mmol) of CuCl and PPh_3 (5.6 mg, 0.02 mmol) for 9.5 h to give 133 mg of a mixture of two compounds (34% yield of **55**, 40% yield of **56** by GLC), which could be separated by preparative TLC by eluting once with 19:1 hexane/EtOAc. Data for the pure compounds are reported below.

***endo*,*exo*-1,3-Dichlorobicyclo[3.2.1]octane-*exo*-1-nitrile (55)**: ^1H NMR (200 MHz, $CDCl_3$) δ 4.54–4.52 (1 H, m), 2.93 (1 H, dd, J = 7.4, 15.1 Hz), 2.85–2.83 (1 H, m), 2.46–2.10 (4 H, m), 1.99–1.85 (4 H, m); IR (film) 2950, 2870, 2250, 1460, 855, 830, 800, 780, 760, 675, 620 cm^{-1}; MS, m/z (relative intensity) 169 (5), 167 (13), 132 (39), 116 (24), 80 (100), 49 (45), 39 (21), 28 (26); exact mass calcd for $C_9H_{11}Cl_2N$ 203.0269, found 203.0278.

***exo*,*exo*-1,3-Dichlorobicyclo[4.2.1]octane-*endo*-1-nitrile (56)**: ^1H NMR (200 MHz, $CDCl_3$) δ 4.55–4.53 (1 H, m), 2.85–2.81 (1 H, m), 2.71–2.51 (3 H, m), 2.34 (1 H, d, J = 12.6 Hz), 2.26–1.81 (5 H, m); IR (film) 2950, 2860, 2250, 1460, 840, 810, 780, 750, 675 cm^{-1}; MS, m/z (relative intensity) 169 (8), 167 (17), 132 (40), 116 (24), 80 (87), 49 (100), 39 (18); exact mass calcd for $C_9H_{11}Cl_2N$ 203.0269, found 203.0273.

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Stereochemical Controls on Exciplex Reactions. Excited State Proton Transfer

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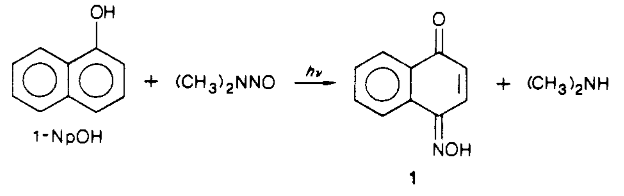
Abstract: By the use of the interaction of excited-state 1-naphthol (1-NpOH) and N-nitrosodimethylamine (NND) as the model, it is shown that excited state proton transfer in organic solvents is a diffusion-controlled process and requires high degrees of geometric arrangements in comparison to energy and charge (electron) transfer processes. During the interaction two identifiable singlet exciplexes can be implicated; one is derived from the direct excitation of the ground-state complex of 1-NpOH and NND and does not proceed to self-nitrosation, while the other is formed from a dynamic collision of *1-NpOH and NND and leads to self-nitrosation to yield 1,4-naphthoquinone monooxime. Each exciplex does not interconvert to the other owing to rapid proton transfer or energy-transfer processes within exciplexes. A possible structure of the ground-state complex was inferred from the NMR chemical shifts displayed by 1-NpOH aromatic protons in the presence of increasing NND concentrations.

We have established that the photoexcitation of polycyclic phenols (ArOH) in the presence of N-nitrosodimethylamine (NND) induces nitrosation of the phenols and that the excited state proton transfer (ESPT) from singlet excited state phenols (*ArOH) to NND is the indispensable step to cause the observed photoreaction.[3] For example, photolysis of 1-naphthol (1-NpOH) in the presence of NND led to the formation of 1,4-naphthoquinone monooxime (**1**). The mechanistic studies of this self-photonitrosation failed to detect a new emission peak of $^*NpO^-$ arising from ESPT, but the presence of an exciplex was assumed. Further investigations show that a ground-state complex between 1-NpOH (and other phenols) and NND is formed in solution and that the mechanism of the interaction of excited state *1-NpOH and NND is more complicated than what had been assumed. In this paper we establish the presence of two exciplexes that are not interconvertible during the lifetime of *1-NpOH.



Results

The UV absorption spectra of 1-NpOH in the presence of NND clearly showed an additional absorption in the 360–450-nm region where both substrates showed no appreciable absorption. The new absorption, assigned to that of a ground-state complex of 1-NpOH–NND (X_S), was partly superimposed with NND absorption in the 360–400-nm region[4] and was unambiguously demonstrated by differential absorption spectra, in dioxane (see Figure 1 in ref 3b), which were taken by using the individual solutions of the substrates in dioxane as the reference. On the assumption of a 1:1 complex formation between 1-NpOH and NND, the association constant, K, was calculated according[5] to eq 1 at various wavelengths (Table I); in this equation, OD°, OD,

Table I. Association Constants (K) of the Ground-State Complex between 1-NpOH and NND in Dioxane[a] at 20 °C

monitoring wavelength, nm	optical density: [NND], M			K, M^{-1}	
	0.030	0.050	0.150	b	c
398	0.0058	0.0095	0.0180	5.5	8.2
400	0.0053	0.0084	0.0160	6.5	8.0
402	0.0050	0.0080	0.0150	6.7	8.5
			average	6.2	8.3

[a] [1-NpOH] = 3 × 10^{-4} M. [b] Calculated from the data of [NND] of 0.030 M and 0.150 M. [c] Calculated from the data of [NND] of 0.050 M and 0.150 M.

$$K = \frac{C_A(OD^\circ - OD') + C_A'(OD - OD^\circ)}{C_A C_A'(OD' - OD)} \qquad (1)$$

and OD′ are the absorbances at a certain wavelength of three solutions containing concentrations of zero, C_A, and C_A' of the component A at a fixed concentration of the component B.

The formation of a ground-state complex, X_S, between 1-NpOH and NND was further demonstrated by NMR spectroscopy, which confirmed the stoicheometry[6-9] of 1:1. The presence of collisional

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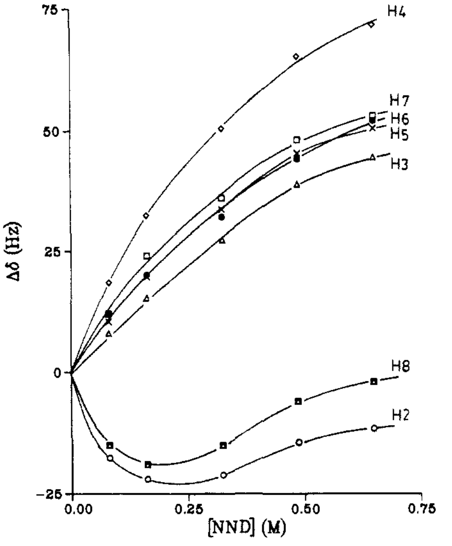

Figure 1. The plots of $\Delta\delta$ against [NND] for the protons in 1-NpOH in CCl_4-$CDCl_3$ (7:3 by volume) at 20 °C.

Table II. Association Constant K and Δ_0 Values by the Monitor of H_3–H_7 of 1-NpOH in CCl_4-$CDCl_3$[a]

protons[b] monitored	H_3 (7.2)	H_4 (7.3)	H_5 (7.7)	H_6 (7.4)	H_7 (7.4)
Δ_0, Hz	139	125	125	73.4	116
K, M^{-1}	1.32	2.14	1.13	2.40	1.46
r	1.000	1.000	1.000	0.998	0.997

[a] For experimental conditions, see Figure 1. [b] The chemical shifts of these protons are indicated in parentheses in ppm.

complexes between NND and aromatic compounds and unequal upfield shifts of two methyl signals of NND have been demonstrated.[6,7] The anti methyl signal in NND shifted upfield faster than the syn methyl signal in the presence of increasing concentrations of 1-NpOH. This phenomenon, however, provides little information on the X_S. The chemical shifts of the aromatic protons of 1-NpOH were determined in the presence of increasing concentration of NND in CCl_4-$CDCl_3$ solution. The shifts ($\Delta\delta$) upfield or downfield from the chemical shift values in the absence of NND are plotted as the function of [NND] (figure 1). The proton signals were assigned according to the published results.[10] The plots of $1/\Delta\nu$ vs $1/[NND]$ for H_3–H, according[8,9] to eq 2

$$1/\Delta\delta = (1/K)(1/\Delta_0)(1/[NND]) + 1/\Delta_0 \qquad (2)$$

indeed gave straight lines[11] (see figure 6 in the supplementary material). Equation 2 was derived on the basis of an assumption of a 1:1 complex formation between two substrates[9] and Δ_0 is the chemical shift difference for a certain aromatic proton in 1-NpOH between the 1:1 complex of X_S and uncomplexed 1-NpOH; these values can be obtained from the reciprocals of the intercepts. The association constants calculated from the slopes and intercepts of these plots agree with each other reasonably within the limit of experimental accuracy and give an average value of 1.7 ± 0.5 M^{-1} (Table II). The results indicate that 1-NpOH and NND indeed form a ground-state complex X_S with 1:1 stoicheometry.

An acetonitrile solution of 1-NpOH and NND when excited at 370 nm (or higher) showed a broad fluorescence at 430–600 nm peaking at 480 nm (Figure 2). Under similar condition neither NND nor 1-NpOH showed this emission. Fluorescence excitation spectra of 1-NpOH in the presence of NND monitored at various wavelengths in the 450–500-nm region show the absorption arising from the ground-state complex in the 380–450-nm region (Figure 3); the valley in the 360-nm region is due to absorption by NND[3]. The comparisons of relative intensities at 390 and 325 nm show that the latter band attenuated rapidly, approaching nil intensity as the excitation spectra were monitored at a longer wavelength; obviously, the 325-nm band consisted of the absorption arising from complexed and uncomplexed 1-NpOH. This was confirmed by the fluorescence excitation spectra of 1-NpOH alone under comparable conditions in which the band at 380–450 nm was not obtained.[11] Therefore the emission at about 480-nm (Figure 2) is assigned to fluorescence of an 1-NpOH–NND exciplex directly attained from the ground-state complex X_S. When a solution of 1-NpOH and NND in dioxane or acetonitrile was irradiated with a light source >380 nm to excite X_S, no quinone monooxime **1** was formed and NND was not photolytically decomposed; the estimated quantum yield for the monooxime formation and NND disappearance were not higher than 6×10^{-4} and 1.5×10^{-3}, respectively. We also reconfirm that photoexcitation of 1-NpOH in the 300-nm region leads to the formation of monooxime **1** and the limiting quantum yield of **1** in dioxane is about[3] 0.1. This unambiguously demonstrates that dynamic collision of *1-NpOH with NND is the sole course of the formation of monooxime **1**.

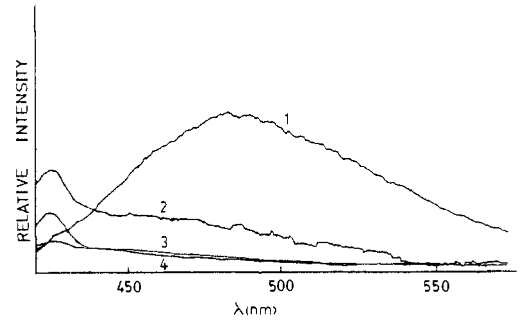

Figure 2. Fluorescence spectra obtained from the excitation of the ground-state complex (X_S absorption at 370 nm) in acetonitrile at room temperature. Curve 1: [1-NpOH], 0.0002 M and [NND], 0.012 M. Curve 2: [1-NpOH], 0.0002 M. Curve 3: [NND], 0.012 M. Curve 4: solvent only.

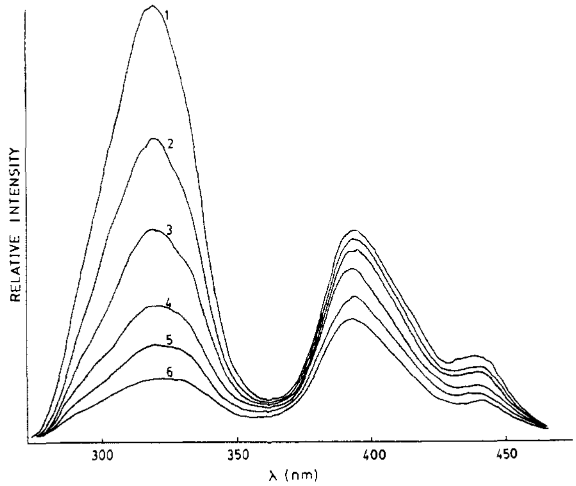

Figure 3. Fluorescence excitation spectra of 1-naphthol (2×10^{-4} M) in the presence of NND (0.012 M) in acetonitrile at 20 °C monitored at 450, 460, 470, 480, 490, and 500 nm for the spectra 1–6, respectively.

The emission peaks from the lowest singlet excited state of *1-NpOH and *1-NpO⁻ in methanol were reconfirmed[11] to be at 340 and 460 nm, respectively; the latter was obtained in methanol solution containing [KOH] = 0.002 M. By use of time-resolved fluorescence spectroscopy, the lifetime and shape of 1-NpOH fluorescence were studied as a function of NND concentrations. The shape of the fluorescence peak (320–520 nm) at various delay times (1–20 ns) was the same as that observed by steady-state fluorescence measurements by the standard method; i.e., no new emission other than that of *1-NpOH was

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Table III. The Quenching of Fluorescence Lifetimes of 1-NpOH and 1-NpOD by NND at Various Emission Wavelengths[a]

	monitoring wavelengths			
	300 nm[b]	345 nm[b]	400 nm[b]	345 nm[c]
$k_q\tau_0$, M^{-1}	80 ± 2	81 ± 3	85 ± 3	90 ± 1
$k_q \times 10^{-9}$, $M^{-1}\ s^{-1}$	7.6 ± 0.2	7.6 ± 0.3	7.9 ± 0.3	8.1 ± 0.1
r	0.997	0.997	0.997	1.000

[a] The samples containing [NND] of 0–25 $\times 10^{-3}$ M in dioxane were excited at 300 nm at room temperature. [b] [1-NpOH] = 2×10^{-4} M. See ref 11 for the experimental data and calculations. [c] [1-NpOD] = 3.4×10^{-4} M.

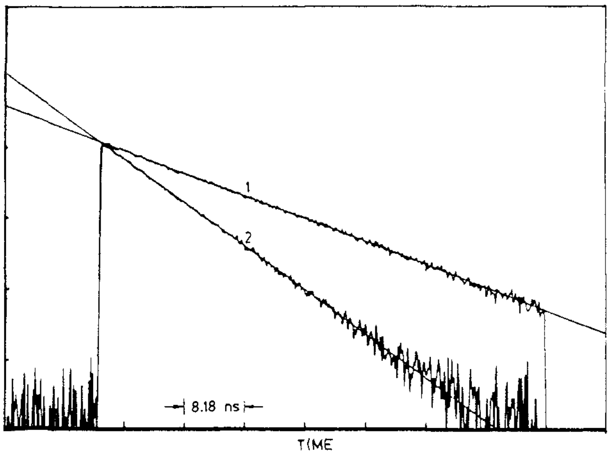


Figure 4. Fluorescence decay curves of 1-NpOH (0.0002 M) in dioxane at room temperature in the absence (curve 1) and presence of NND (0.012 M, curve 2); the samples were excited at 300 nm and monitored at 345 nm. The exponential decay times obtained from the two straight-line fits were 10.70 and 5.10 ns for curves 1 and 2, respectively. The vertical markers are decades of intensity.

observed. In the presence of high concentrations of NND, the fluorescence spectra of *1-NpOH were distorted because of reabsorption of the emitted light by NND in the 340-nm region. The details of these time-dependent spectra were described in the thesis submitted by Wu.[11] The decay patterns of fluorescence intensities in dioxane monitored at three different wavelengths (300, 345, and 400 nm, Table III) were single exponential either in the presence or absence of NND (Figure 4). The fluorescence lifetimes determined were plotted according to eq 3 or 3′ to afford

$$\tau^{\circ}/\tau = 1 + k_q\tau_0[\mathrm{NND}] \qquad (3)$$

$$1/\tau^{\circ} = 1/\tau_0 + k_q[\mathrm{NND}] \qquad (3')$$

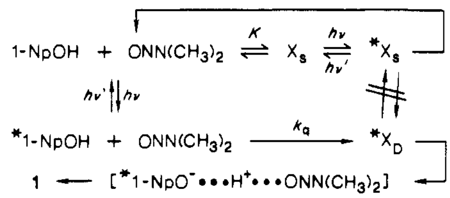
k_q values (Table III). O-Deuteriated 1-naphthol, 1-NpOD, was also used to study its fluorescence lifetimes in the presence and absence of NND under stringently anhydrous conditions. The close similarity of k_q values for 1-NpOH and 1-NpOD was shown in Table III clearly indicates the fact that no deuterium isotope effect exists in the ESPT of *1-NpOH to NND as has been shown in the quantum yield studies described previously.[3]

Under comparable conditions, the self-photonitrosation of 1,5-dihydroxynaphthalene with NND proceeded much more rapidly than that of 1-NpOH; this reaction, unfortunately, gave a complex mixture, probably owing to secondary photoreactions, and could not be studied quantitatively.[11] The limiting quantum yield of substrate disappearance in the presence of increasing amounts of NND was roughly estimated to be 0.2–0.3, much higher than that of the 1-NpOH–NND system[3] of 0.1.

Discussion

In addition to the information described previously,[3] we have now established that (i) 1-NpOH and NND do form a ground-state complex (X_S), (ii) the direct excitation of X_S does not cause the self-nitrosation of 1-NpOH, and (iii) while the ESPT step is involved, no deuterium isotope effect is detected. These new observations are incorporated in an expanded mechanistic proposal (Scheme I), which also contains an evident conclusion that the collisional interaction between *1-NpOH and NND (i.e. the dynamic quenching process) alone leads to a different exciplex *X_D followed by a sequence of reactions giving the oxime.[3] The rapidly decreasing ratios of the peak intensities at 325 nm to those at 390 nm in the fluorescence excitation spectra (Figure 3) clearly indicate that the latter is the absorption of the ground-state complex X_S and, more importantly, that *X_D does not transform to *X_S within its lifetime.

Scheme I



On the basis of Scheme I, steady-state quenching of fluorescence intensities (I°/I) is related to NND concentrations by the quadratic equation[12,13] 4. In a low concentration range of NND, where the $[\mathrm{NND}]^2$ term is insignificant, eq 5 can be applied as an approximation. At this [NND] range, the slope represents

$$I^{\circ}/I = \{1 + K[\mathrm{NND}]\}\{1 + k_q\tau_0[\mathrm{NND}]\} \qquad (4)$$

$$I^{\circ}/I \cong 1 + (k_q\tau_0 + K)[\mathrm{NND}] \qquad (5)$$

overall Stern–Volmer quenching constant,[3] K_{SV} = 117 M^{-1}, and contains a static quenching term arising from the ground state complex, X_S, formation and a dynamic quenching term arising from encounters of *1-NpOH and NND. Experimentally the latter term can be determined by fluorescence lifetime measurements ($k_q\tau_0 \cong 82\ M^{-1}$ in Table III). These data allow us to estimate K according to eq 5, giving much higher K values than those determined by UV and NMR spectroscopy as shown above. It is assumed that these higher K values (from eq 5) contain a substantial margin of errors arising from the use of NND concentrations significantly lower than those used in the UV and NMR determinations. Experiments with higher concentrations of NND are frustrated because of serious reabsorption by NND of emitted light.[3] However the validity of eq 4 has been established in 1-anthrol fluorescence intensity quenching by NND where the emitted light is not reabsorbed.[11]

The fact that the self-nitrosation of 1-NpOH is induced solely from the dynamic quenching process is confirmed by the close agreement of $k_q\tau_0$ determined from fluorescence lifetime quenching (82 M^{-1} from Table III) with that determined from the monooxime quantum yields (Φ_{ox}) on the basis of eq 6 (74 M^{-1} from ref 3a). Equation 6 has been derived on the basis of the mechanism proposed in the previous paper[3] to express the relation of $1/\Phi_{ox}$ and 1/[NND]. Under the expanded mechanism proposed in Scheme I, validity of eq 6 still holds true since the kinetic effects on the oxime formation (Φ_{ox}) by the presence of X_S is only secondary, arising from the absorption of incident light by increments of X_S. This should cause a slightly lower $k_q\tau_0$ value for that obtained from eq 6 as compared to that derived from the lifetime determinations, e.g. 74 vs 82 M^{-1} as shown above. Therefore, the $k_q\tau_0$ value obtained from these plots must represent the dynamic quenching process; that is, the monooxime is formed from the dynamic quenching process.

$$(\Phi_{ox})^{-1} = (\alpha\beta)^{-1} + (\alpha\beta k_q\tau_0[\mathrm{NND}])^{-1} \qquad (6)$$

As the rate constant of the dynamic quenching process approaches the diffusion-controlled rate constants in various organic solvents (Table III), the conclusion derived above implies that the ESPT step in these organic solvents is limited by the diffusion-controlled collision process, and ESPT occurs within the exciplex *X_D, i.e. the exciplex formed from the dynamic quenching process. The lack of deuterium isotope effects in the self-photonitrosation

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process is in agreement with this observation and means that the ESPT step possesses very small or negligible activation energy such as that that occurs within a complex. Lack of deuterium isotope effects has been observed in diffusion-controlled quenching processes.[14] Indeed, in a related study on dynamic quenching of the excited-state 1-anthrol by NND, the activation energy E_a has been determined to be 2.5 kcal/mol,[11] which is in the range of E_a found for diffusion-controlled reactions in organic solvents.[14] It should be mentioned that in water solution, ESPT from *1-NpOH operates by a different mechanism with the rate constant of 2.5×10^{10} s^{-1} with water clusters as acceptors and transmitters.[15,16]

Having established the dual deactivation pathway of *1-NpOH with NND as shown in Scheme I, we propose the presence of two exciplexes, each of which reacts by its own pathway without being able to interconvert to the other during their lifetimes. The present phenomenon finds analogy with those found in the exciplexes of energy and charge (electron) transfer interactions[17-20] where geometric requirements of the exciplexes have been discussed on the basis of optimum orbital overlaps.[20] As far as a few examples reported[17-19] there exists some evidence that energy and charge (electron) transfer interactions do occur efficiently whether by dynamic collision of excited molecules or by excitation of a ground-state complex and exhibit identical or very similar fluorescence spectra and chemical behavior by either pathway.[21-23]

These observations could be taken as indications that geometric requirements are less stringent for energy and electron transfer and that reorientation to a favorable exciplex geometry occurs faster than other processes. The assumptions are further supported by a number of bimolecular photochemical reactions initiated by energy or charge (electron) transfer interactions wherein the excitation of the CT band of ground-state complexes generally leads to successful photoreactions.[24-29]

In spite of these reports on energy and charge (electron) transfer interactions, the present observation is puzzling in that the excitation of X_S absorption at >400 nm causes no self-nitrosation of 1-NpOH. Since an exciplex is a loosely bound complex possessing an enthalpy of dissociation of <10 kcal/mol,[30-32] cases of the reorientation of an exciplex faster than its reaction processes are known.[20-29] However, in H abstraction from alkylbenzenes by the π,π^* triplet states of aromatic ketones (by CT mechanism), two distinct and *irreversible* exciplexes have been identified to explain observed H-abstraction selectivity.[33] The present case must mean that the geometry of *X_S deviates significantly from that required for ESPT, and, further, ESPT occurs much faster than the reorientation of substrates within the exciplex.

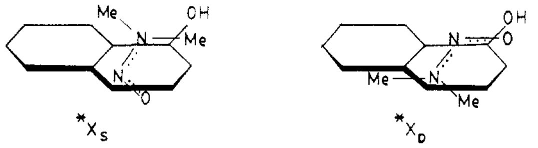

Figure 5. Proposed geometry for exciplexes.

Thus, we propose that the failure to observe *$X_X \rightarrow$ *X_D could arise from a limitation imposed by the short lifetime of the exciplexes combined with a high degree of stereospecificity required in the ESPT step. For example, while reorientation of *X_S is feasible, it does not occur fast enough to bring the substrate to a required geometry; in the meantime, an alternative process, such as energy transfer from *1-NpOH to NND competes favorably to depopulate the excited state. We have demonstrated that fluorescence of 1-NpOCH$_3$ is quenched by NND by energy transfer ($k_q = 4 \times 10^{10}$ M^{-1} s^{-1}) without causing any chemical reaction.[3] The rapid decay of singlet excited NND is known.[4] Recently it was demonstrated that proton transfer between a radical cation and a radical anion requires more stringent geometric reorientations within an encounter complex.[34]

In spite of extensive search,[11] the failure to observe emission from the proton-transferred complex [*1-NpO$^-$...H$^+$...ONN(CH$_3$)$_2$] has been a missing link in the proposed mechanism in the dynamic quenching process. The straightforward single exponential decay of *1-NpOH fluorescence intensities suggests that reverse proton transfer of this complex to *X_D does not occur to any appreciable extent. This may be due to a rapid deactivation of this complex by subsequent energy transfer followed by dissociation on the course to the nitrosation process. Thus, this complex may have a lifetime too short to show other reactions such as reverse proton transfer and emission.

Undoubtedly the difference between the two exciplexes *X_S and *X_D rests on the orientation of the two substrates. For their formations, substrates are assumed to orient with their molecular planes parallel to each other (Figure 5) for maximum overlap of interacting orbitals;[20] they are the LUMO (π^* orbitals) of the substrates in the present case. From the Franck–Condon principle, *X_S must inherit the geometric features of the ground-state complex X_S. As ESPT is established to be a necessary step in the self-photonitrosation of 1-NpOH,[3,11] the failure to produce quinone monooxime **1** on excitation of the ground-state complex X_S must mean that *X_S (and therefore X_S) does not have structural features that allow ready proton transfer. This conclusion appears unusual in view that ground-state complexes between phenols and general bases are generally assumed to be formed through H bonding where there is no other significant binding force.[5,35] Indeed in some cases where bases are as strong as amines, the presence of H bonding has been demonstrated by IR spectroscopy.[35] We advance an argument that in the geometry of X_S having parallel molecular planes, H bonding is probably weak and unimportant owing to nonlinear arrangement of the interacting centers OH···ON.

In the absence of a clearly established correlation of NMR chemical shifts and stereochemistry, the chemical shifts of protons in 1-NpOH generated by NND (Table II) may be intuitively interpreted with the structure shown in Figure 5. It is assumed that a high electron density in the N=O portion induces large upfield shifts for the C-3, C-4, and C-5 protons and that a low electron density of the (CH$_3$)$_2$N moiety causes downfield shifts for the C-2 and C-8 protons. Since the exciplex *X_S does not have a chance of undergoing ESPT, it either emits, albeit weakly, or dissipates the excited state by energy transfer to NND within its lifetime; these naturally cause no net chemical reactions.[3] The induced shifts of the chemical shifts of C-2 and C-8 by NND (Figure 1) appears to be a composite of two opposing effects; the weaker effects of upfield shifts occur at higher concentrations of NND and probably arise from shieldings in terms of anisotropic

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effects of the nitrosamino group.[6,7] In a hope to gain some understanding on the geometric arrangement of the ground-state complex X_S, molecular-mechanics computations based on the force field MM2 method[36] was applied to the interaction of 1-NpOH and NND. These computations certainly confirmed the parallel orientation of the molecular planes of 1-NpOH and NND but also yielded widely fluctuating minimal energies with small rotations of substrate orientations. While the intuitive geometry (Figure 5) is one of relatively low energy species, it is not the geometry possessing lowest relative energy (see supplementary material, Figure 7).

The structure of the exciplex $^*X_D$ is suggested to have NND oriented in the direction so ESPT can occur. Among all conceivable geometrical arrangements for the encounter complex formation from random collisions of *1-NpOH and NND, only those arrangements with the probability of ESPT can develop into the exciplex $^*X_D$ within which proton transfer and energy migration can occur in the correct sequence to give a successful reaction. The encounter complexes of other geometrical arrangements decay to the ground state by energy transfer to NND as discussed above. Owing to such stringent geometric requirements, it is consistent that the self-photonitrosation of 1-NpOH with NND gives low quantum yields in spite of the efficient quenching process by NND. While there are other unknown factors involved, the more facile self-photonitrosation of 1,5-dihydroxynaphthalene may be interpreted as increased availability of ESPT and supports the proposed geometry of exciplex $^*X_D$ in Figure 5.

Experimental Section

The instrumentation, chemicals and general conditions of experiments followed those described in the previous paper.[3] Fluorescence lifetime determinations used, as the excitation source, a synchronously pumped, cavity dumped, and mode locked dye laser system operating at 600 nm with 4 MHz repetition rate and a 10-ps pulse width at 300 nm after frequency doubling. A fast photomultiplier tube operating in single-photon counting mode was used as the signal detector. A detailed description of the apparatus is given in a previous publication[37] and in the thesis submitted by one of us.[38]

Transient fluorescence spectra of 1-NpOH (0.0006 M) in dioxane or THF ranging from 320 to 520 nm were recorded at room temperature at several time windows (0-1, 1-3, 3-8, 8-14, 14-20 and 20-40 ns) after pulsing with the 300-nm laser source. Similar transient fluorescence spectra of 1-NpOH in the presence of NND were recorded. The logarithmic decays of fluorescence intensity vs time at three different wavelengths were measured and plotted, and τ_0 and τ were obtained from the slopes. Lifetime measurements involving 1-NpOD used either a vacuum transfer method or drybox operation to prepare solutions: glasswares were flame-dried and materials were freshly prepared and dried.

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Registry No. 1, 4965-30-4; 1-NpOH, 90-15-3; $(CH_3)_2NNO$, 62-75-9.

Supplementary Material Available: Plot of $1/\Delta\delta$ against 1/[NND] for C-3 to C-7 protons of 1-N_pOH (Figure 6) and the energy-minimized geometry of the ground-state complex X_s obtained by the force field MM-2 computation (Figure 7) (3 pages). Ordering information is given on any current masthead page.

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Intramolecular 2 + 2 Photocycloadditions of 4-(3′-Alkenyl)- and 4-(3′-Pentynyl)-2,5-cyclohexadien-1-ones

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Abstract: The first examples of the intramolecular 2 + 2 photocycloaddition of 4-(3′-alkenyl)-2,5-cyclohexadien-1-ones are described. 2,5-Cyclohexadienones **11a-f**, **24a-b**, and **26a-e** undergo photocyclization to tricyclo[4.3.1.^{1,5}0^{7,10}]dec-2-en-4-ones **12a-h**, **25a-b**, and **27a-e**, respectively, in excellent yields without competition from the type A photorearrangement. Tricyclodecenones **12g** and **12h** undergo slower but efficient secondary photorearrangements to oxetanols **16a** and **16b**, presumably by γ-hydrogen atom transfer from the C(5)-methoxy substituent to the photoexcited enone carbonyl group to give the intermediate biradicals **15a** and **15b**. Stereochemical studies with the enantiomerically pure 4-(3′-butenyl)-2,5-cyclohexadienone **22** demonstrated that 2 + 2 photocycloaddition to give **23** occurs without racemization. Irradiation of the (*cis*-3′-pentenyl)-2,5-cyclohexadienone **26a** and the *trans*-3′-pentenyl isomer **26b** revealed that the cycloaddition is nonstereospecific and probably involves biradicals of type **28**. Preliminary characterization of the excited state responsible for cyclobutane formation also is presented. The C(4)-substituted 3′-pentynyl derivative **30** gave the unstable cyclobutene **31** in high yield. The conversion of **31** to oxidation and reduction products **32**, **33**, and **27b** demonstrates potential synthetic utility of the intramolecular acetylene to 2,5-cyclohexadienone cycloaddition.

Intramolecular cycloadditions of oxyallyl zwitterions **2** generated from consecutive photorearrangements of 4-substituted 2,5-cyclohexadien-1-ones **1** have been shown to be useful for the construction of carbocyclic and heterocyclic ring systems. The zwitterionophile (X) tethered at C(4) of **1** can be an azide 1,3-dipole,[1,2] a diene,[2,3] or an alkene.[4]

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