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# Naphthoylnaphthvalene → naphthoylnaphthalene valence isomerization via an intermediate generated form the lowest excited singlet state

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## Abstract

At room temperature, sub-picosecond laser photolysis of naphthoylnaphthvalene (NNV) and naphthoylnaphthalene (NN) reveals that their lowest excited singlet states ($^1$NNV* and $^1$NN*, respectively) have an identical lifetime (0.7 ps). In comparison with the results obtained by nanosecond laser photolysis and steady-state photolysis of NNV (cf. Nakayama et al., Chem. Phys. Lett. 266 (1997) 601), however, it is concluded that the decay channels of $^1$NNV* are intersystem crossing to the lowest excited triplet state and valence isomerization yielding ground-state NN; of course, the decay channel of $^1$NN* is only intersystem crossing to the lowest excited triplet state. Interestingly, steady-state photolysis of NNV at 77 K and then measurements of the absorption and fluorescence spectra really indicate the existence of an intermediate (P-77) for $^1$NNV* → NN valence isomerization. Although no clear solvent effects on the absorption and fluorescence spectra of P-77 are observed, it is proposed that P-77 is either a bond-cloven species or a valence isomer of NNV generated from $^1$NNV*. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Naphthoylnaphthvalene; Laser photolysis; Steady-state photolysis

## 1. Introduction

In the context of the recent importance of photo-responsiveness of molecules in the wide range of molecular devices, we are studying the photophysics and photochemistry of polycyclic aromatic compounds which undergo photoinduced valence isomerization yielding the Dewar-type [1–4] or valence-type [4–6] isomers. Our findings are as follows: (a) the reactant absorptions can be extended up to 550 nm; (b) both the reactants and products are kinetically stable, and no by-products are formed by the forward and backward photoreactions.

Owing to the large strain energy and the peculiar *sp*$^9$ hybridization in the bicyclobutane moiety [7], the photochemistry of valence-type compounds is also of great interest and Turro et al. [8] reported that the lowest excited singlet state of naphthvalene underwent valence isomerization forming the lowest excited triplet state of naphthalene. Neither population of the lowest excited triplet state of the original compound (naphthvalene) nor formation of the lowest excited singlet state of the photoproduct (naphthalene) was observed. By a choice of appropriate triplet sensitizers, however, Renner et al. [9] reported that not the lowest excited singlet state but the second excited triplet state of benzvalene underwent valence isomerization forming the lowest excited triplet state of benzene which is again capable of sensitizing valence isomerization of another benzvalene molecule.

Generally, intersystem crossing from the lowest excited singlet to triplet states of aromatic carbonyl compounds is very rapid. And, the results reported by Turro et al. [8] and Renner et al. [9] intrigued us with a view of finding out which of the lowest excited singlet and triplet states of valence-type aromatic carbonyl compounds could undergo valence isomerization as well as whether the electronically excited products were formed or not. From these viewpoints, we performed nanosecond laser photolysis and steady-state photolysis of naphthoylnaphthvalene (NNV) with the naphthoyl group at a bridgehead carbon atom of the naphthvalene moiety [10]. At room temperature in benzene, the results obtained were as follows: (a) nanosecond pulse excitation of NNV revealed no population of the lowest excited triplet state ($^3$NN*) of NN, i.e. only the triplet–triplet ($T' \leftarrow T_1$) absorption spectrum due to the lowest excited triplet state ($^3$NNV*) of NNV could be seen and $^3$NNV* was quenched by dissolved oxygen (1–3 mM) with a rate constant of (3.1–1.0) × $10^9$ $M^{-1}$ $s^{-1}$; (b) steady-state photolysis

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of NNV revealed no effect of oxygen on the rate of formation of NN from NNV.

All the results stated above indicate that the lowest excited singlet state ($^1NNV^*$) of NNV undergoes valence isomerization yielding ground-state NN finally. As an extension of our studies on the excited-state dynamics of sterically strained aromatic carbonyl compounds [2,3,11–17], therefore, the present paper deals with the decay channels of $^1NNV^*$ compared with that of the lowest excited singlet state ($^1NN^*$) of NN. On the basis of the results obtained by steady-state photolysis of NN at 77 K in EPA (diethyl ether : isopentane : ethanol = 5 : 5 : 2 in volume ratio), furthermore, we proposed the existence of an ionic intermediate for $^1NNV^* \rightarrow NN$ valence isomerization [18]. Hence, the solvent effects on the absorption and phosphorescence spectra of this intermediate are also examined.

## 2. Experimental details

By the treatment of naphthvalene (prepared following the method of Katz et al. [19]) with *n*-butyllithium in the presence of *N*, *N*, *N′*, *N′*-tetramethylethylenediamine, a lithionaphthvalene (with a lithiated bridgehead carbon atom) was obtained at first and then its reaction with 2-naphthaldehyde followed by $CrO_3$/pyridine oxidation yielded NNV. NN was synthesized by the reaction of 2-naphthyllithium with 2-naphthaldehyde yielding dinaphthylcarbinol followed by successive Jones oxidation. Crude NNV and NN thus obtained were recrystallized from diisopropyl ether and ethanol, respectively. The solvents used were benzene, ethanol, 2-MP (2-methylpentane), 3-MP (3-methylpentane), MTHF (2-methyl-tetrahydrofuran), EPA and ME (methanol : ethanol = 1 : 1 in volume ratio). Although spectral-grade benzene (Dojin) and Uvasol diethyl ether (Merck) were used without further purification, GR-grade 2-MP, 3-MP and isopentane from Wako were purified by passing them through an alumina column. Spectral-grade methanol (Dojin) and ethanol (Nacalai) were dried using a molecular sieve 3A (Wako) preheated in a crucible over Bunsen burner and cooled in vacuo. Under a nitrogen atmosphere, GR-grade MTHF (Wako) was refluxed in the presence of calcium hydride and then distilled. The sample solutions used for sub-picosecond laser photolysis in a flow cell of 2 mm path length were deoxygenated by bubbling of Ar gas, while those used for steady-state photolysis in a cell of 10 mm path length were degassed by several freeze–pump–thaw cycles.

Sub-picosecond laser photolysis was performed by a pump-probe method using a laser photolysis system comprising a femtosecond mode-locked Ti : sapphire oscillator (Tsunami, model 3960) and a regenerative amplifier (model TSA-50) from Spectra-Physics [20]; both intensities of the excitation light pulse (the 267-nm third harmonic) and the probing light pulse (the white-light continuum generated by focusing the 800-nm fundamental into water) were approximated by a Gaussian function with a full width at the half-maximum intensity (FWHM) of 0.25 ps.

Steady-state photolysis was carried out using the 313-nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp, and the absorption and phosphorescence spectra were recorded using a Hitachi 200-20 spectrophotometer and a Hitachi MPF-4 spectrophosphorimeter, respectively; measuring the intensity changes of reactant and product absorptions with time, the quantum yields for formation of NN from NNV in benzene and ethanol were determined by the Hatchard–Parker potassium ferrioxalate actinometry method [21].

## 3. Results

The transient absorption spectra shown in Fig. 1 are obtained by sub-picosecond laser photolysis of NNV and NN at room temperature in ethanol. For both NNV and NN, Fig. 2 indicates that the buildup of transient absorption with time (closed or open circles monitored at 440 nm) can well be reproduced by a single-exponential function (the solid curve) with a time constant of $\tau_R = 0.7$ ps. Since the dotted lines in Fig. 1 are the normalized $T' \leftarrow T_1$ absorption spectra due to $^3NNV^*$ and $^3NN^*$ obtained by nanosecond laser photolysis at 77 K in EPA [10], it can be concluded that the buildup time of $T' \leftarrow T_1$ absorption originating from $^3NNV^*$ is equal to that originating from $^3NN^*$.[1]

In the previous paper [18], we reported that steady-state photolysis of NNV at 77 K in EPA caused a reaction different from NNV → NN valence isomerization observed at room temperature in ethanol and benzene [10]; after steady-state photolysis of NNV at 77 K in EPA, elevation of temperature up to room temperature followed by re-cooling down to 77 K gave rise to the appearance of the absorption spectrum due to NN. By nanosecond laser photolysis of the photoproduct (P-77) formed at 77 K in EPA, furthermore, the transient absorption spectrum thus obtained was found to be somewhat different from the $T' \leftarrow T_1$ absorption spectrum due to $^3NN^*$ but rather similar to that due to $^3NNV^*$; the lifetime of transient absorption obtained for P-77 was equal to its phosphorescence lifetime, i.e. 0.57 s which was shorter than the lifetime (1.0 s) of $^3NNV^*$ or $^3NN^*$ [10].

In the present study, measurements of the $T' \leftarrow T_1$ absorption spectra by nanosecond laser photolysis of P-77 at 77 K in ME and MTHF are impossible owing to the crack of sample solutions but the corresponding phosphorescence lifetimes are found to be 0.49 and 0.80 s, respectively. As shown by the solid lines in Fig. 3(a) and (b), steady-state photolysis of NNV at 77 K in ME and MTHF causes the

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[1] Taking into account of the spectral overlap due to the absorptions of NNV and NN, the quantum yield for NNV → NN valence isomerization is determined to be 0.25–0.30 in both benzene and ethanol. Hence, the identical lifetime obtained for $^1NNV^*$ and $^1NN^*$ is reasonable.

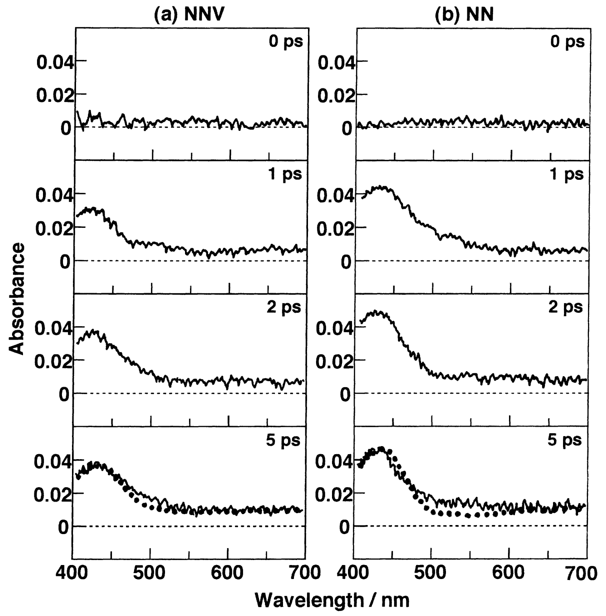


Fig. 1. Transient absorption spectra obtained by sub-picosecond laser photolysis of NNV and NN at room temperature in ethanol. The dotted lines are the normalized $T' \leftarrow T_1$ absorption spectra due to $^{3}\mathrm{NNV}^{*}$ and $^{3}\mathrm{NN}^{*}$ obtained by nanosecond laser photolysis at 77 K in EPA [10].

absorption spectral change similar to that observed in EPA [18]. In accordance with this, we have obtained the following results: (1) As shown in Fig. 4(a), steady-state photolysis of NNV at room temperature in EPA and then measurements of the phosphorescence spectra at 77 K reveal that the solid and dashed spectra thus obtained are clearly different from the phosphorescence spectrum (the dotted line) due to $^{3}\mathrm{NNV}^{*}$ [10]. Since the dashed spectrum is identical with the phosphorescence spectrum due to $^{3}\mathrm{NN}^{*}$ [10], it can again be concluded that steady-state photolysis of NNV at room temperature really yields NN. (2) As shown in Fig. 4(b)–(c), steady-state photolysis of NNV and then measurements of the phosphorescence spectra both at 77 K in ME and MTHF reveal that the solid spectra thus obtained are clearly different from the phosphorescence spectra due to $^{3}\mathrm{NNV}^{*}$ and $^{3}\mathrm{NN}^{*}$. After then, elevation of temperature up to room temperature followed by re-cooling down to 77 K changes the solid spectra to the dashed spectra which are again identical with the phosphorescence spectrum due to $^{3}\mathrm{NN}^{*}$; the identical results were obtained in EPA [18]. (3) Fig. 4(b′)–(c′) indicate that the phosphorescence excitation spectra (the dashed-dotted lines) obtained for P-77 at 77 K

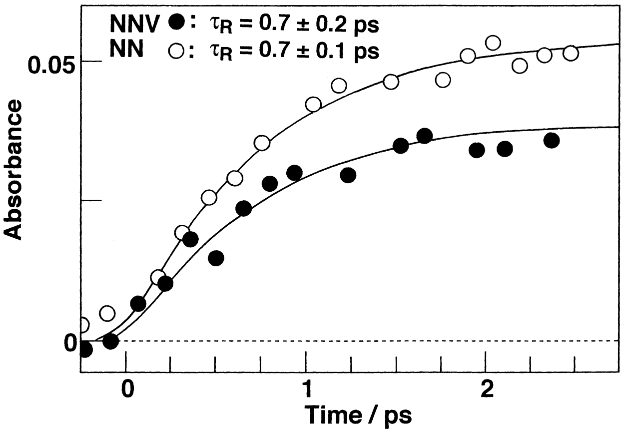


Fig. 2. Buildup of the transient absorptions with time (monitored at 440 nm) obtained by sub-picosecond laser photolysis of NNV (●) and NN (○) at room temperature in ethanol. The smooth curves are the best-fit single-exponential functions with a build-up time of $\tau_R = 0.7$ ps.

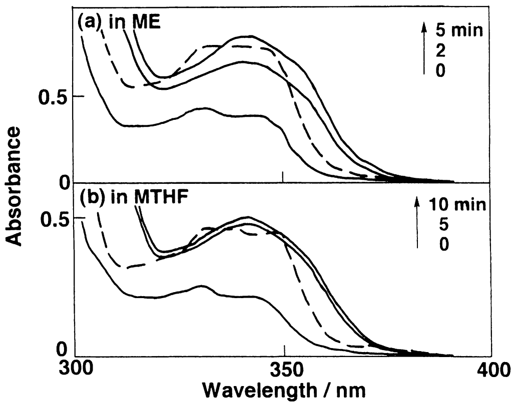


Fig. 3. Absorption spectral changes caused by steady-state photolysis of NNV at 77 K in ME and MTHF (———). The dashed absorption spectra are obtained by elevation of temperature up to room temperature (after photolysis) followed by re-cooling down to 77 K.

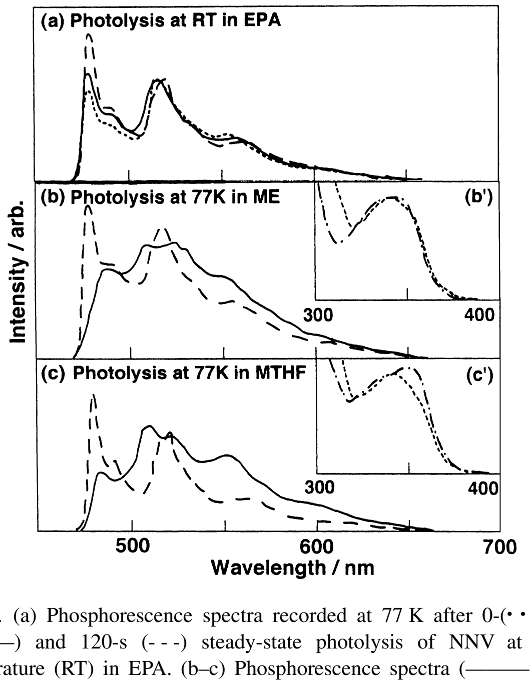


Fig. 4. (a) Phosphorescence spectra recorded at 77 K after 0-(• • •), 4-(———) and 120-s (- - -) steady-state photolysis of NNV at room temperature (RT) in EPA. (b–c) Phosphorescence spectra (———), and (b′–c′) absorption (• • •) and phosphorescence excitation (– • –) spectra recorded at 77 K after steady-state photolysis of NNV at 77 K in ME and MTHF, where photolysis times are 1 and 30 min, respectively. After photolysis at 77 K, elevation of temperature up to room temperature followed by re-cooling down to 77 K gives rise to the appearance of dashed phosphorescence spectra.

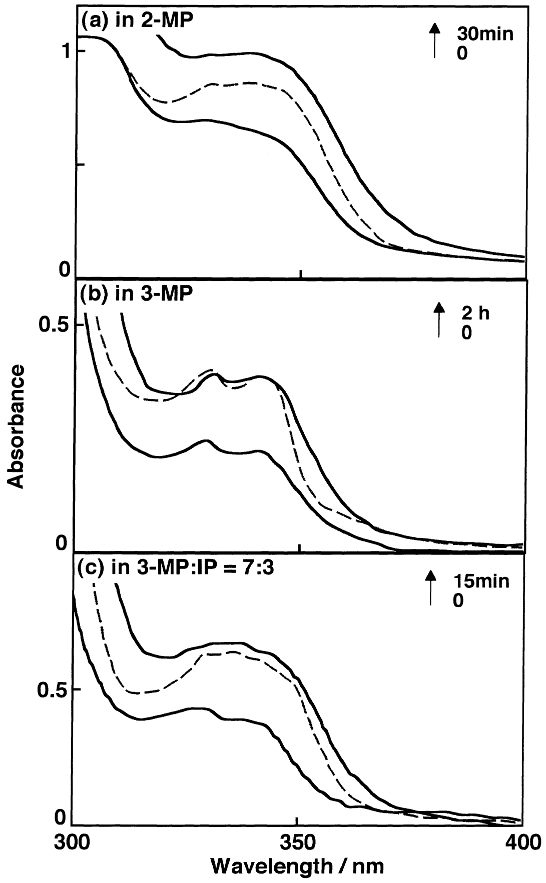


Fig. 5. Absorption spectral changes caused by steady-state photolysis of NNV at 77 K in 2-MP, 3-MP and a 3-MP/IP mixed solvent (———). The dashed absorption spectra are obtained by elevation of temperature up to room temperature (after photolysis) followed by re-cooling down to 77 K.

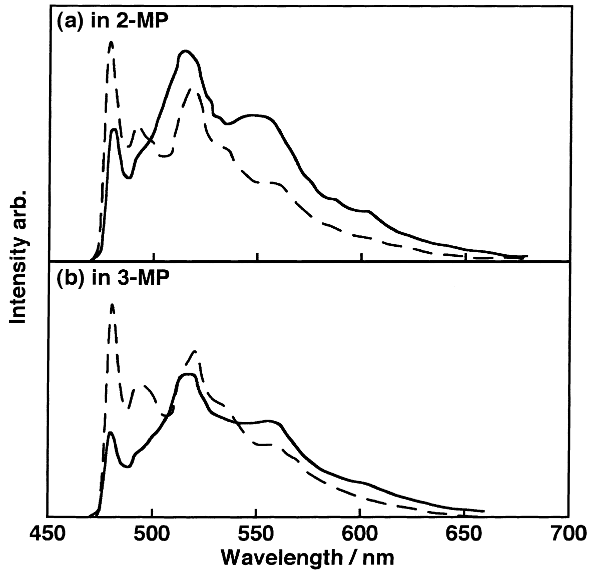


Fig. 6. Phosphorescence spectra (———) recorded at 77 K after steady-state photolysis of NNV at 77 K in 2-MP and 3-MP, where photolysis times are 1 and 2 h, respectively. After photolysis at 77 K, elevation of temperature up to room temperature followed by re-cooling down to 77 K gives rise to the appearance of dashed phosphorescence spectra.

are consistent with the corresponding absorption spectra (the dotted lines).

Fig. 5 shows the absorption spectral changes (the solid lines) caused by steady-state photolysis of NNV at 77 K in 2-MP, 3-MP and a mixed solvent of 3-MP and isopentane (IP) in 7 : 3 volume ratio. Although the spectral change in 3-MP is very slow compared with that in 2-MP, addition of IP to 3-MP accelerates the absorption spectral change. As shown in Fig. 6, however, the phosphorescence spectra obtained in 2-MP and 3-MP are somewhat different from those obtained in ME and MTHF (cf. Fig. 4). In comparison with the phosphorescence spectra shown in Fig. 4(a), it is clear that P-77 (major) and NN (minor) are formed in 2-MP, but NN (major) and P-77 (minor) are formed in 3-MP. Since this solvent is a well-known soft solvent even at 77 K, addition of 30 vol% IP to 3-MP may suppress the P-77 → NN conversion.

## 4. Discussion

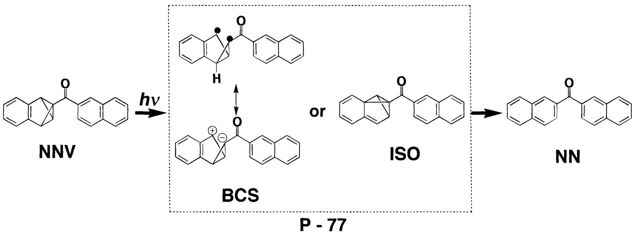
Upon excitation of naphthvalene at 77 K in methylcyclohexane, Turro et al. [8] observed only the phosphorescence originating from the lowest excited triplet state of naphthalene. On the basis of this fact, as stated previously, they concluded that the lowest excited singlet state of naphthvalene underwent valence isomerization forming the lowest excited triplet state of naphthalene. Formation of $^1$NN$^*$ and/or $^3$NN$^*$ from $^1$NNV$^*$ (or conversion of $^3$NNV$^*$ to $^3$NN$^*$) upon excitation of NNV, however, can be ruled out on the basis of the following results obtained previously [10]: (i) Excitation of NNV at 77 K in EPA gave rise to the appearance of phosphorescence and $T' \leftarrow T_1$ absorption spectra only due to $^3$NNV$^*$, i.e. neither phosphorescence nor $T' \leftarrow T_1$ absorption spectrum reflecting the superposition of phosphorescences (or $T' \leftarrow T_1$ absorptions) originating from both $^3$NNV$^*$ and $^3$NN$^*$ could be seen; although steady-state photolysis of NNV at room temperature and then measurements of phosphorescence spectra at 77 K in EPA revealed the change of phosphorescence spectra with the photolysis time, this could be interpreted in terms of independent excitation of the original compound (NNV) and the photoproduct (NN) resulting in the superposition of phosphorescences originating from both $^3$NNV$^*$ and $^3$NN$^*$. (ii) Nanosecond laser photolysis of NNV at room temperature in benzene revealed no population of $^3$NN$^*$, i.e. only the $T' \leftarrow T_1$ absorption spectrum due to $^3$NNV$^*$ could be seen.

For aromatic carbonyl compounds, it is well known that internal conversion from the lowest excited singlet state to the ground state is negligible compared with intersystem crossing from the lowest excited singlet to triplet states. We thus believe that $^1$NNV$^*$ undergoes valence isomerization yielding ground-state NN, i.e. valence isomerization of ground-state but vibrationally activated NNV can be ruled out. Formation of P-77 upon steady-state photolysis of NNV at 77 K is observed not only in alcohol or ether solvents (EPA, ME and MTHF) but also in hydrocarbon solvents (2-MP, 3-MP and a 3-MP/IP mixed solvent). This indicates that P-77 is different from the ketyl radicals of NNV and NN which are generated by hydrogen-atom abstraction of $^3$NNV$^*$ from ethanol at room temperature [10]. Hence, P-77 may be an intermediate for $^1$NNV$^* \rightarrow$ NN valence isomerization.

Many thermal reactions of the valene-type compounds in solutions are well known. For examples, Turro et al. [22] observed quantitative formation of benzene from benzvalene, and Bryce-Smith and Longuet-Higgins [23] postulated bicyclo[3.1.0]hex-2-en-4,6-diyl biradical as an intermediate for benzene → fulvene valence isomerization. Hence, formation of benzofulvene from naphthvalene might be interpreted in terms of the stepwise scission of C–C bonds in the bicyclobutane skeleton, i.e. generation of 2,3-benzo-bicyclo[3.1.0]hexen-4,6-diyl biradical and then indenyl carbene followed by migration of the benzylic hydrogen atom to the carbene center. For naphthvalene, however, formation of benzofulvene in the liquid phase was reported by Katz et al. [24], but Kjell and Sheridan [25] observed formation of naphthalene in the gas phase and proposed that benzofulvene was formed by an unknown catalyzed process in the liquid phase. Formation of a benzofulvene-type compound upon heating of NNV in the liquid phase observed by us can thus be ascribed to a catalyzed process similar to that proposed by Kjell and Sheridan [25].

On the basis of the conjecture stated above, the previous proposal that a biradical of NNV is the intermediate for thermal formation of a benzofulvene-type compound [18] is incorrect. Hence, a plausible candidate fot P-77 may be a bond-cloven species (BCS) shown in Scheme 1, i.e. observation of this species at 77 K can be ascribed to the stabilization of two radicals (and/or positive and negative charges) owing to their delocalization over the benzene ring and the naphthoyl group, respectively. However, no solvent effects on the absorption and phosphorescence spectra of P-77 can be observable. Also, no explanation can be given to the solvent effect on the phosphorescence lifetime obtained for P-77, i.e. the phosphorescence lifetimes in MTHF, EPA and ME are 0.80, 0.57 and 0.49 s, respectively, but that in methylcyclohexane is 0.34 s. If P-77 is really BCS, therefore, its major character may be of a biradical type.

As stated previously, the phosphorescence and transient absorption spectra obtained for P-77 are rather similar to those obtained for NNV. Furthermore, Renner et al. [9] proposed [1,3]-sigmatropic rearrangement in order to interpret the photochemical deuterium scrambling observed for a deuterium labeled benzvalene. Although it seems to be much less plausible, an alternative candidate for P-77 may be a valence isomer (ISO) of NNV also shown in Scheme 1, i.e. 8-naphthoyltetracyclo[4.4.0.0$^{1,9}$.0$^{8,10}$]deca-2,4,6-triene formed by [1,3]-sigmatropic rearrangement. In the case of [1,3]-sigmatropic rearrangement of benzvalene stated above, however, the photoproduct is also benzvalene itself, and Turro et al. [22] and Dewar and Kirschner [26] reported a small activation enthalpy (25.9 or 21.5 kcal/mol, respectively) for thermal benzvalene → benzene valence isomerization. In contrast, owing to the loss of the benzene structure for the valence isomer (ISO) of NNV, the structural strain of ISO is expected to be much greater than that of NNV. Hence, conversion of P-77 to NN at a higher temperature than 77 K might be reasonable.



Scheme 1.

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