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ARTICLES

Significant Effects of Substituents on Substituted Naphthalenes in the Higher Triplet Excited State

Masanori Sakamoto, Xichen Cai, Michihiro Hara, Mamoru Fujitsuka, and Tetsuro Majima*

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

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Substituent effect on the lifetimes of a series of substituted naphthalenes (Np) in the higher triplet excited state (T_n) was studied with transient absorption measurements using the two-color two-laser flash photolysis technique. Lifetimes of Np(T_n) in cyclohexane solution were determined from the triplet energy transfer quenching by carbon tetrachloride to be 0.98−63 ps. The different lifetimes of Np(T_n) were explained by the energy gap law for the internal conversion from Np(T_n) to Np(T_1), indicating that Np(T_n) quenched by carbon tetrachloride is assigned to Np(T_2) with the longest lifetime among Np(T_n). The lifetime of Np(T_n) was correlative with the Hammett σ_p constant. Electronic characters of substituents showed a more significant influence on the energy of the T_2 state than that of the T_1 state.

1. Introduction

Properties of molecules in the higher triplet excited states (T_n) are an attractive subject in the fields of photochemistry, photophysics, and photobiology.[1−32] However, information on molecules in the T_n states is limited, because the direct detection of the T_n states is extremely difficult due to their short lifetimes and no emissive character. Some indirect approaches have been employed to estimate the lifetimes of molecules in the T_n state. One of the indirect methods is the analysis of the product resulting from triplet energy transfer (ENT) from the T_n state. Ladwig et al. determined the lifetime of naphthalene (T_2) using high-concentration benzene which acts as the triplet quencher and triplet energy carrier to *endo*-dicyclopentadiene, giving norbornene from the T_1 state.[14−16] Saltiel et al. reported a similar approach in which the sensitized photoisomerization of stilbene or 2,4-hexadiene is used as a probe of the triplet energy quenching of anthracene (T_2).[23] Recently, two-color two-laser flash photolysis was used to estimate the lifetimes of the T_n states from the ENT quenching of the T_n state molecules by an appropriate triplet quencher that has the lowest excited triplet energy ($E(T_1)$) between $E(T_1)$ and $E(T_n)$ of the target molecules.[17,24−27] Since molecules in the T_n states decay to the T_1 state through fast internal conversion, no change of the T_1 state transient absorption was observed during the nanosecond laser excitation of the T_1 state. However, bleaching of the transient absorption of the T_1 state was observed in the presence of the triplet quencher of the T_n state. For example, carbon tetrachloride (CCl_4) quenches naphthalene in the T_n state (naphthalene (T_n)) through the ENT quenching mechanism, but does not quench naphthalene (T_1).[17,24−27] We have estimated the lifetime of naphthalene (T_n) to be 4.5 ps in acetonitrile based on the CCl_4 concentration dependence of the ENT quenching efficiency.[17] This value is well consistent with those obtained by theoretical calculation and product analysis.[14,28,29]

Properties in the T_n state are affected by the substituent, while there are only a few reports about substituent effect on aromatic hydrocarbons in the T_n states. For example, the anthracene S_1-T_2 energy gap varied by changing the solvent and substituent.[30,31] Bohne et al. reported that the lifetime of substituted anthracene (T_2) depends on the T_2-T_3 vibronic coupling.[32] Our previous work on a variety of substituted benzophenones (T_n) revealed that the lifetime is also affected by the substituent on the benzene ring.[26,27] Therefore, the substituent is one of the important factors governing the lifetime of the T_n state molecules. Although naphthalene is a fundamental and important aromatic hydrocarbon particularly in photochemistry, limited numbers of theoretical and experimental studies have been reported on its higher excited states.[14−17,28,29] Moreover, no systematic study has been reported on the substituent effect on the properties of substituted naphthalenes (Np) in the T_n states (Np(T_n)). In this paper, we describe the substituent effect on the lifetime of Np(T_n) based on transient absorption measurement using two-color two-laser flash photolysis.

2. Experimental Section

2.1. Materials. Structures of all naphthalene derivatives (Np) are shown in Chart 1. 2-Methylnaphthalene, 1-cyanonaphthalene, naphthalene, and benzophenone were recrystallized two or three times from ethanol before use. Other compounds were of the highest grade available and used as received. Sample solutions were prepared in cyclohexane and deoxygenated by bubbling with argon gas for 30 min before irradiation. All laser experiments were carried out at room temperature.

2.2. Phosphorescence Measurement at 77 K. Phosphorescence spectra were recorded at 77 K in 1-methylpentane glass using a HITACHI 850 spectrophotometer.

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* Corresponding author. E-mail: majima@sanken.osaka-u.ac.jp.

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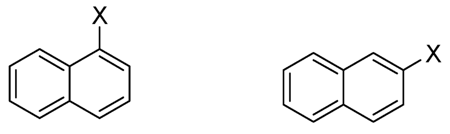
CHART 1: Molecular Structures of 1- and 2-Substituted Naphthalenes



X = H, CN, CH_2CN, CH_3, CH_2CH_3, $CH(CH_3)_2$, OCH_3

X = H, CH_2CN, CH_3, CH_2CH_3, $CH(CH_3)_2$, OCH_3

2.3. Transient Absorption Measurement Using Two-Color Two-Laser Flash Photolysis. Two-color two-laser flash photolysis experiment was carried out using the third harmonic oscillation (355 nm) of an Nd^{3+}:YAG laser (Quantel, Brilliant; 5 ns fwhm) as the first laser and the 425-nm flash from an OPO laser (Continuum, Surelite OPO) pumped by an Nd^{3+}:YAG laser (Continuum, Surelite II-10; 5 ns fwhm) as the second laser. The delay time of two laser flashes was adjusted to 70 ns by three four-channel digital delay/pulse generators (Stanford Research Systems, Model DG 535). Two laser beams were adjusted to overlap at the sample. The monitor light source was a 450 W Xe lamp (Osram XBO-450) synchronized with the laser flash. The monitor light perpendicular to the laser beams was focused on a monochromator (Nikon G250). The output of the monochromator was monitored using a photomultiplier tube (PMT) (Hamamatsu Photonics, R928). The signal from the PMT was recorded on a transient digitizer (Tektronix, TDS 580D four-channel digital phosphor oscilloscope). To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were employed. The samples were contained in a transparent rectangular quartz cell (1.0 × 1.0 × 4.0 cm) at room temperature.

3. Results

3.1. Triplet−Triplet Absorption Spectra of Np. In the present paper, substituents of Np were selected to examine the effects of their electronic characters and positions on the lifetime of $Np(T_n)$. CCl_4 was used as a quencher of $Np(T_n)$, since our previous work demonstrated that CCl_4 quenches naphthalene (T_n) but not naphthalene (T_1).[17] $Np(T_1)$ was generated from the triplet sensitization with benzophenone (BP) during irradiation with the first laser (355 nm, 3 mJ $pulse^{-1}$) of the mixtures. The triplet−triplet (T−T) absorption spectra of Np were observed as shown in Figures 1 and 2. At the Np concentrations used, ENT from $BP(T_1)$ to Np is quantitative. Thus, the extinction coefficients (ϵ) of Np can be estimated from a comparison of signal intensity with that of naphthalene (24 500 M^{-1} cm^{-1} at 415 nm in nonpolar solvent).[33] The estimated ϵ values of Np are summarized in Table 1. The T−T absorption band of naphthalene at 415 nm has been assigned to the $^3B_{3g}{}^- \leftarrow {}^3B_{1u}{}^+$ transition, which is long-axis polarized.[34−36] Relatively large ϵ values were observed for 2-substituted naphthalenes compared with those for 1-substituted naphthalenes. The shape of T−T absorption of 1-methoxynaphthalene was largely deformed, indicating that another short-axis-polarized transition such as the $^3A_g{}^- \leftarrow {}^3B_{1u}{}^+$ transition is possibly induced by the substitution of the methoxy group at the 1-position.[34−36]

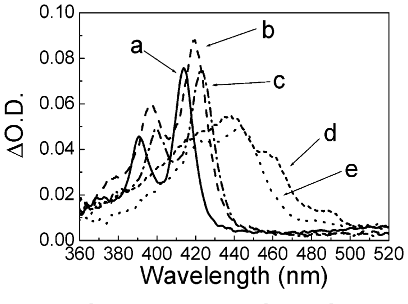


Figure 1. Transient absorption spectra observed at 200 ns after 355-nm laser excitation of 1-substituted Np (naphthalene (a), 1-methylnaphthalene (b), 1-ethylnaphthalene (c), 1-methoxynaphthalene (d), and 1-cyanonaphthalene (e)) (7.0×10^{-3} M) in the presence of BP (7.0×10^{-3} M) in Ar-saturated cyclohexane solution at room temperature.

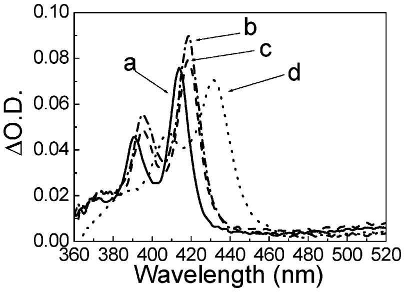


Figure 2. Transient absorption spectra observed at 200 ns after 355-nm laser excitation of 2-substituted Np (naphthalene (a), 2-methylnaphthalene (b), 2-ethylnaphthalene (c), and 2-methoxynaphthalene (d)) (7.0×10^{-3} M) in the presence of BP (7.0×10^{-3} M) in Ar-saturated cyclohexane solution at room temperature.

TABLE 1: Peak of T−T Absorption (λ_{max}) and Extinction Coefficient (ϵ) of Np at the Peak Position

Np	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
1-cyanonaphthalene	442	16 000
1-naphthaleneacetonitrile	415	14 000
naphthalene	415	24 500[a]
1-methylnaphthalene	419	29 000
1-ethylnaphthalene	424	25 000
1-isopropylnaphthalene	424	26 000
1-methoxynaphthalene	440	18 000
2-naphthaleneacetonitrile	416	28 000
2-methylnaphthalene	419	28 000
2-ethylnaphthalene	419	29 000
2-isopropylnaphthalene	420	29 000
2-methoxynaphthalene	431	23 000

[a] Reference 33.

3.2. Two-Color Two-Laser Excitation Experiments. $Np(T_n)$ can be generated by the excitation of $Np(T_1)$ with the second laser (425 nm, 9 mJ $pulse^{-1}$) at 70 ns after the first laser. No change of the transient absorption of $Np(T_1)$ was observed during the irradiation with the second laser in the absence of CCl_4. It is suggested that the fast $T_n \rightarrow T_1$ internal conversion (IC) occurs within the laser flash duration (5 ns).

In the presence of CCl_4, the bleaching of the transient absorption of $Np(T_1)$ was observed after the second laser irradiation, as shown in Figures 3 and 4. The yield of bleaching

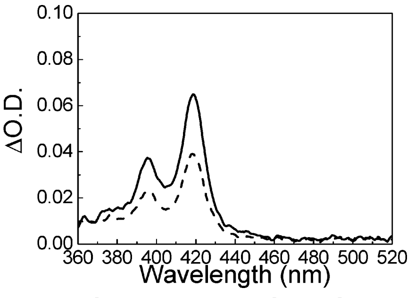


Figure 3. Transient absorption spectra observed at 200 ns after the first laser pulse during two-color two-laser photolysis (355 and 425 nm, broken line) and one-laser photolysis (355 nm, solid line) of a mixture of 2-methylnaphthalene (7.0×10^{-3} M) and BP (7.0×10^{-3} M) in Ar-saturated cyclohexane solution in the presence of CCl_4 (1.0 M) at room temperature.

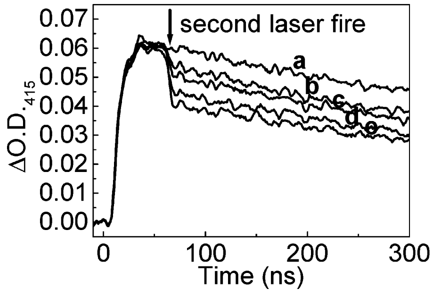
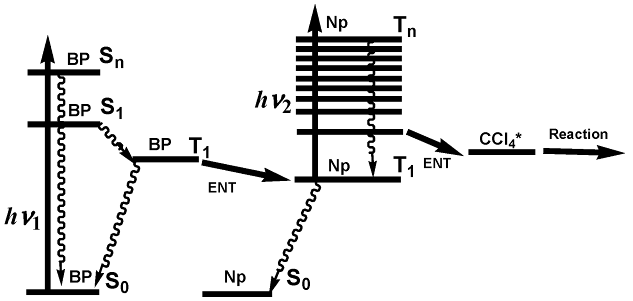


Figure 4. Kinetic traces of ΔOD at 415 nm during two-color two-laser flash photolysis of a mixture of 2-methylnaphthalene (7.0×10^{-3} M) and BP (7.0×10^{-3} M) in Ar-saturated cyclohexane solution in the absence (a) and presence of CCl_4 (0.1 (b), 0.2 (c), 0.3 (d), and 0.4 M (e)) at room temperature.

SCHEME 1: Schematic Energy Diagram for BP, Np, and CCl_4 in Their Ground and Excited States[a]



[a] Wavy lines indicate relaxation processes.

of 2-methylnaphthalene (T_1) during the second laser irradiation increased with an increase in the concentration of CCl_4 (Figure 4). Similar transient absorption changes were observed with the other Np. This bleaching indicates that Np(T_n), produced by irradiation of the second laser, disappeared through a process (or processes) which does not (or do not) regenerate Np(T_1). The supposed photoinduced processes are shown in Scheme 1.

4. Discussion

4.1. Reactions from Np(T_n). Since the formation and decay of Np(T_n) occur within the duration of the second laser flash (5 ns), Np(T_n) cannot be monitored directly. The bleaching of ΔOD at the peak assigned to Np(T_1) in the presence of CCl_4 within the second laser flash ($\Delta\Delta OD = \Delta OD_{before} - \Delta OD_{after}$, where ΔOD_{before} and ΔOD_{after} refer to ΔOD before and after the second laser flash, respectively) results from the quenching of Np(T_n) by CCl_4. Limited numbers of studies on the photoinduced reactions from the T_n state have been reported.[4−27] Most of them are ENT from T_n to the triplet quenchers. However, Wang et al. reported the electron transfer (ELT) quenching of anthracene (T_n) by bromoethyl acetate in acetonitrile.[13] Thus, we used cyclohexane as a solvent to suppress the ELT from Np(T_n). No generation of radical cations was observed, suggesting that ELT does not occur in the present system. Back intersystem crossing ($T_n \rightarrow S_1$) can also be neglected since no fluorescence from Np(S_1) was observed after the second laser irradiation.

4.2. Determination of lifetime of Np(T_2). Assuming that the ENT quenching of Np(T_n) occurs by the bimolecular reaction process, ΔΔOD can be represented as a function of the concentration of CCl_4 ([CCl_4]) as shown in eq 1:[17,37,38]

$$\frac{1}{\Delta\Delta OD} = \beta\left(1 + \frac{1}{k_q\tau[CCl_4]}\right) \qquad (1)$$

where β is a constant that depends on the reaction system,[17,37,38]

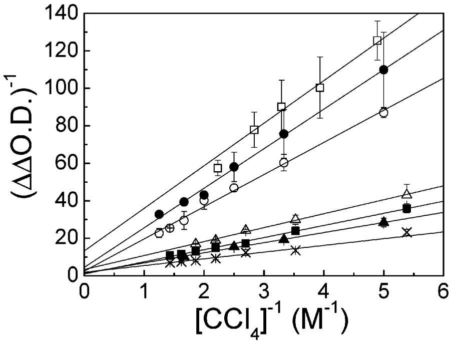


Figure 5. Plots of $(\Delta\Delta OD)^{-1}$ vs $[CCl_4]^{-1}$ during two-color two-laser photolysis of naphthalene (●), 1-cyanonaphthalene (○), 1-naphthaleneacetonitrile (■), 1-methylnaphthalene (▲), 1-ethylnaphthalene (△), 1-isopropylnaphthalene (×), and 1-methoxynaphthalene (□) in the presence of various concentrations of CCl_4.

k_q is the ENT quenching rate constant of Np(T_n) by CCl_4, and τ is the lifetime of Np(T_n). According to eq 1, the plots of $(\Delta\Delta OD)^{-1}$ vs $[CCl_4]^{-1}$ showed a linear relation as shown in Figure 5.

The ENT quenching mechanism of Np(T_n) by CCl_4 cannot be explained by the simple diffusion-controlled process because of the quite short τ of Np(T_n) and high concentration of CCl_4. For such systems, the quenching rate constant k_q is represented as a sum of the lifetime-independent and -dependent terms. The lifetime-independent term refers to a dynamic process. The lifetime-dependent term (i.e., static quenching) refers to the process by which a donor is quenched at the instant of the excitation by a ground state quencher that locates sufficiently close to the donor.[32,39−41] Assuming that σ' is a true collisional distance between two reactive molecules A* and B (A* is an electronically excited molecule) and D is the sum of diffusion coefficients of A* and B, the classical theory leads to the analytical expression of k_q (eq 2):[17,39−41]

$$k_q = k_{diff}\left(1 + \frac{\sigma'}{(\pi D\tau)^{0.5}}\right) \qquad (2)$$

where k_{diff} is a diffusional constant given by[17,39−41]

$$k_{diff} = 4\pi N\sigma' D \qquad (3)$$

where N is Avogadro's number. We employed $\sigma' = 0.6$ nm and $D = 0.8 \times 10^{-5}$ cm^2 s^{-1}.[17] From eqs 2 and 3 and the parameters obtained from Figure 5, the τ values of Np(T_n) were estimated and are summarized in Table 2.

4.3. Assignment of Triplet Manifold of Np(T_n). From the energy gap law, the energy gap for IC (ΔE) and τ have the relation of eq 4:[17,24−27,34,43]

$$\frac{1}{\tau} = k_{IC} \sim 10^{13}\exp(-\alpha\Delta E) \qquad (4)$$

where k_{IC} is the rate constant of IC and is given by a reciprocal of τ. α is a proportionality constant and is calculated to be 3.8 using the energy gap between naphthalene (T_2) and naphthalene (T_1) and the τ value in cyclohexane.[28] The estimated α is almost the same as the previously reported value,[32] supporting the IC between T_2 and T_1. For other naphthalenes, the ΔE values estimated using the α and τ values are listed in Table 2.

The T−T absorption of naphthalene (T_1) has been assigned to the $T_1 \rightarrow T_{10}$ transition.[29,32,44] However, the contribution of the T_n ($n = 3-10$) seems to be small because the IC ($T_{10} \rightarrow T_2$) is too fast for the bimolecular reaction due to a quite small energy gap for T_n ($n = 2-10$).[29] Additionally, in the present

TABLE 2: Lifetimes of Np(T_n) (τ), Energies of the Lowest and Higher Triplet Excited States (E(T_1) and E(T_2)), and Energy Gaps between the Lowest and Higher Triplet Excited States (ΔE)

	τ (ps)	E(T_1) (eV)	E(T_2) (eV)	ΔE (eV)
1-cyanonaphthalene	0.98 ± 0.53	2.52[a]	3.1	0.6
1-naphthaleneacetonitrile	14 ± 1.2	2.61[b]	3.9	1.3
naphthalene	9.4 ± 2.0	2.64[a]	3.8	1.2
1-methylnaphthalene	9.5 ± 0.77	2.63[a]	3.9	1.3
1-ethylnaphthalene	18 ± 4.3	2.59[a]	4.0	1.4
1-isopropylnaphthalene	45 ± 2.7	2.58[b]	4.2	1.6
1-methoxynaphthalene	61 ± 8.6	2.65[a]	4.3	1.7
2-naphthaleneacetonitrile	16 ± 4.8	2.60[b]	3.9	1.3
2-methylnaphthalene	34 ± 6.5	2.62[a]	4.2	1.6
2-ethylnaphthalene	36 ± 9.2	2.62[a]	4.2	1.6
2-isopropylnaphthalene	48 ± 10	2.58[b]	4.2	1.6
2-methoxynaphthalene	63 ± 13	2.62[a]	4.3	1.7

[a] References 33 and 42. [b] Calculated from the phosphorescence spectra.

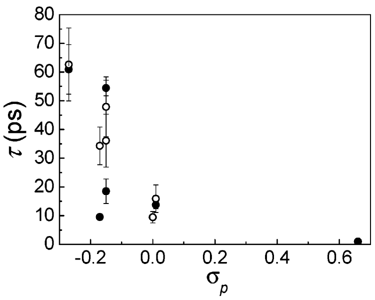


Figure 6. Plots of τ of 1-substituted naphthalene (●) and 2-substituted naphthalene (○) vs Hammett constant σ_p in cyclohexane.

experimental condition, an interaction between Np and CCl_4 in the ground state can be ignored. Therefore, ENT is expected to proceed mainly from Np(T_2) with the longest lifetime among T_n ($n = 2-10$).[29,32,43] The ENT processes from the T_2 state have been also reported for a series of aromatic hydrocarbons in the T_n state.[14-16,18-21,23,32]

4.4. Substituent Effects on τ of Np(T_2). In the case of methyl- and chloro-substituted anthracenes (T_2), the τ values depend more significantly on the position of substitution than on the electronic properties of the substituents.[32] In the present case, the τ values of 2-methyl- and 2-ethylnaphthalenes (T_2) are 3.9 and 2.5 times larger than those of 1-methyl- and 1-ethylnaphthalenes (T_2), respectively. Differences in the τ values of the other Np(T_2) are small.

It is indicated that an electron-donating substituent increases the τ value while an electron-withdrawing substituent decreases it. The τ values of Np in cyclohexane increase in the order of $OCH_3 > CH_2CH_3 > CH_3 > H = CH_2CN > CN$. This is the same order as the Hammett constant σ_p.[33] As shown in Figure 6, the τ values of 1- and 2-substituted naphthalenes decreased with increasing σ_p.

It seems that the τ values of Np(T_2) depend significantly on the electronic property of the substituent. The τ value has a close relation with the energy gap (ΔE) as indicated by eq 4. As shown in Figure 7, the E(T_1) values of Np are almost constant. In contrast, E(T_2) values depend on σ_p significantly. The T_2 state (B_{2u}) consists mainly of two-electronic configurations, namely HOMO $-$ 1 → LUMO and HOMO → LUMO $+$ 1.[29,34] The electron-withdrawing group is expected to reduce the antibonding character of the LUMO $+$ 1, reducing E(T_2) as evidenced in Figure 7. Therefore, the substitution of the electron-withdrawing group seems to decrease ΔE, leading to shorter τ.

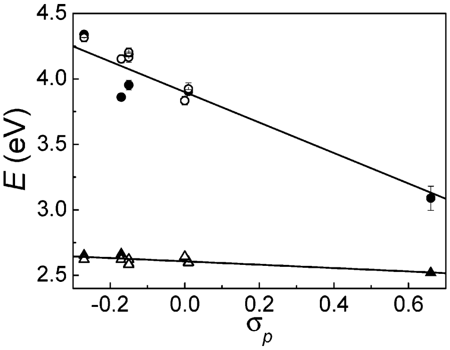


Figure 7. Plots of E(T_1) (▲) and E(T_2) (●) of 1-substituted naphthalene and E(T_1) (△) and E(T_2) (○) of 2-substituted naphthalene vs Hammett constant σ_p in cyclohexane.

5. Conclusions

We determined τ values of substituted Np in the T_2 state using two-color two-laser flash photolysis. Effects of the substituents on the τ values of Np(T_2) were systematically studied. It is found that the electronic characters of the substituents influence more significantly the Np(T_2) state than the Np(T_1) state. The τ values of 1- and 2-substituted Np(T_2) showed Hammett type correlation with the σ_p value.

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