ORGANIC
LETTERS

2007
Vol. 9, No. 3
453−456

Positive Photocatalysis of a Diels–Alder Reaction by Quenching of Excited Naphthalene–Indole Charge-Transfer Complex with Cyclohexadiene

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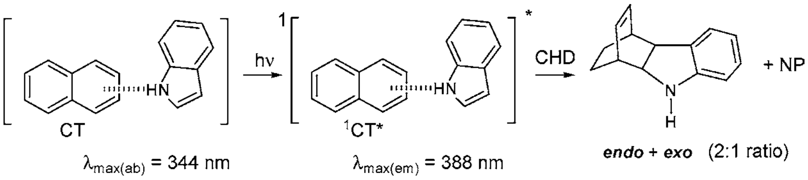
Received November 15, 2006

ABSTRACT



Naphthalene photocatalyzes formation of cyclohexadiene–indole cycloadducts in a wavelength-dependent process. Steady-state irradiation and time-resolved fluorescence studies agree well with NP–InH ground-state charge transfer (CT) complexes as the key species responsible for the photocatalyzed process.

Unlike most photocatalytic processes, focused on degradation of pollutants to manage environmental problems, the term “positive photocatalysis”[1] has been coined for applications of the concept with synthetic purposes. In this context, naphthalene (NP) has rarely been used as photocatalyst in organic transformations.[2] However, substituted naphthalenes, such as cyano-, carboxy-, and alkoxynaphthalenes, photocatalyze a variety of reactions, such as cyclizations,[3] addition of alcohols to alkenes,[4] dimerizations,[5] cross-cycloadditions,[6] and cycloreversions.[7]

For example, cyanonaphthalenes are known to induce the [4 + 2] photocycloaddition of electron-rich dienes (i.e., 1,3-cyclohexadiene, CHD) to electron-rich dienophiles (i.e., *β*-methylstyrene).[8,9] This reaction was labeled as a triplex Diels−Alder reaction, since it was postulated to occur by formation of an excited ternary complex (^{1}S*−dienophile−diene) arising from trapping of the (^{1}S*−dienophile) exciplex by the diene. To our knowledge, there is no report on the cross-cycloaddition between indole (InH) and 1,3-cyclohexadiene (CHD) photocatalyzed by naphthalenes.

The fact that the NP singlet excited state (^{1}NP*) reacts with conjugated dienes[10] and azaaromatic compounds such

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[1] (a) Corma, A.; García, H. *Chem. Commun.* **2004**, 1443. (b) Sanjuan, A.; Alvaro, M.; Corma, A.; García, H. *Chem. Commun.* **1999**, 1641.

[2] (a) Chow, Y. L.; Marciniak, B.; Mishra, P. *J. Org. Chem.* **1984**, *49*, 1458. (b) Cohen, S. G.; Paola, A.; Parson, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141. (c) Bartholemew, R. F.; Brimage, D. R. G.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 3482.

[3] Görner, H.; Warzecha, K. D.; Demuth, M. *J. Phys. Chem. A* **1997**, *101*, 9964.

[4] (a) Fukuhara, G.; Mori, T.; Wada, T.; Inoue, Y. *Chem. Commun.* **2006**, 1712. (b) Asaoka, S.; Wada, T.; Inoue, Y. *J. Am. Chem. Soc.* **2003**, *125*, 3008.

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[6] Mattay, J.; Vondenhof, M.; Denig, R. *Chem. Ber.* **1989**, *122*, 951.

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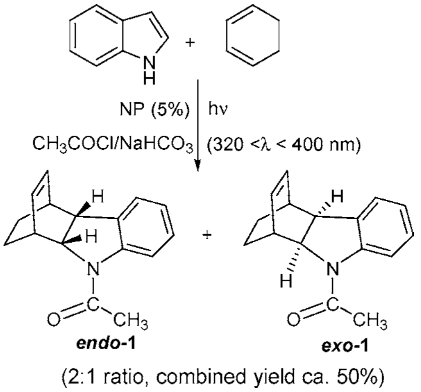
[10] (a) Kimura, M.; Sagara, S.; Morosawa, S. *J. Org. Chem.* **1982**, *47*, 4344.(b) Yang, N. C.; Libman, J. *J. Am. Chem. Soc.* **1972**, *94*, 9228.

10.1021/ol062783k CCC: $37.00

as pyrrole[11] appeared, in principle, to be incompatible with its possible use as a photocatalyst in the Diels−Alder reaction between InH and CHD; nevertheless, this reaction is catalyzed by triarylpyrylium salts, via photochemically generated radical cations, and by 2-benzoylthiophene, via triplet triplexes. [12]

Herein, we report that NP photocatalyzes formation of CHD−InH cycloadducts **1** (Scheme 1) in a wavelength-dependent process. Steady-state irradiation and time-resolved fluorescence studies strongly agree with NP−InH ground-state charge transfer (CT) complexes as the key species responsible for the photocatalyzed process. This is further supported by product studies using light of different wavelengths for the preparative photolysis.

Scheme 1. Diels−Alder Reaction Photocatalyzed by NP



Typically, a deaerated dichloromethane solution of NP (0.001 M), CHD (0.04 M), and InH (0.02 M) was irradiated for 6 h with the pyrex-filtered light of a broad emission lamp ($280 < \lambda < 360$ nm, maximum at 320 nm). An acylation reagent (acetyl chloride/$NaHCO_3$) was also added to the reaction mixture prior to irradiation.[13] Analysis of the photolyzate by GC revealed the presence of trace amounts of Diels−Alder cycloadducts, although polymerization was the main reaction. By contrast, irradiation at $320 < \lambda < 400$ nm (maximum at 350 nm) gave ca. 50% of the Diels−Alder cycloadducts, together with traces of cyclohexadiene dimers (with a typical ratio of a radical cation photosensitized dimerization).

In order to investigate the nature of the excited-state involved in the process, steady-state and time-resolved emission experiments were performed. The fluorescence spectrum of NP was measured in dichloromethane solution (absorbance 0.3 at the excitation wavelength $\lambda_{exc} = 310$ nm), and the maximum was found at 335 nm. Figure 1 shows the normalized emission and excitation spectra for NP in dichloromethane. The intersection between both spectra allowed us to locate the 0−0 transition and to estimate the singlet excited-state energy (E_S) for NP in this solvent as $E_S = 90$ kcal/mol.[14]

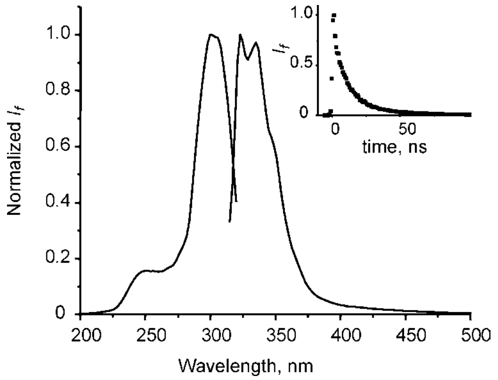


Figure 1. Normalized fluorescence (right) and excitation spectra (left) of NP (2.5×10^{-3} M) in deaerated dichloromethane. Inset: Fluorescence decay trace monitored at 335 nm.

The fluorescence quantum yield was determined as 0.04[15] by comparison with quinine sulfate in 0.5 M sulfuric acid,[16] using 301 nm as the excitation wavelength. From the monoexponential decay (see inset in Figure 1), a singlet lifetime of 10.6 ns was determined.

Both, the dienophile and the diene used in this study were effective quenchers of $^1NP^*$ (Figure 2). Hence, the kinetic evaluation of the quenching process at room temperature was performed by monitoring the singlet lifetime at 330 nm as a function of the quencher concentration (Figure 2). The data fitted well with eq 1

$$\tau_0/\tau - 1 = \tau_0 k_q[Q] \qquad (1)$$

where τ_0 is the lifetime of the NP singlet and $\tau_0 k_q$ is the Stern−Volmer parameter.

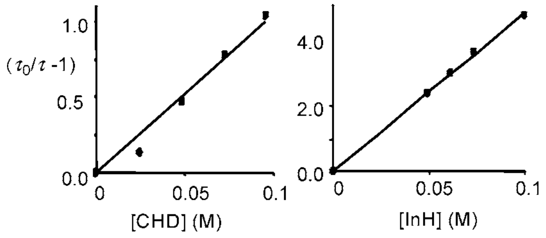


Figure 2. Stern−Volmer plots for the fluorescence quenching of NP in the presence of increasing concentrations of quenchers: CHD (left) and InH (right).

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[11] The excited singlet of naphthalene has been proposed as the reactive state, since the fluorescence of NP is quenched by pyrrole with high efficiency: Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.

[12] (a) Wiest, O.; Steckhan, E. *Tetrahedron Lett.* **1993**, *34*, 6391. (b) Gieseler, A.; Steckhan, E.; Wiest, O.; Knoch, F. *J. Org. Chem.* **1991**, *56*, 1405.(c) González-Béjar, M.; Stiriba, S. E.; Domingo, L. R.; Pérez-Prieto, J.; Miranda, M. A. *J. Org. Chem.* **2006**, *71*, 6932.

[13] Previous studies (ref 9) on this reaction using triarylpyrylium salts as photosensitizers have mentioned the need to protect the amine group of the photoadduct, since no products are isolated in its absence.

[14] Another value ca. 92 kcal/mol has been reported in polar and nonpolar solvents: Murov, S.; Carmichael, I.; Hug, G. L. In *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

Stern−Volmer plots (Figure 2) showed a linear dependence of $\tau_0/\tau - 1$ on [Q] at concentrations up to 0.1 M. The slopes provided the second-order rate constant of ^{1}NP* deactivation by the quencher multiplied by the ^{1}NP* lifetime ($\tau_0 k_q$). Thus, values of 1.8×10^9 and 8.4×10^9 M^{-1} s^{-1} were obtained for CHD[17] and InH, respectively, from the kinetic evaluation.

Interestingly, as the concentration of InH was increased, the fluorescence of NP decreased, and a new emission band was observed at wavelengths longer than those of NP fluorescence (see Figure 3). The excitation spectrum at λ_{em} = 388 nm evidenced that the species responsible for the emission between 370 and 450 nm was not a (^{1}NP*−InH) exciplex but an excited NP−InH charge transfer (^{1}CT*) complex absorbing between 300 and 370 nm, with λ_{max} at 344 nm (see Figure 4 and Scheme 2i,ii).[18,19,20] From the monoexponential fluorescence decay (see inset in Figure 3) ^{1}CT* lifetime was estimated as ca. 3 ns; it was only slightly (although linearly) dependent on [InH], evidencing a weak interaction between ^{1}CT* and InH (Scheme 2iii).

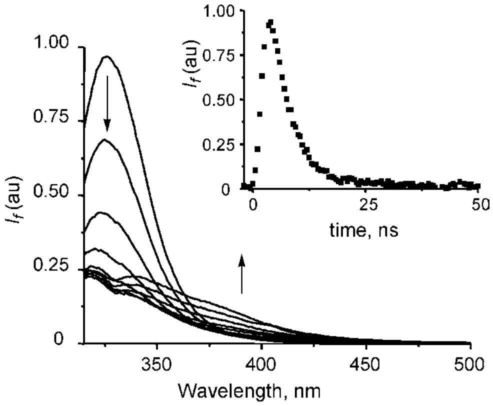

Figure 3. Fluorescence spectra of NP (2.5×10^{-3} M) in the presence of increasing amounts (from 0.004 to 0.170 M) of indole in dichloromethane. Inset: fluorescence decay trace (λ_{exc} = 337 nm, λ_{em} = 388 nm) of NP−InH (CT) complex.

Interestingly, the intensity of the ^{1}CT* emission decreased as CHD was added to the solution, at the same time that a very low intensity new emission was observed at wavelengths longer than those of the ^{1}CT* fluorescence (see Figure 5).

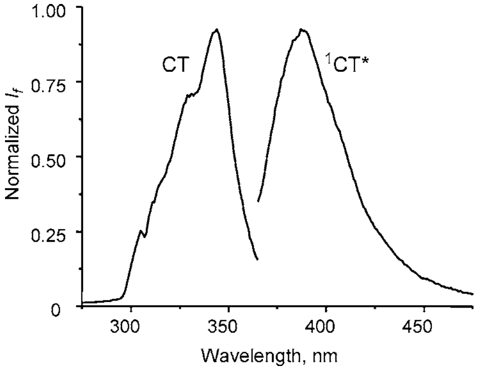

Figure 4. Normalized fluorescence at λ_{exc} = 344 nm (right) and excitation spectra at λ_{em} = 388 nm (left) of NP−InH CT complex in dichloromethane.

Scheme 2. Processes Involved in the Photoexcitation−Deactivation of NP in the Presence of InH and CHD

$\text{NP + InH} \longrightarrow \text{NP---InH (CT)}$ (i)

$\text{CT} \xrightarrow{h\nu} {}^1\text{CT*}$ (ii)

${}^1\text{CT* + InH} \longrightarrow \text{NP + 2 InH}$ (iii)

${}^1\text{CT* + CHD} \longrightarrow \textbf{CA} + \text{NP}$ (iv)

$\text{NP---InH+ CHD} \longrightarrow \text{NP---InH---CHD (TCT)}$ (v)

$\text{TCT} \xrightarrow{h\nu} {}^1\text{TCT*}$ (vi)

The excitation spectrum at λ_{em} = 405 nm evidenced that the species responsible for the long-wavelength emission (reaching 600 nm) was not a (^{1}CT*−CHD) exciplex. In other words, it was not co-incident with that of the CT (λ_{max} =

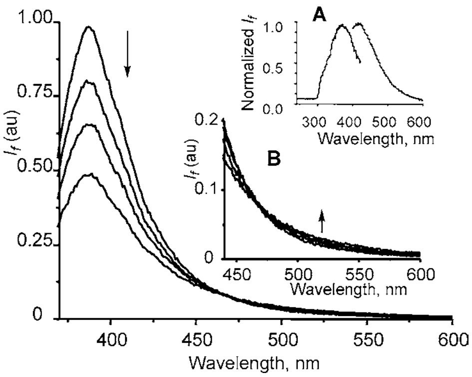

Figure 5. Fluorescence spectra (λ_{exc} = 344 nm) of ^{1}CT* in the presence of increasing amounts of CHD in dichloromethane. (Inset A) Right: normalized fluorescence (λ_{exc} = 376 nm) of ^{1}TCT*. Left: excitation spectra (λ_{em} = 405 nm) of the ternary NP−InH−CHD TCT complex. (Inset B) Amplification showing the emission of ^{1}TCT*.

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(15) It has been shown that chloromethanes quench the fluorescence of some substituted naphthalenes: (a) Boscá, F.; Canudas, N.; Marín, M. L.; Miranda, M. A. *Photochem. Photobiol.* **2000**, *7*, 173. (b) Behera, P. K.; Mukherjee, T.; Mishra, A. K. *J. Lumin.* **1995**, *65*, 131.

(16) Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* **1971**, *75*, 901.

(17) A value of 2.2×10^9 M^{-1}s^{-1} in benzene has been previously reported: Stephenson, L. M.; Whitten, D. G.; Vesley, G. F.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 3665.

(18) No comparable emission was observed in the case of CHD.

(19) For a series of pseudopeptides, the formation of intramolecular CT complexes between NP and InH moieties in the 260−320 nm absorption region has been previously detected. In methanol, the emission spectrum of the CT complexes is centered at 380 nm. These complexes are not detected in dioxane: Pispisa, B.; Stella, L.; Venanzi, M.; Palleschi, A. *J. Peptide Res.* **1999**, *54*, 353.

(20) Hydrogen-bonding interactions between indole and benzenoid-π-bases in carbon tetrachloride solutions have been previously detected by FTIR: Muñoz, M. A.; Ferrero, R.; Carmona, C.; Balón, M. *Spectrochim. Acta Part A* **2004**, *60*, 193.

344 nm), but showed an excitation maximum at 376 nm (see inset A in Figure 5). Hence, it could be ascribed to a NP−InH−CHD ternary ground-state charge transfer (TCT) complex (Scheme 2v,vi).

Stern−Volmer analysis of the emission quenching at 388 nm by CHD revealed that lifetime did not decrease linearly with concentration (Figure 6) but followed a quadratic law (2) instead, which is consistent with quenching of both $^1NP^*$ and $^1CT^*$ fluorescence.

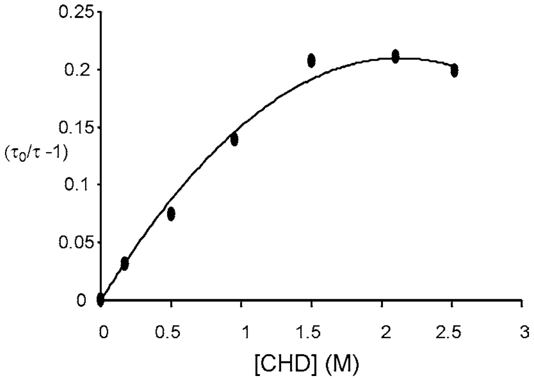

Figure 6. Stern−Volmer analysis of the quenching of $^1CT^*$ emission by CHD (λ_{exc} = 337 nm, λ_{em} = 388 nm).

$$\tau_0/\tau - 1 = -0.215[\mathrm{CHD}]^2 + 0.038[\mathrm{CHD}] \qquad (2)$$

Apparently, the NP singlet excited-state is not involved in the cycloaddition process, since irradiation at wavelengths where naphthalene has an intense absorption band led mainly to polymerization. To check whether the cycloadducts (**CA** in Scheme 2iv) originated from NP−InH or NP−InH−CHD ground-state complexes (CT and TCT, respectively), selective irradiation at 344 and 400 nm, using a 65 W Xe arc lamp incorporating a grating monochromator, was performed. As NP does not absorb at the former wavelength, light is absorbed by both the CT and the TCT complex. On the other hand, at the latter wavelength only the TCT absorbs. Analyses of the photolyzates by GC showed that the Diels−Alder products were only formed upon 344 nm irradiation.[21]

In summary, we have found an unprecedented naphthalene-photocatalyzed [4+2] cycloaddition between indole and cyclohexadiene based on selective irradiation of a naphthalene-indole ground-state charge-transfer complex, which reacts in the presence of 1,3-cyclohexadiene. The scope and limitations of this reaction are currently under study.

Acknowledgment. We thank the Ministerio de Educación y Ciencia (Project CTQ2005-00569, doctoral fellowship to M.G.-B.) and Generalitat Valenciana (GV-ACOMP06/134) for generous support of this work.

Supporting Information Available: Details of synthesis and characterization of the known compounds **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] **Standard Procedure.** To a deaerated dichloromethane solution of InH (0.5 mmol), CHD (1.0 mmol), and powdered $NaHCO_3$ (1.0 mmol) were added acetyl chloride (0.5 mmol) and later NP (0.025 mmol) under nitrogen atmosphere. After irradiation, water was added, and the organic phase was separated and dried (Na_2SO_4). Final separation was achieved by column chromatography (hexane/ethyl acetate, 7:1).