

Intramolecular dimer radical cations of α,ω -di(2-naphthyl)alkanes in solutions studied by near-IR transient absorption spectroscopy

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Abstract

Formation of intramolecular dimer radical cations in a series of α,ω -di(2-naphthyl)alkanes (DN n , where n is the number of carbon atoms in the methylene chain) in solutions was investigated by near-IR transient absorption spectroscopy, which enables one to quantitatively evaluate the equilibrium constant (K) for the formation of the intramolecular dimer radical cations and stabilization energy (E_{CR}) due to charge delocalization. The dependence of K on n corresponds to the probability of ring closure in a *syn* fashion where the chain attaches at the same side of the two naphthalene (Np) moieties. The dependence of E_{CR} on n is similar to that of K except at $n = 3$. For DN n with a shorter chain, the mutual configuration of the two Np moieties cannot be optimal because the ring closure itself is difficult owing to the restriction by the short chain. For DN n with a longer chain, the two Np moieties are in a more stable configuration because of the loose restriction of the long chain. The small value of E_{CR} at $n = 3$ indicates that the optimal configuration for the dimer radical cation of Np is not a sandwich-like one, but a distorted one.

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1. Introduction

Bichromophoric compounds are favorable systems for investigation of interactions between two chromophores [1–14]. Especially, bichromophoric compounds, in which two chromophores attach at both ends of an alkane chain, are useful for investigation of dimer formation [4–14]. Since the reaction is closely related to ring-closure probability [15] and molecular motion of the chain, its efficiency and kinetics are indicative of chain conformation and dynamics in solutions [5–14]. For example, it is known that formation yields of excimers [7–11], exciplexes [12] and photochemical cyclic adducts [13] of bichromophoric compounds are largely affected by the number of carbon atoms (n) in the chain. Hirayama reported for the first time that intramolecular excimers of diphenyl and triphenyl alkanes can be formed only in compounds in which two phenyl groups are separated by three carbon atoms ($n = 3$ rule) along the main alkane chains [7]. Previously, we also reported that an intramolecular excimer of α,ω -di(2-naphthyl)alkanes (DN n , $n = 3$ –12) is observed only for $n = 3$ sample [9].

On the other hand, Zachariasse and co-workers performed detailed experiments using dipyranyl alkanes and found that intramolecular excimers are formed in a wide range of n , although the yields are remarkably dependent on n [10,11]. Many works have been reported so far using a variety of chains besides alkane chains [11] and different detection methods [4,7,13,14]. These researches showed that intramolecular reactions are governed by static and dynamic characters of the chain molecules examined. At the same time, the quantitative studies on characters of the reactions provide invaluable information on the characters of the chain. However, as seen in the examples of naphthyl [9] and pyrenyl [10,11] alkanes, the results are also affected by the kinds of chromophoric unit used in the experiments, probably due to the interaction energy between two units [9].

On the contrary, there have been no systematic studies for dimer radical cations [14,16] in a series of bichromophoric compounds with various chain lengths n , probably due to difficulty of spectroscopic evaluation for an amount of a dimer radical cations especially when the ratio of a dimer radical cations to a monomer radical cations is low. Absorption of monomer radical cations overlaps that of dimer radical cations in a UV-Vis region, which is covered by conventional transient absorption spectroscopy. We have overcome

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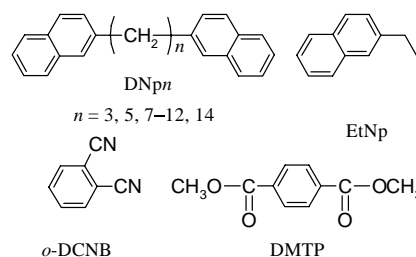
this problem by near-IR transient absorption spectroscopy [14], a powerful tool for evaluation of dimer radical cations. This method allows one to quantitatively evaluate not only stabilization energy due to charge delocalization between two chromophores [16] (charge resonance (CR) stabilization) but also an amount of a dimer radical cation as well as that of a monomer radical cation. Since there is no other absorption in the near-IR region except for charge resonance bands, which originate from the charge delocalization, an amount of a dimer radical cations can be quantitatively evaluated even if the formation ratio of a dimer radical cations is low.

Here, we investigated the intramolecular dimer radical cations in a series of DN n in solutions by near-IR transient absorption spectroscopy. We discuss quantitatively for the first time the dependence of the equilibrium constant for the formation of the intramolecular dimer radical cations of naphthalene (Np) on the chain length n as well as the dependence of stability due to the CR stabilization on the chain length n .

2. Experimental

2.1. Materials

A series of DN n ($n = 3, 5, 7-12, 14$) was synthesized from Wolff–Kishner reduction of the corresponding ketones. The ketones were prepared as follows. For DNp3, 1,3-di(2-naphthyl)propan-1-one was prepared by the hydrogenation of the product obtained from the condensation of 2-naphthaldehyde and 2-acetonaphthone in an alkaline ethanol solution [8]. For DNp5, 1,5-di(2-naphthyl)pentan-3-one was prepared by the hydrogenation of the product obtained from the condensation of 2-naphthaldehyde and acetone by the same method as that for DNp3. For DN n ($n = 7-12, 14$), α,ω -di(2-naphthyl)alkanes were prepared by the Grignard reactions between 2-naphthonitrile and the corresponding dibromoalkanes. Details of the synthesis of DN n have been described elsewhere [9]. A monomeric compound of 2-ethylnaphthalene (EtNp) was purchased from Tokyo Kasei Kogyo Co. and used without further purification. Electron acceptors of *o*-dicyanobenzene (*o*-DCNB) and dimethylterephthalate (DMTP) were purchased from Tokyo Kasei Kogyo Co. and from Nacalai Tesque, respectively, and used after several times of recrystallization. Acetonitrile (spectroscopic grade) was purchased from Nacalai Tesque and used without further purification. The chemical structures of the compounds used in this study are shown in Scheme 1. The solutions in 1 cm quartz cells were degassed by the freeze–pump–thaw method. The concentration of the naphthalene compounds was adjusted to be 0.3 mmol l^{-1} where intermolecular formation of dimer radical cations of Np is negligible. The concentrations of *o*-DCNB and DMTP were 0.1 and 0.01 mol l^{-1} , respectively.



Scheme 1. Chemical structures of the compounds used in this study.

2.2. Measurements

A nanosecond laser pulse (308 nm, $<10 \text{ mJ cm}^{-2}$, FWHM 17 ns) from a XeCl excimer laser (Lambda Physik EMG101MSC) was used as an excitation light source to ionize the Np compounds. A steady-state 150 W xenon lamp (Hamamatsu Photonics, L2175) was used as a monitor light source. The monitor light in the direction normal to the excitation light was passed through a monochromator (Ritsu, MC-10N) before detection. Transient absorption spectra were measured with a photomultiplier tube (Hamamatsu Photonics, R1477) for the visible region from 400 to 850 nm and with an InAs photovoltaic detector (Hamamatsu Photonics, P838) for the near-IR region from 780 to 2000 nm. Transient absorption decay at 675 and 1050 nm in a short time region was measured with a photomultiplier tube (Hamamatsu Photonics, R5188). The temperature of a sample cell settled in a quartz Dewar was controlled by precooled nitrogen gas.

3. Results and discussion

Fig. 1 shows the transient absorption spectra for radical cations of EtNp in acetonitrile solutions with 0.1 mol l^{-1} *o*-DCNB (solid line) and 0.01 mol l^{-1} DMTP (broken line), $1 \mu\text{s}$ after laser excitation. The concentration of EtNp and the temperature is as follows: (a) $[\text{EtNp}] = 0.3 \text{ mmol l}^{-1}$, at room temperature; (b) $[\text{EtNp}] = 6 \text{ mmol l}^{-1}$, at room temperature; (c) $[\text{EtNp}] = 6 \text{ mmol l}^{-1}$, at 233 K. At a low concentration of $[\text{EtNp}] = 0.3 \text{ mmol l}^{-1}$ (Fig. 1a), a sharp absorption band at 675 nm was observed. This band is ascribable to the monomer radical cation of EtNp formed by photoinduced electron transfer from an excited EtNp molecule to an *o*-DCNB molecule [14]. Rapid rise of the absorption of the monomer radical cation was observed in a few 10 ns, which corresponds to the width of the laser pulse. This rapid rise shows that the monomer radical cation is formed by the photoinduced electron transfer from the lowest singlet excited state of an EtNp molecule to an acceptor molecule, because the rate constant of intersystem crossing of 2-methylnaphthalene is reported to be as slow as ca. $4.3 \times 10^6 \text{ s}^{-1}$ [17]. At a high concentration of $[\text{EtNp}] = 6 \text{ mmol l}^{-1}$ (Fig. 1b), two broad absorption bands appeared at 590 and 1100 nm in addition to the sharp

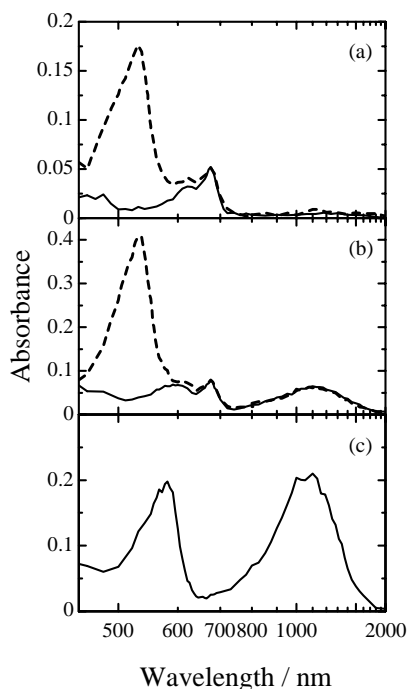


Fig. 1. Transient absorption spectra of radical cations of EtNp in acetonitrile solutions with 0.1 mol l^{-1} *o*-DCNB (solid line) and 0.01 mol l^{-1} DMTP (broken line), $1 \mu\text{s}$ after laser excitation: (a) $[\text{EtNp}] = 0.3 \text{ mmol l}^{-1}$, at room temperature; (b) $[\text{EtNp}] = 6 \text{ mmol l}^{-1}$, at room temperature; (c) $[\text{EtNp}] = 6 \text{ mmol l}^{-1}$, at 233 K.

absorption band at 675 nm. At a low temperature of 233 K, as shown in Fig. 1c, the intensity of these broad absorption bands increased whereas the sharp absorption band due to the monomer radical cation disappeared. Thus, these broad bands are ascribable to a dimer radical cation intermolecularly formed by diffusive encounters between two EtNp molecules. The absorption band at 590 nm is ascribed to the local excitation band and that at 1100 nm to the CR band of the intermolecular dimer radical cation of EtNp [14].

To discuss quantitatively the formation of the dimer radical cations, we evaluated molar absorption coefficients of the cations from transient absorption spectra of EtNp solutions with DMTP whose radical anion has an absorption peak at 530 nm with a molar absorption coefficient of $12\,300 \text{ mol}^{-1} \text{ l cm}^{-1}$ [18]. The molar absorption coefficients of the monomer radical cation and the dimer radical cation were evaluated to be $4500 \text{ mol}^{-1} \text{ l cm}^{-1}$ at 675 nm and $4400 \text{ mol}^{-1} \text{ l cm}^{-1}$ at 1100 nm, respectively, on the basis of that of DMTP. For the monomer radical cation, the molar absorption coefficient was evaluated from the transient absorption spectrum of the dilute EtNp solution (0.3 mmol l^{-1} , Fig. 1a) where the amount of the monomer radical cation of EtNp formed should be the same as that of the radical anion of DMTP. For the dimer radical cation, the molar absorption coefficient of the CR band was evaluated from the transient absorption spectrum of the concentrated EtNp solution (6 mmol l^{-1} , Fig. 1b) where the dimer radical cation is

Table 1

Peak wavelengths and molar absorption coefficients for the monomer absorption band, the CR band of EtNp radical cations and the absorption band of DMTP radical anion

	λ_{max} (nm)	ϵ ($\text{mol}^{-1} \text{ l cm}^{-1}$)
EtNp $^{\bullet+}$	675	4500
(EtNp) $_2^{\bullet+}$	1100	4400
DMTP $^{\bullet-}$	530	12300 ^a

^a Ref. [18].

formed in addition to the monomer radical cation. First, the amount of the monomer radical cation was calculated with the molar absorption coefficient previously evaluated and the absorbance at 675 nm where the dimer radical cation has little absorption as shown in the transient absorption spectrum at 233 K (Fig. 1c). Next, the amount of the dimer radical cation was evaluated from the difference in the amounts of the monomer radical cation and the DMTP radical anion of DMTP. The molar absorption coefficients thus obtained are summarized in Table 1.

3.1. Dependence of the formation of the intramolecular dimer radical cation on the chain length

Here, we discuss the dependence of the formation of the intramolecular Np dimer radical cations of DNp $_n$ on the chain length. Fig. 2 shows transient absorption spectra for a series of DNp $_n$, $1 \mu\text{s}$ after laser excitation at room temperature. In all the spectra, a broad absorption band ascribed to the CR band was observed in the near-IR region. These spectra show that the dimer radical cations of Np can be intramolecularly formed in all DNp $_n$ molecules in contrast to the intramolecular Np excimer, which can be formed only for DNp3. The intramolecular pyrene excimer is also formed for dipyrenyl alkanes with a longer methylene chain. The excited state of pyrene monomer has a longer lifetime of 300 ns and its excimer has larger stabilization energy of ca. 40 kJ mol^{-1} than those of Np [9]. The monomer radical cation of Np had a lifetime as long as a few microseconds and, as mentioned later, the intramolecular dimer radical cations of Np had CR stabilization energy as large as ca. 50 kJ mol^{-1} . These properties are why intramolecular dimer radical cations were observed for all DNp $_n$ molecules. In addition to the CR band, the monomer band at 675 nm was also observed except for DNp3. Both bands decayed with the ratio maintained over a time range of our measurement from 1 to $9 \mu\text{s}$ after excitation.

Fig. 3 shows the time evolution of the ratio of the absorbance at 1050 nm to that at 675 nm, for DNp7 at 273 K. There are two characteristic time domains in the time evolution. In the first domain from laser excitation to $1 \mu\text{s}$, the ratio increased, indicating that the intramolecular dimer radical cation of DNp7 is dynamically formed after excitation. In the second domain after $1 \mu\text{s}$ from laser excitation, on the other

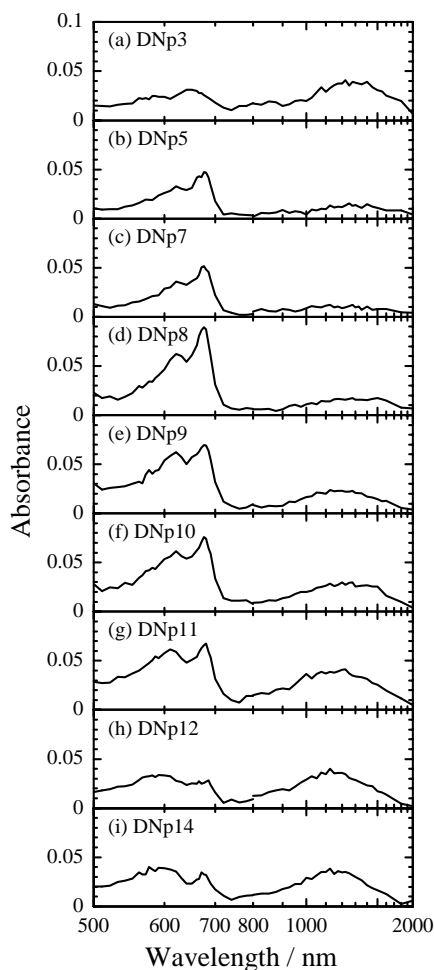


Fig. 2. Transient absorption spectra for radical cations of DNpn in acetonitrile solutions with 0.1 mol l^{-1} *o*-DCNB, $1 \mu\text{s}$ after laser excitation at room temperature. The chain length n is 3, 5, 7–9, 10–12 and 14 in order from (a) to (i).

hand, the ratio was constant, which shows that the monomer and the dimer radical cations of DNp7 reach equilibrium, $1 \mu\text{s}$ after excitation. A similar tendency was observed for the other DNpn. Therefore, the equilibrium constant K ($=[\text{D}^+]/[\text{M}^+]$) for each DNpn used in this study can be obtained from the saturated ratio, $1 \mu\text{s}$ after the excitation. We will discuss later the dependence of K on the chain length n .

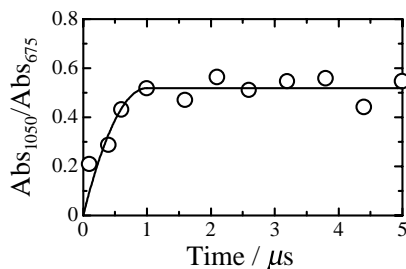


Fig. 3. Time evolution of the ratio of the absorbance at 1050 nm to that at 675 nm, for DNp7 at 273 K.

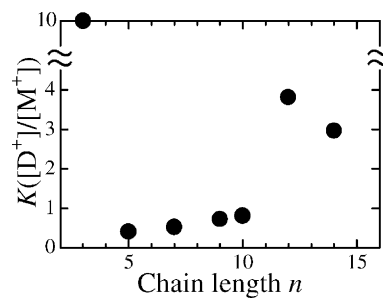


Fig. 4. Dependence of K at 273 K on the chain length n .

Fig. 4 shows the dependence of K at 273 K on the chain length n . For DNp3, the K was estimated to be larger than 10 because no absorption of the monomer radical cation was observed at 675 nm. K was largest at $n = 3$, which is consistent with the Hirayama rule [7], and rapidly decreased to less than unity in a region of $n = 5$ –10, above which it increased, showed a maximum at $n = 12$, and then decreased again at $n = 14$. This chain-length dependence of K qualitatively corresponds to the ring-closure probability of polymethylene chains calculated by Sisido [15], provided that our result is shifted toward higher n by three. The shift toward higher n by three was also reported in the dependence of formation of intramolecular pyrene excimers on the chain length between two pyrene moieties [10,11]. Zachariasse and co-workers explained that two pyrenyl moieties in a sandwich-like configuration, which is generally accepted to be an optimal configuration for excimer interaction, are considered as three methylene groups forming a half part of a cyclohexane ring in the chair conformation [10,11]. This explanation can be also applied to dimer radical cations, because the sandwich-like configuration is considered to be one of optimal configurations for dimer radical cations as well as excimers. Therefore, it is safe to say that the K between the monomer radical cation and the dimer radical cations formed in DNpn depends on the ring-closure probability of the chain.

There are two types of ring closure, i.e., the terminal bonds from the end groups to the chain are in the same direction (*syn*-type) or in the opposite direction (*anti*-type). Generally, *anti*-type ring closure reactions require longer chains compared with *syn*-type reactions. The shift toward higher n by three implies *syn*-type of ring closure. Nishijima and co-workers reported the dependence of a photochemical reaction yield of *anti*-type ring closure on the chain length n [13]. They found that the reaction yield had a maximum at $n = 18$ whereas the yield was very low in a range of $n = 2$ –12. The maximum for the intramolecular formation of the dimer radical cations in the series of DNpn appeared at a shorter chain length of $n = 12$ compared with the *anti*-type. Therefore, we conclude that the dimer radical cations of DNpn are formed in a *syn* fashion where the chain attaches at the same side of the two Np moieties.

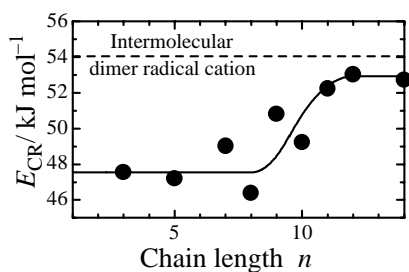


Fig. 5. Dependence of E_{CR} on the chain length n .

3.2. Dependence of the charge resonance stabilization on the chain length

Here, we discuss the CR stabilization energy E_{CR} of the dimer radical cations, which was directly evaluated from the absorption spectra in Fig. 2 as half of the energy required for the CR transition. Fig. 5 shows the dependence of E_{CR} on the chain length n . The horizontal broken line at 54 kJ mol^{-1} shows the E_{CR} for the intermolecular dimer radical cation of EtNp. E_{CR} was almost constant in a region of $n = 3$ –8, gradually increased around $n = 9$, and saturated above $n = 12$, i.e., came close to that for the intermolecular dimer radical cation of EtNp. Except for $n = 3$, the dependence of E_{CR} on the chain length n was similar to that of K . This is because E_{CR} is affected by mutual configurations of two aromatic moieties, which are restricted by a chain linking the two moieties. This dependence can be explained in terms of degree of freedom between two Np moieties. For EtNp without the chain, the mutual configuration of the two Np moieties should be optimal because there is no restriction due to the chain. Thus, the intermolecular dimer radical cation is most stable and has the largest E_{CR} . Badgar and Brocklehurst proposed a distorted dimer radical cation of Np where a displacement of the two Np rings minimizes the inter-ring π -electron repulsion [19]. For DNp3, this optimal displacement for the stabilization is inhibited by the shortest propane chain. This is why E_{CR} is small for DNp3 in spite of the largest K . For DNpn with a shorter methylene chain ($n = 3$ –8), the mutual configuration of the two Np moieties cannot be optimal because the ring closure itself is difficult owing to the restriction by the short chain. For DNpn with a longer methylene chain ($n > 9$), the two Np moieties are in a more stable configuration because of the loose restriction of the chain.

4. Conclusions

The equilibrium constant K for the formation as well as the CR stabilization energy of the intramolecular dimer radical cations in a series of α,ω -di(2-naphthyl)alkanes in acetonitrile solutions were quantitatively investigated with transient absorption spectroscopy from the visible to the near-IR re-

gion. This is the first quantitative and systematic study for influence of a chain linking two chromophores on intramolecular dimer radical cations formed in bichromophoric compounds. The intramolecular dimer radical cations of Np were observed for all the chain lengths $n = 3, 5, 7$ –12, 14, whereas the Np excimer can be formed only for $n = 3$. The molar absorption coefficients were evaluated to be $4500 \text{ mol}^{-1} \text{ l cm}^{-1}$ at 675 nm for the monomer radical cation of Np and $4400 \text{ mol}^{-1} \text{ l cm}^{-1}$ at 1100 nm for the dimer radical cation of Np. On the basis of the absorbance of each species, K between the monomer and the dimer radical cation was evaluated for the series of DNpn. The dependence of K on the chain length n corresponds to the probability of ring closure in a *syn* fashion. The CR stabilization of the dimer radical cations formed in DNpn increased with increasing chain length: Longer chains enable the mutual configuration of the two Np moieties to be optimized. These findings provide a basis for understanding of formation and stabilization of dimer radical cations in complex systems such as polymers bearing chromophores at their side chains.

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