{M}^*$ )
	8.7(4H, 2q)	1415,1150		280( $\text{M}+2$ )
3b	4.25-4.5(1H, m), 4.8-5.1(2H, m)	3060,2950	276,322	312( $\text{M}^*$ ), 314( $\text{M}+2$ )
	8.7(4H, 2q)	2880,1415		316( $\text{M}+4$ )
4b	4.9(2H, s), 8.65(4H, q)	3080,2940	275,321	346( $\text{M}^*$ ), 348( $\text{M}+2$ )
		1410,1110		350( $\text{M}+4$ ), 352( $\text{M}+6$ )
5b	2.9-3.4(2H, m), 4.05-4.70(3H, m)	3045,2980	270,325	288( $\text{M}^*$ )
	8.6(4H, q)	2940,1410		290( $\text{M}+2$ )
6b	2.3(3H, s), 2.8-3.9(2H, m)	3040,2950	276,325	302( $\text{M}^*$ )
	4.2-5.05(2H, m), 8.7(4H, 2q)	1400,835		304( $\text{M}+2$ )
7b	3.1-3.6(2H, m), 4.1-4.9(2H, m)	3060,2960	275,320	269( $\text{M}^*$ )
	8.6(4H, 2q)	2260,1410		271( $\text{M}+2$ )
8b	2.6-3.55(3H, m), 4.1-4.55(2H, m)	3020,2980	273,325	235( $\text{M}^*$ )
	8.6(4H, q)	2940,2250		
8c	2.45-3.49(2H, m), 3.7-4.55(3H, m)	3020,2950	274,325	235( $\text{M}^*$ )
	8.6(4H, 2q)	2250,1480		

fluorescence in benzene is quenched by dimethyl fumarate<sup>10</sup>, and a weakly emitting exciplex is observed at high dimethyl fumarate concentration. On the other hand, the fluorescence of TAP is quenched by dimethyl fumarate and fumaronitrile without giving any cycloaddition product or exciplex emission (Table 3). However, the fluorescence of TAP is not quenched by *trans*-1,2-dichloroethylene which yields a cycloadduct. On the other hand, the phosphorescence of TAP is efficiently quenched by *trans*-1,2-dichloroethylene (Figure 2) indicating that the photochemical reaction of TAP with olefins proceeds from the triplet manifold.

**Reaction Mechanism.** The following kinetic scheme for the photoreaction of TAP with olefins can be suggested, where T = TAP, S = Sensitizer, O = Olefin, A = Adduct, and Q = Quencher.

Scheme I.



The quantum yield,  $\Phi_A^0$ , of cycloadduct formation is:

$$\Phi_A^0 = \frac{\alpha k_{TO}[O]}{k_a + \alpha k_{TO}[O] + (1-\alpha)k_{TO}[O]} = \frac{\alpha k_{TO}[O]}{k_a + k_{TO}[O]} \quad (5)$$

$$\text{and, } \frac{1}{\Phi_A^0} = \frac{1}{\alpha} \left( 1 + \frac{1}{k_{TO}\tau_T[O]} \right) \quad (6)$$

If the quencher (Q) is present, the following step should be added to Scheme I.



In this case, the quantum yield of cycloadduct formation,  $\Phi_A^q$ , is:

$$\Phi_A^q = \frac{\alpha k_{TO}[O]}{k_a + k_{TO}[O] + k_{TQ}[Q]} \quad (8)$$

$$\text{and, } \frac{\Phi_A^0}{\Phi_A^q} = \frac{k_a + k_{TO}[O] + k_{TQ}[Q]}{k_a + k_{TO}[O]} = 1 + \frac{k_{TQ}[Q]}{k_a + k_{TO}[O]} \quad (9)$$

In the triplet-sensitized photoreaction, the following steps have to be considered.



Like above,

$$\Phi_A^s = \frac{k_{ST}[T]}{\Sigma k_s + k_{ST}[T] + k_{SO}[O]} \times \Phi_A^0 \quad (15)$$

$$\Phi_A^{s,q} = \frac{k_{ST}[T]}{\Sigma k_s + k_{ST}[T] + k_{SO}[O] + k_{SQ}[Q]} \times \Phi_A^0 \quad (16)$$

where  $\Phi_A^0$  is the quantum yield of adduct formation in the triplet-sensitized photoreaction and  $\Phi_A^{s,q}$  is the quantum yield

**Table 4.** The azulene effect on the direct and sensitized photocycloaddition reaction of TAP with *trans*-1,2-dichloroethylene at 366 nm\*

Concentration of xanthone/M	Concentration of azulene/M	$\Phi$	$\Phi^0/\Phi$
0	0	0.038	1.0
	$1 \times 10^{-4}$	0.028	1.36
	$2 \times 10^{-4}$	0.021	1.81
	$4 \times 10^{-4}$	0.016	2.38
0.01	0	0.045	1.0
	$1 \times 10^{-4}$	0.034	1.32
	$2 \times 10^{-4}$	0.024	1.88
	$4 \times 10^{-4}$	0.018	2.5

\*Concentration of TAP is  $3 \times 10^{-3}$ M. ( $\lambda_{max}$  of TAP is 280 nm).

in the presence of both the sensitizer and the quencher. And,

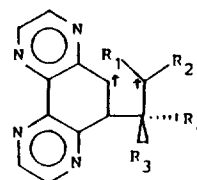
$$\frac{\Phi_A^s}{\Phi_A^{s,q}} = \frac{\Sigma k_s + k_{ST}[T] + k_{SO}[O] + k_{SQ}[Q]}{\Sigma k_s + k_{ST}[T] + k_{SO}[O]} \times \frac{\Phi_A^0}{\Phi_A^q} \quad (17)$$

If we assume that all  $S^1$  are quenched by T, O, or Q, and the quenching of  $S^1$  by Q is negligible compared with the quenching by T and O, i.e.,  $\Sigma k_s \ll k_{ST}[T] + k_{SO}[O] + k_{SQ}[Q]$ ,  $k_{ST}[T] + k_{SO}[O] \gg k_{SQ}[Q]$ , eq(18) can be derived.

$$\frac{\Phi_A^s}{\Phi_A^{s,q}} = \frac{\Phi_A^0}{\Phi_A^q} \quad (18)$$

Azulene (quencher) quenches the direct and triplet sensitized photoreaction very efficiently giving the same slope in the Stern-Volmer plot (Table 4) which is consistent with eq(18).

A triplet biradical intermediate can account for the stereoselectivity of the reaction and the failure to preserve the stereochemistry of the olefinic moiety in the cycloadduct.



Triplet biradical

To minimize the repulsion of  $\pi$ -electron cloud of pyrazine ring in TAP with halogen atom electron cloud, rotation of C-C bond precedes ring closure in the triplet biradicals. Due to this repulsion, the reaction proceeds stereoselectively and the cycloadducts have the *exo cis* configuration. In the photoreaction of TAP with 2-chloroacrylonitrile (7a), the reaction proceeds stereoselectively due to the double effect, the repulsion of  $\pi$ -electron clouds and the overlap interaction of  $\pi$ -orbitals in the transition state.

From the stereochemistry of photocycloadducts, it appears reasonable to conclude that the triplet state photoreaction of TAP with olefins proceeds through a triplet biradical intermediate.

## Experimental

**Materials.** TAP was synthesized by the reported method<sup>11</sup>

starting from pyrazine carboxylic acid and recrystallized from acetone. Extra pure n-hexane, ethyl ether, acetonitrile, and methanol(Merck Chemical Co.) were used without further purification for HPLC. Dimethyl fumarate, fumaronitrile was recrystallized twice from benzene. Trans-1,2-dichloroethylene, vinyl bromide, acrylonitrile, 2-chloroacrylonitrile, vinylidene chloride, trichloroethylene, tetrachloroethylene, 2-bromopropene, 2,3-dimethyl-2-butene, methyl crotonate (all from Aldrich Chemical Co.) were used without further purification. Benzophenone and xanthone(both from Aldrich) were recrystallized from cyclohexane. Azulene(Aldrich) was purified by vacuum sublimation. Kiesel Gel GF<sub>254</sub>(Merck) and Kiesel Gel 60(70-230 mesh) (Merck) were used for silica gel thin layer chromatography and column chromatography, respectively.

**Spectra and Physical Data.** UV spectra were recorded on a Cary-17 spectrophotometer. IR spectra were taken on a Perkin-Elmer 267 spectrophotometer by using KBr pellets. <sup>1</sup>H NMR spectra were obtained on a Varian FT-80A NMR spectrometer at 79.542 MHz or a Varian T-60A NMR spectrometer in chloroform-d. Mass spectra were obtained on a Hewlett Packard 5985A GC/MS system using electron impact(EI) method. Elemental analyses were carried out on a F&M Scientific Cooperation C.H.N. Analyzer Model 180. Fluorescence and phosphorescence spectra were recorded on an Aminco-Bowman spectrofluorophotometer with an Aminco X-Y recorder at room temperature and at 77K with modification of cell compartment. High performance liquid chromatogram was obtained on a Waters Associates Model 244 liquid chromatograph equipped with Model 6000A solvent delivery system and Model 440 absorbance detector(254 nm and 280 nm). HPLC analyses were performed by using a  $\mu$ -Bondapak CN column with n-hexane/ ethyl ether/acetonitrile(v/v, 11/3/1) as an isocratic eluting solvent.

**Quantum Yield Measurements.** Ethyl acetate solutions of TAP and olefins were placed into Pyrex ampoules and degassed by three freeze-pump-thaw cycles( $<10^{-4}$  mmHg) with cooling in liquid nitrogen, and then the ampoules were sealed. Thus prepared samples were irradiated in a merry-go-round unit with a 450 W Hanovia medium-pressure mercury arc lamp(Type 679A36). Corning glass filters(No. 0-52 and 7-37) were used to isolate mono-chromatic light of 366 nm. The light intensity was measured by tris(oxalato) ferrate(III) actinometry<sup>12</sup>. The amount of photochemical cycloadducts with olefins were measured by HPLC.

**Preparative Photolysis.** Preparative photolysis was generally carried out in chloroform(60 ml) by using 0.6 mmol of TAP and 30 mmol of olefins. Samples were degassed by bubbling oxygen-free nitrogen through the solutions and irradiated at room temperature in a Rayonet Photochemical reactor(The Southern New England Ultraviolet Co.) equipped with 300 nm UV lamps for 35-60 hours until TAP is disappeared. The progress of the reaction was monitored by TLC and the reaction mixtures were analyzed by HPLC and NMR.

**Photocycloaddition of TAP with trans-1,2-dichloro-**

**ethylene, vinyl bromide, 2-chloroacrylonitrile.** Degassed chloroform solutions of TAP and trans-1,2-dichloroethylene (1a), vinyl bromide(6a), and 2-chloroacrylonitrile(8a), were irradiated with 300 nm UV light. After the irradiation for 40-60 hours, the solutions were concentrated in vacuo, and the photoadduct was recrystallized from chloroform(1 ml) and n-hexane (15 ml). The photoadducts (1b), (6b), and (8b) were obtained, respectively.

**Photocycloaddition of TAP with acrylonitrile.** TAP and acrylonitrile dissolved in chloroform was deoxygenated for 30 mins by bubbling nitrogen gas. The resulting solution was irradiated with 300 nm UV light for 50 hours. The residue was concentrated in vacuo and the two photoadducts were separated by preparative thin layer chromatography using acetone-ethyl acetate(7:3, v/v) as an eluting solvent, and the photoadducts (9b) and (9c) were recrystallized from chloroform and n-hexane.

**Photocycloaddition of TAP with vinylidene chloride, trichloroethylene, tetrachloroethylene, and 2-bromopropene.** Degassed chloroform solutions of TAP with vinylidene chloride, trichloroethylene, tetrachloroethylene, and 2-bromopropene were irradiated with 300 nm UV light for 60 hours. The photoreaction mixtures were concentrated in vacuo. The photoadducts (3b), (4b), (5b), and (7b) were isolated by silica gel column chromatography with acetone-ethyl acetate(3:2, v/v) as an eluting solvent, and the products were recrystallized from n-hexane.

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