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Evidence for photo-rearranged isomer of 2-(bromomethyl)naphthalene in solution studied by one-color and two-color laser-excitation transient-absorption techniques

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Abstract

Photochemical reaction of 2-(bromomethyl)naphthalene (2-BMN) in hexane solution was studied at room temperature using one-color and two-color laser excitation transient absorption techniques. After the excitation of 2-BMN with the 308 nm laser, a new transient species, X, which has longer lifetime and a broad absorption band around 340 nm, was found in addition to 2-naphthylmethyl radical (2-NPM). In the two-color laser excitation experiment, 2-NPM turned out to react by the irradiation of the 355 nm light. The excitation of the X species by the 355 nm light led to the generation of 2-NPM. The appropriate candidate for the X species would be the rearranged isomer of 2-BMN in view of an ab initio calculation. The production and photoreaction mechanisms were also discussed. © 2001 Published by Elsevier Science B.V.

Keywords: 2-(Bromomethyl)naphthalene; Photoexcitation; 2-Naphthylmethyl radical; Photo-rearranged isomer; Transient absorption; Two-color laser excitation

1. Introduction

Photoexcitation of several halogen-substituted aromatic compounds is known to induce carbon–halogen bond homolysis and to generate the corresponding aryl radical and halogen atom. The photodissociation mechanisms of halomethyl naphthalenes [1–9] and the properties of the naphthylmethyl radicals in the ground and excited states [10–15] have been studied for these several decades. Rentzepis and co-workers studied the photodissociation of 1- and 2-(halomethyl)naphthalenes at room temperature by means of picosecond emission and absorption spectroscopies [4,5]. Two channels of energy dissipation were proposed when the (halomethyl)naphthalenes were excited into the $S_2(\pi, \pi^*)$ state with the 266 nm light. One is internal conversion to the $S_1(\pi, \pi^*)$ state followed by fluorescence to S_0 , and the other is intersystem crossing to an upper triplet state which itself, or crosses to, a dissociative (σ, σ^*) triplet state that leads to homolysis of the carbon–halogen bond. Kawai et al. investigated photolysis of 1-(chloromethyl)naphthalene by the irradiation at 308 nm and triplet photosensitization in benzene solution using the time-resolved ESR technique [8]. 1-Naphthylmethyl

radical is formed even in the low vibrational levels of the T_1 state. Slocum and Schuster investigated the solvent effect of the photolysis of 1-(halomethyl)naphthalenes [6]. They employed spectroscopic measurements and product analyses in methanol and in cyclohexane solution, and observed carbon–halogen bond heterolysis in methanol, while only homolysis was observed in cyclohexane. Recently, we reported the excitation energy effect on photochemical reaction of 2-(bromomethyl)naphthalene (2-BMN) in acetonitrile solution [9]. Intense T–T absorption band appeared at 415 nm in the transient absorption spectra of 2-BMN excited at 248 nm, while the absorption of 2-naphthylmethyl radical (2-NPM) was predominantly observed in the spectra excited at 308 nm. The excitation energy effect on the reaction should reveal the relaxation and reaction dynamics of the S_1 and S_2 states.

Tokumura et al. measured doublet–doublet fluorescence spectra of several naphthylmethyl radicals using the two-step laser excitation spectroscopy [11,12]. They also studied the coupling reactions of the naphthylmethyl radicals in the ground state. Scaiano and co-workers investigated the excited-state properties of 1-naphthylmethyl radical using two-laser excitation techniques [10,13,14]. They reported the absorption spectrum, the lifetime, and the reactivity of naphthylmethyl radicals in the excited state at room

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temperature. We recently reported with time-resolved thermal lensing technique that 2-NPM would react through the excited state, while the main relaxation process of excited 1-NPM is internal conversion [15].

Hiratsuka et al. studied reaction intermediates produced upon the photolysis of benzyl chloride in glassy matrix and in solution [16]. In addition to benzyl radical, another transient species was observed, and assigned to the structural isomers of benzyl chloride produced by the recombination of the benzyl radical and chlorine atom in solvent cage. They also reported 1,3-trimethylsilyl-shifted intermediate by photolyzing trimethylsilyldiphenylmethane [17]. On 2-BMN in hexane solution excited at 308 nm, a long-lived species, which has a broad absorption band similar to that of the structural isomers of benzyl chloride or 1,3-trimethylsilyl-shifted intermediate of trimethylsilyldiphenylmethane, was observed in addition to 2-NPM. In this article, we examine the long-lived transient species using one-color and two-color laser excitation transient absorption methods, and discuss the property of the species with the help of ab initio calculation.

2. Experimental

The 2-BMN (Tokyo Kasei Indus.) and benzophenone (Tokyo Kasei Indus., GR grade) were purified by recrystallization in methanol. Hexane (Kanto Chemical Co. Inc., GR grade) and acetonitrile were used as received. The samples were deoxygenated by bubbling with argon gas (purity 99.95%) saturated with the solvent (hexane or acetonitrile) for 0.5 h before use. To eliminate the influence of photoproducts, all of the sample solutions were flowed in a cuvette (NSG T59FL-UV-10; 10 mm light path length).

In the conventional one-color transient absorption experiment, we used an excimer laser (COMPex 102; XeCl, 308 nm, 10–50 ns pulse duration) as a photolysis light source and a steady-state or a pulsed Xe lamp (Ushio UXL-300DO; 300W) as a monitoring light source. Besides them, in the two-color transient absorption experiment, we used a frequency tripled Nd³⁺: YAG laser (Quantel; Brilliant ω , 355 nm, 5 ns pulse duration, 55 mJ/pulse), which was synchronously fired with the photolysis laser, as an excitation light source. The two lasers were irradiated perpendicularly to the monitoring light. The frequency tripled Nd³⁺: YAG laser was used as an excitation light source in the photosensitization experiment. The monitoring light passed through a sample cuvette and a monochromator was detected with a photomultiplier tube (Hamamatsu; 1P28), and converted into the voltage with a 50 or 500 Ω load resistor, digitized with a digital oscilloscope (Sony Tektronix; TDS-380, 2 GHz/sampling) and transferred to a personal computer.

Ab initio calculations were performed using the GAUSSIAN 98 program. Geometries and energies of 2-BMN and the transient rearranged isomers in the ground state were

calculated by the B3LYP/6-31G* level of theory. CI-Singles calculations were also carried out to estimate the energy of the excited states.

3. Results and discussion

3.1. Transient absorption spectra of 2-BMN excited at 308 nm

Fig. 1 shows the transient absorption spectra of 2-BMN excited at 308 nm in hexane solution. After the excitation (2 μ s), a sharp absorption band with a peak at 380 nm and a broad band around 340 nm were observed. The sharp band completely disappeared within 250 μ s, while the broad band was found to still remain (\sim several ms). The spectrum consisting only of the sharp absorption component is identical with that of 2-NPM obtained by the photolysis of 2-(chloromethyl)naphthalene (2-CMN) at 266 nm [5]. The broad band did not appear in the spectrum of 2-CMN, but in that of 2-BMN. These facts strongly suggest the existence of a new transient species including a bromine atom, different from 2-NPM. Here, we tentatively name the transient species X. The long lifetime and the broad spectral feature of X are analogous to those of the structural isomers of benzyl chloride, observed by photoexcitation of benzyl chloride [16]. Therefore, the X species may be the rearranged isomer of 2-BMN. The detailed discussion will be shown below.

3.2. Two-color laser excitation transient absorption measurement

Time profile of the two-color laser excitation transient absorption of 2-BMN in hexane monitored at 345 nm is shown in Fig. 2. When the excitation light (355 nm) was irradiated, obvious bleaching was observed and did not recover within the time window (20 μ s). We previously reported the

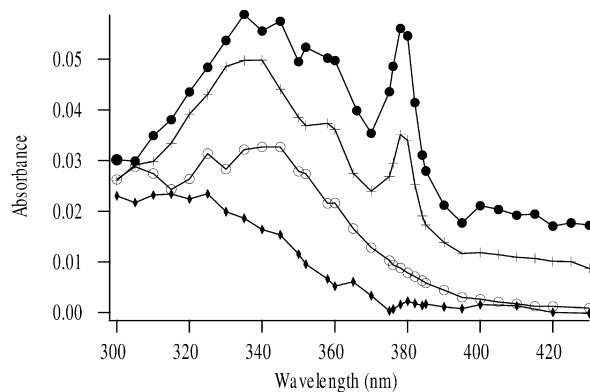


Fig. 1. (a) Transient absorption spectra of 2-BMN in hexane observed at 2 μ s (●), 10 μ s (+), 250 μ s (○), and 5 ms (◆) after the 308 nm excitation. A sharp absorption band with a peak at 380 nm should be ascribed to 2-NPM, and a broad band around 340 nm to the transient species named "X". The absorption spectrum at 5 ms is due to final stable products.

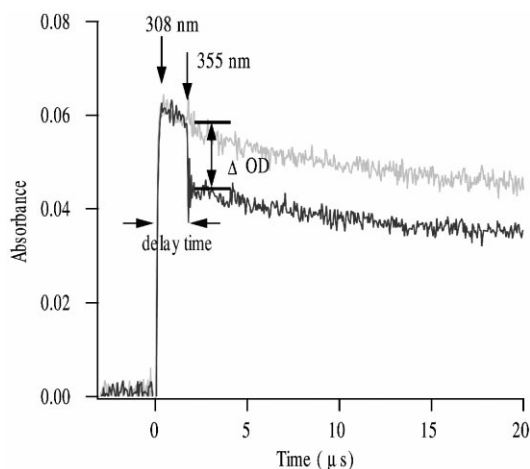


Fig. 2. Time profile of the two-color laser excitation transient absorption of 2-BMN in hexane monitored at 345 nm (black line). The time profile without the irradiation of 355 nm light is also shown (gray line). The bleaching was observed by the excitation laser irradiation.

excited state reaction of 2-NPM [15]. However, it becomes explicit that the 355 nm light was absorbed by both 2-NPM and X, so that either or both the species would contribute to the bleaching. Here, the influence of the final products on the bleaching is negligible because the absorbance is very small as shown in Fig. 1. The magnitude of the bleaching (ΔOD) immediately after the excitation was plotted against

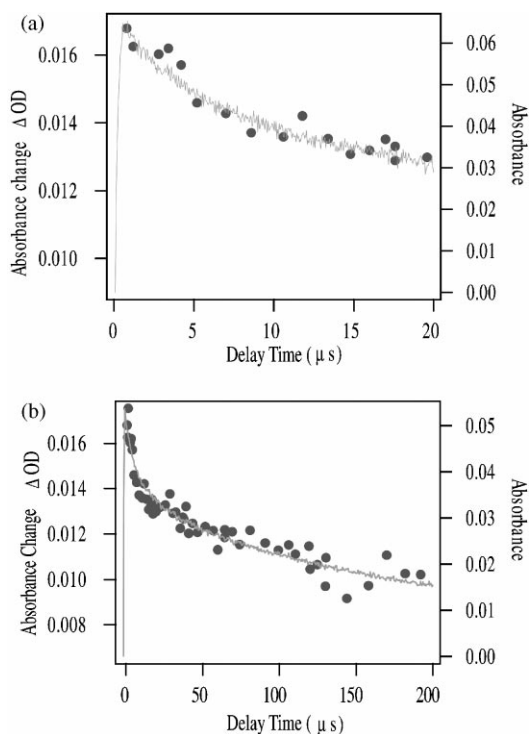


Fig. 3. Plots of the absorbance change (ΔOD) vs. delay time of the two lasers monitored at 345 nm (●). Time profiles of the transient absorption monitored at (a) 380 and (b) 355 nm are also shown. The scale for the transient absorption is indicated on the right axis.

the time interval between the two laser pulses, shown in Fig. 3. The time profile of the transient absorption monitored at 380 nm, mainly due to 2-NPM, was superimposed on the plots (Fig. 3a). As 2-NPM disappeared, ΔOD decreased. Within the time range in Fig. 3a (0–20 μs), the concentration of the X species hardly change, while 2-NPM decays distinctly. If the bleaching is due to only the X species, the plots of the ΔOD should be constant against time interval of the two beams. Therefore, the plots in Fig. 3a revealing that 2-NPM should react through the excited states. For the X species, the same result was obtained as shown in Fig. 3b. It is concluded that not only 2-NPM, but also X should react by the excitation with the 355 nm light.

Fig. 4a shows time profile of the two-color laser excitation transient absorption of 2-BMN in hexane monitored at 380 nm (black line). The second laser was fired at 10 μs after the photolysis laser when the X species dominantly absorbs the light. Compared with the one-color laser excitation transient absorption of 2-BMN (gray line), it is evident that some transient absorption was superimposed in addition to the bleaching observed in Fig. 2. The difference between the time profiles with and without the second laser pulse is shown in the inset of Fig. 4a. The lifetime was estimated to be about 8 μs, which is very similar to that of 2-NPM. The ΔOD value immediately after the

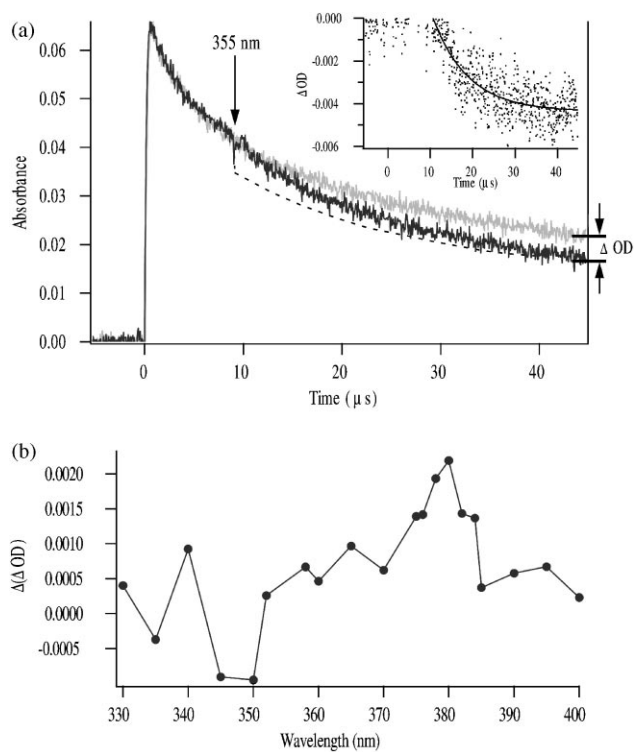
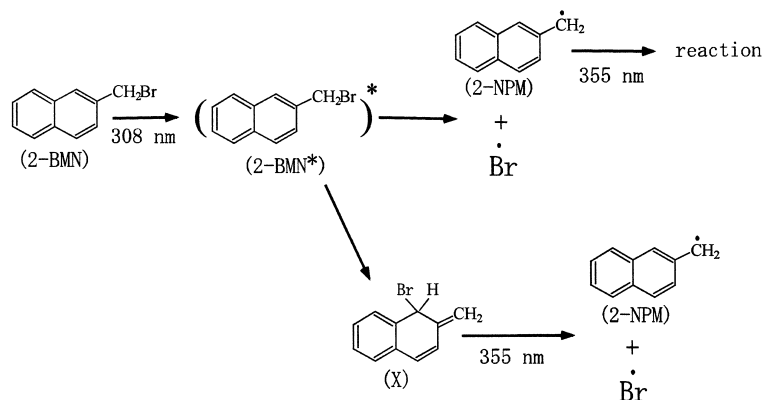


Fig. 4. (a) Time profile of the two-color laser excitation transient absorption of 2-BMN in hexane monitored at 380 nm (black line). The time profile without the irradiation of 355 nm light is also shown (gray line). The difference between the time profiles with and without the second laser is shown in the inset. (b) Plots of $\Delta(\Delta OD)$ at various wavelengths, where $\Delta(\Delta OD) = \Delta OD$ (at 45 μs) – ΔOD (at 10 μs). See text for details.



Scheme 1. A schematic mechanism of the generation and photoreaction of the photorearranged isomer of 2-BMN.

excitation light shown in the inset of Fig. 4a was nearly equal to zero, which indicates that the extinction coefficient of the X species should be identical with that of 2-NPM at 380 nm. The absorption spectrum of $\Delta(\Delta OD) (= \Delta OD \text{ (at } 45 \mu\text{s)} - \Delta OD \text{ (at } 10 \mu\text{s)})$ is shown in Fig. 4b. The spectral feature, especially the sharp band around 380 nm, is identical to that of 2-NPM. It is obvious that the X species should produce 2-NPM after the excitation, and therefore, these results insist that the X species would be the rearranged isomer of 2-BMN. A schematic mechanism of the generation and photoreaction of the photorearranged isomer of 2-BMN is briefly summarized in Scheme 1.

3.3. Triplet sensitization

Triplet sensitization experiment was carried out using benzophenone as a triplet sensitizer. Fig. 5 shows time profiles of the transient absorption in acetonitrile solution obtained by the 355 nm excitation monitored at (a) 545 nm, (b) 380 nm, and (c) 345 nm. Direct excitation of 2-BMN is negligible, because 2-BMN hardly absorbs the 355 nm light. The transient absorption observed at 545 nm (Fig. 5a) could be attributed to triplet benzophenone, and the lifetime was estimated to be about 0.3 μs . Because the lifetime of the triplet benzophenone in acetonitrile solution without 2-BMN is 8 μs (gray line in Fig. 5a), the triplet benzophenone should be effectively quenched by 2-BMN. Production of benzophenone ketyl radical was not observed. As for 1-(chloromethyl)naphthalene, triplet-triplet energy transfer from triplet benzophenone followed by the generation of 1-naphthylmethyl radical was reported [8]. In the case of 2-BMN, in addition to the transient absorption due to triplet benzophenone, the transient absorption attributable to 2-NPM and X was observed at 380 nm (Fig. 5b) and 345 nm (Fig. 5c), respectively. The transient absorption spectra obtained by triplet photosensitization of 2-BMN with benzophenone excited at 355 nm are shown in Fig. 5d. In the spectrum observed at 2 μs after the laser pulse, the absorptions of the triplet benzophenone and triplet 2-BMN

can be excluded, because the triplet benzophenone is completely quenched (see Fig. 5a) and the triplet 2-BMN is also deactivated [9] within 2 μs after the irradiation of the 355 nm light. There are both the sharp absorption band with a peak at 380 nm due to 2-NPM and the broad absorption band around 340 nm due to X in Fig. 5d. Compared with the transient spectra obtained by direct excitation of 2-BMN (Fig. 1), it is explicit that X is dominantly produced by the sensitization than 2-NPM. It indicates that X would be mainly generated through triplet manifolds.

The difference in the formation ratio of between 2-NPM and X will be explained as follows. One reason is the difference in the excess energy above the dissociation potential of the C–Br bond. The energies of the S_1 state of 2-BMN and the T_1 state of benzophenone are about 90 [7] and 69 kcal/mol [18], respectively. In the case of direct photodissociation, relatively higher internal energy is supplied to the photofragments, resulting in easier escape of a bromine atom from the solvent cage. On the other hand, photosensitization supplies less energy to the fragments, resulting in accelerative formation of X, the rearranged isomer of 2-BMN. Another appropriate reason may be the difference in the property of the dissociative states. The dissociation of 1-(chloromethyl)naphthalene occurs through the triplet manifolds. It is also reported that two dissociative triplet states ($^3\pi\sigma^*$ and/or $^3\sigma\sigma^*$) lying near the lowest triplet state were speculated by ab initio calculation for chlorobenzene [19]. Some dissociative states will be lying above the T_1 state in the case of 2-BMN. The production of 2-NPM or the formation of X may result from the character of the dissociative states.

3.4. Structure and properties of the rearranged isomer of 2-BMN

The ground state geometries of the rearranged isomers of 2-BMN was optimized using the B3LYP/6-31G* level of theory. The optimized geometries of 1, 3, 6, 8, and 9-isomer, in which a bromine atom (Br) is combined with carbon in 1,

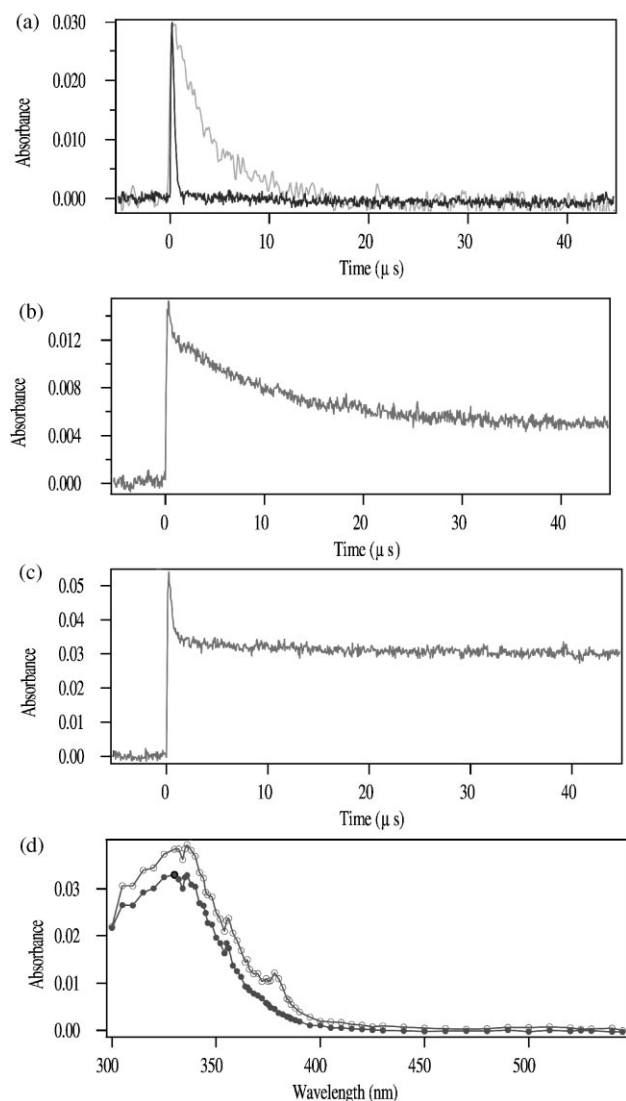


Fig. 5. Time profiles of the transient absorption of 2-BMN sensitized by triplet benzophenone with the 355 nm light irradiation in acetonitrile solution monitored at (a) 545, (b) 380, and (c) 345 nm. (d) The transient absorption spectra of 2-BMN and benzophenone in acetonitrile observed at 2 (○) and 130 (●) μs after the 355 nm excitation. The sharp band at 380 nm and the broad band around 340 nm similar to that in Fig. 1 are also observed in the spectra. However, the ratio of X to 2-NPM is much larger than that obtained by direct excitation.

3, 6, 8 and 9-positions (C(1), C(3), C(6), C(8), and C(9)), are determined (see Fig. 6). Their stabilization energies against the isolated free radical pair of 2-NPM and Br are summarized in Table 1. 1-Isomer has the stabilization energy of 39 kcal/mol and is the most stable one in the five types of isomers. The Mulliken spin densities of 2-NPM were calculated by the UB3LYP/6-31G* level of theory. The spin density at C(1) is 0.39, which is the highest next to 0.75 at C(12), and Br may prefer to interact with C(1). Therefore, the most probable isomer would be 1-isomer.

A difference in energy between 2-BMN and the free radical pair of 2-NPM and Br was also calculated. The value of

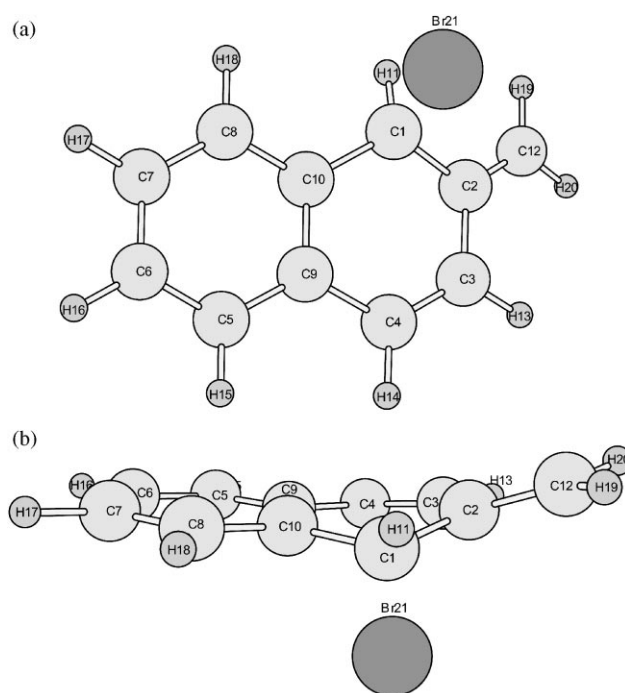


Fig. 6. Ground state geometry of 1-isomer optimized by the B3LYP/6-31G* level of theory (a) from the top and (b) from the side view.

the stabilization energy of 1-isomer (39 kcal/mol) is found to be smaller than the difference in energy between 2-BMN and the free radical pair (61 kcal/mol), namely, the bond energy of C(12)–Br. The optimized geometry of 1-isomer is shown in Fig. 6. The distance between Br and C(1) was estimated to be about 2.1 Å, which well agrees with the calculated distance between Br and C(12) of 2-BMN (2.0 Å). The Mulliken spin densities of 1-isomer were also calculated at the UB3LYP/6-31G* level. The spin densities at all of the atoms were nearly equal to zero, indicating 1-isomer does not have the character of biradicals.

CI-Singles calculations of 2-BMN and 1-isomer were also carried out. The S_1 state of 1-isomer was mainly generated by HOMO–LUMO transition, since the contribution of the transition is estimated to be as large as 70%. The energy of the S_1 state of 1-isomer (4.69 eV) was derived to be smaller than that of 2-BMN (5.17 eV). It agrees with

Table 1

Stabilization energy of 1, 3, 6, 8, and 9-isomers and 2-BMN against the energy of free radical pair of 2-NPM and Br calculated at the B3LYP/6-31G* level

Species	Stabilization energy (kcal/mol)
Free radical pair of Br and 2-NPM	0
1-Isomer	39.0
3-Isomer	19.2
6-Isomer	23.7
8-Isomer	21.2
9-Isomer	13.7
2-BMN	60.8

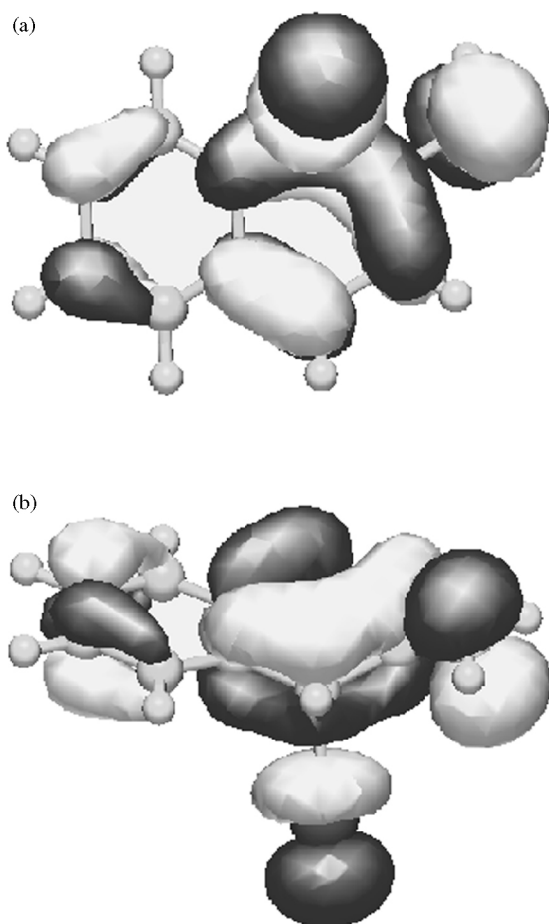


Fig. 7. LUMO of 1-isomer, of which the geometry has been already optimized in Fig. 6. The side view (b) clearly indicates the antibonding property of the C(12)–Br bond.

the experimental results that the absorption spectrum of X (about 340 nm) was observed at longer wavelength than that of 2-BMN (325 nm). As shown in Fig. 7, the LUMO of 1-isomer has antibonding character of the C(12)–Br bond. It is consistent with the experimental result that X reacts by the excitation with the 355 nm light to yield 2-NPM. These calculation results strongly support our assignment of the X species to the rearranged isomer of 2-BMN.

4. Summary

Photochemical reaction of 2-BMN in hexane solution was studied at room temperature. A new transient species, X, was

produced in addition to 2-NPM by the excitation of 2-BMN with the 308 nm light. Further excitation of the X species with the 355 nm light resulted in disappearance of the X species to yield 2-NPM. Photosensitization of 2-BMN with benzophenone produced the large amount of the X species, which indicates that the X species would be mainly generated through triplet manifolds. Ab initio calculations were also carried out. The geometry for the rearranged isomer of 2-BMN was optimized. The most probable candidate for the X species was proved to be 1-isomer (Figs. 6 and 7).

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