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Reactive intermediates formed by the consecutive photolyses of naphthalenetetracarboxylic dianhydrides: direct observation of reactive intermediates generated by laser-induced reaction in low-temperature argon matrices

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Abstract

Photolyses of 1,2;5,6- and 2,3;6,7-naphthalenetetracarboxylic dianhydrides (**1** and **2**), which would be precursors of 1,5- and 2,6-naphthdiynes, respectively, were studied by matrix isolation and wavelength-selective irradiation techniques in order to directly observe intermediates produced stepwise. The photolyzed products in the matrices were characterized by FT-IR and UV–Vis spectroscopies with the aid of density functional theory calculations. As a result of decarboxylation and decarbonylation of dianhydride precursors, the generation of naphthyne intermediates was confirmed in both the cases of **1** and **2**. The photolyses of these naphthyne intermediates resulted in the formation of acetylenic compounds as in the case of benzdiynes. In the photolysis of **1**, the final compound was assigned to deca-5-ene-1,3,7,9-tetrayne, although it was unidentified in the case of **2**.

Keywords: Matrix isolation; Reactive intermediate; Laser photolysis; Density functional theory calculation; Naphthalenetetracarboxylic dianhydride; Naphthdiyne

1. Introduction

Arynes, benzyne and its congeners have attracted great interest because of their ability to participate in a wide variety of organic reactions and their peculiar structures containing a strained triple bond. Only the simplest member among them, *o*-benzyne, has been thoroughly characterized by its direct observation using matrix isolation spectroscopy [1–6]. Recently, its peculiar structure has been discussed on the basis of both experimental and theoretical results. The length of triple bond in *o*-benzyne, which was estimated by ^{13}C dipolar NMR [7], showed that theoretical calculations, particularly calculations at the density functional theory (DFT) level, provided reasonably accurate geometries of the unstable species [7,8]. Although *o*-benzyne has been studied extensively, matrix isolation and characterization of larger arynes such as naphthyne have seldom been carried out. These didehydrogenated polyaromatic hydrocarbons (PAH) are of interest as reactive intermediates for organic reactions [9,10], while they have been studied theoretically as the interstellar compounds responsible for unidentified infrared (UIR) emission bands [11,12]. Recently, we reported the direct observation of 1- and 2-naphthynes in argon matrices, and discussed the changes in geometries and reactivities induced by the fusion of an additional benzene nucleus to benzyne [13,14].

On the other hand, benzdiyne and naphthdiyne, in which two triple bonds are contained within one aromatic system, are further challenging reactive intermediates. We reported the direct observation of a benzdiyne structure by the photolysis of 1,4-bis(trifluoromethyl)-2,3;5,6-benzenetetracarboxylic dianhydride in a low-temperature argon matrix in 1997, which was the first finding that a benzdiyne structure could be trapped by a matrix isolation method [15]. However, we could not confirm the generation of unsubstituted benzdiynes by the consecutive photolysis of the corresponding precursors [16–18]. These compounds should be highly unstable because of large ring strain. The expansion of the conjugated system would contribute to the stabilization of such highly unsaturated species by reducing the ring strain. Naphthdiynes were proposed as reactive intermediates

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participating in some organic chemical reactions [19,20]. These intermediates should be formed in the photolyses of naphthalenetetracarboxylic dianhydrides.

Here, we wish to report the consecutive photolyses of 1,2;5,6- and 2,3;6,7-naphthalenetetracarboxylic dianhydrides in low-temperature argon matrices. The wavelength-selective photolyses using several lasers have been executed in order to identify intermediates formed consecutively.

2. Experimental

2.1. Materials

1,2;5,6-Naphthalenetetracarboxylic dianhydride (**1**) was synthesized from 2,6-dimethylnaphthalene in the following way. 1,5-Dibromo-2,6-dimethylnaphthalene was obtained from bromine and 2,6-dimethylnaphthalene by the method of Arnold and Liggett [21]. Then 1,5-dicyano-2,6-dimethynaphthalene was obtained from copper cyanide and 1,5-dibromo-2,6-dimethylnaphthalene by the method of Friedman and Shechter [22]. 1,5-Dicyano-2,6-dimethylnaphthalene was oxidized to 1,2,5,6-naphthalenetetracarboxylic acid and then converted to the dianhydride by Dozen's method [23]. The final product was purified by recrystallization from acetic anhydride. 2,3,6,7-Naphthalenetetracarboxylic dianhydride (**2**) was synthesized according to the literature procedure [24] and was purified by recrystallization from acetic anhydride.

2.2. Matrix isolation experiments

Matrix isolation experiments were performed with a closed-cycle helium cryostat (Air Products Displex CS-202). Pressure in the sample chamber was kept at 10^{-6}–10^{-7} Torr during the experiments. For FT-IR measurement, a CsI plate cooled to 11 K was used as a substrate, on which vaporized **1** or **2** was co-deposited with argon (99.9999%) at 11 K. KBr plates were used as optical windows for FT-IR measurements, which were carried out on a Perkin-Elmer Spectrum-GXI spectrometer with a resolution of $1\,\mathrm{cm}^{-1}$. For the measurement of UV–Vis absorption spectra, a CaF_2 and quartz plates were used as the substrate and the optical windows, respectively. UV–Vis spectra were measured with a Shimadzu UV-3100 spectrometer.

Wavelength-selective photoirradiation was carried out with the following light sources: (1) third harmonic pulses (THG) of a Nd:YAG laser ($\lambda = 355$ nm: Lotis LS-2125 with YHG-34), whose repetition rate and laser fluence were 10 Hz and ca. $4\,\mathrm{mJ\,cm}^{-2}\,\mathrm{pulse}^{-1}$, respectively; (2) fourth harmonic pulses (FHG) of a Nd:YAG laser ($\lambda = 266$ nm), whose repetition rate and laser fluence were 10 Hz and ca. $3\,\mathrm{mJ\,cm}^{-2}\,\mathrm{pulse}^{-1}$, respectively; (3) a XeCl excimer laser ($\lambda = 308$ nm: MPB Technologies, PSX-100), whose repetition rate and laser fluence were 10 Hz and ca. $1\,\mathrm{mJ\,cm}^{-2}\,\mathrm{pulse}^{-1}$, respectively; (4) a KrF excimer laser ($\lambda = 248$ nm, Lambda-Physik EMG201), whose repetition rate and laser fluence were 5 Hz and ca. $8\,\mathrm{mJ\,cm}^{-2}\,\mathrm{pulse}^{-1}$, respectively.

2.3. Computational methods

All DFT calculations were performed with the Gaussian 98 program package [25]. Geometries of compounds were optimized using the B3LYP method [26,27] and the 6-31G** basis set. The nature of the stationary points was assessed by means of vibrational frequency analysis. All of the calculations were done on the IBM RS/6000-SP system at the

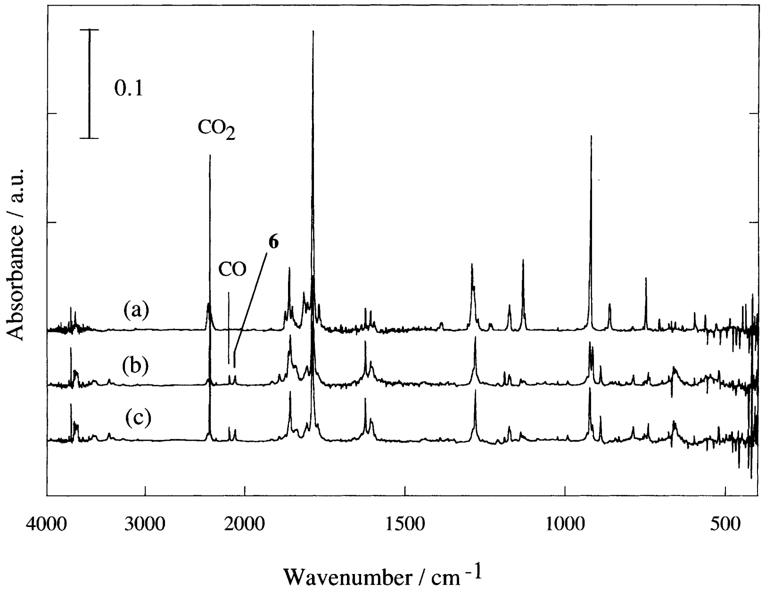


Fig. 1. The FT-IR spectra observed in the photolysis of **1**: (a) before irradiation; (b) after irradiation at 355 nm; (c) after irradiation at 308 nm.

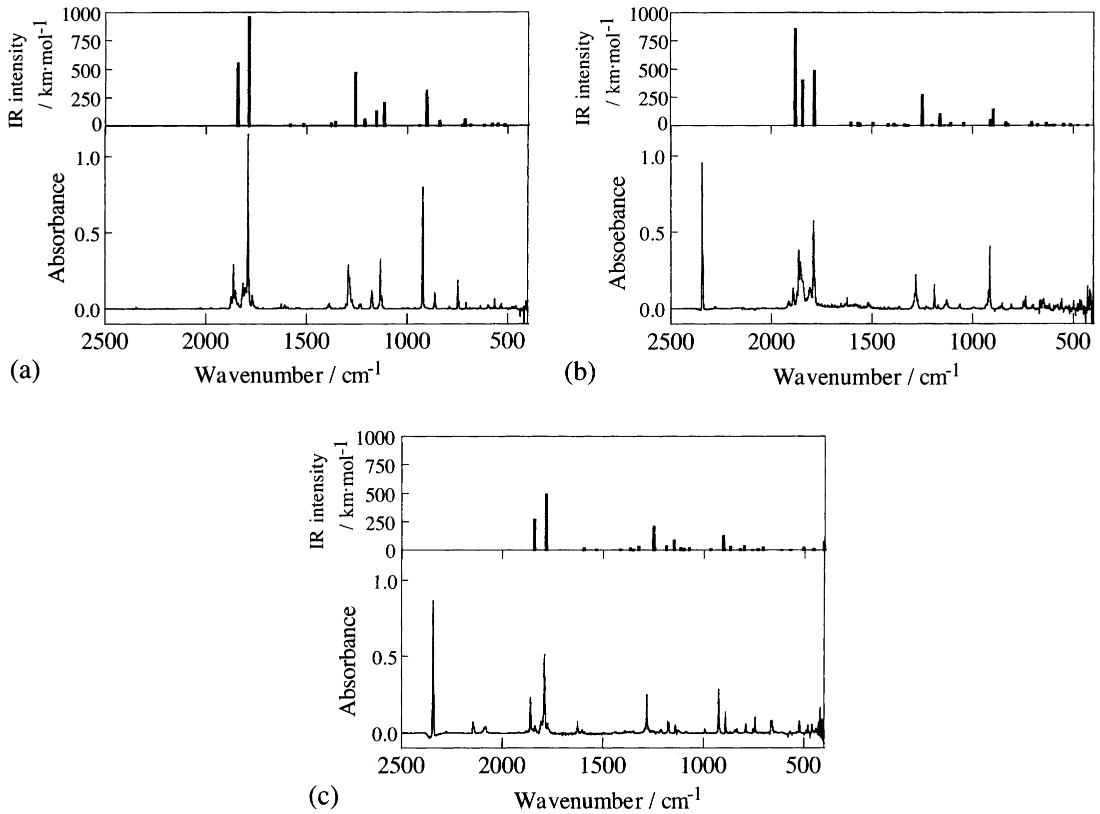


Fig. 2. The observed and calculated IR spectra of **1** (a), **4** (b), and **5** (c).

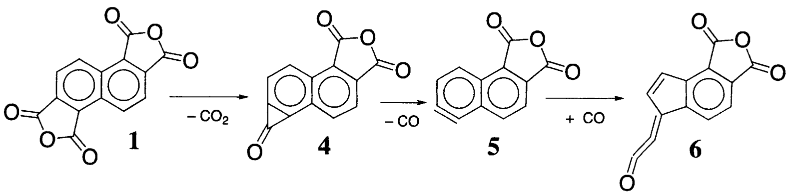
Tsukuba Advanced Computing Center (TACC) and on the IBM 32 node SP system at the National Institute of Material and Chemical Research (NIMC).

3. Results and discussion

3.1. Naphthyne intermediate from 1,2,5,6-naphthalenetetracarboxylic dianhydride

Crystallines of **1** was vaporized at 145°C and co-deposited with argon onto a cold substrate. Figs. 1(a) and 2(a) show IR spectra of matrix-isolated **1**. The precursor **1** showed the lowest transition band at 362 nm, which is 6 nm longer than that of 1,2-naphthalenedicarboxylic anhydride (**3**). In the previous report, **1** in the argon matrix was photolyzed with a XeCl laser ($\lambda = 308$ nm) to form directly a naphthyne intermediate (**5** in Scheme 1) [28]. Meanwhile, the consecutive photolysis was observed for **3**: stepwise decarboxylation and decarbonylation were induced by the wavelength-selective irradiation [13]. Since the lowest transition band of **1** (362 nm) located close to that of **3** (356 nm), the photolysis using THG pulses of Nd:YAG laser ($\lambda = 355$ nm) was examined. Upon the irradiation, new IR peaks ascribable to photo-generated species appeared, while the peaks of **1** decreased, as shown in Fig. 1(b). In contrast to the case of **3**, the appearance of peaks due to CO and CO_2 indicated that both decarboxylation and decarbonylation of **1** were induced upon the irradiation. IR spectrum observed after the photolysis was not in agreement with the calculated spectrum of **4**.

The further change in IR spectra was observed upon irradiation with a XeCl excimer laser (Fig. 1(c)). The spectrum observed upon this irradiation was in good agreement with the calculated spectra of **5** as shown in Fig. 2(c). Careful analysis of these spectra revealed that the decarbonylation did not completely proceed upon irradiation at 355 nm.



Scheme 1.

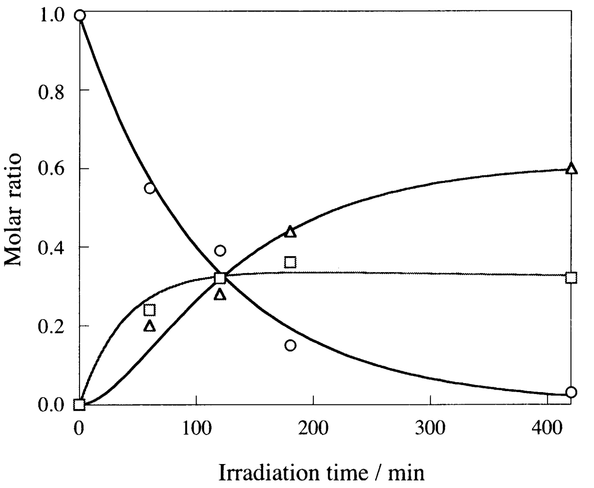
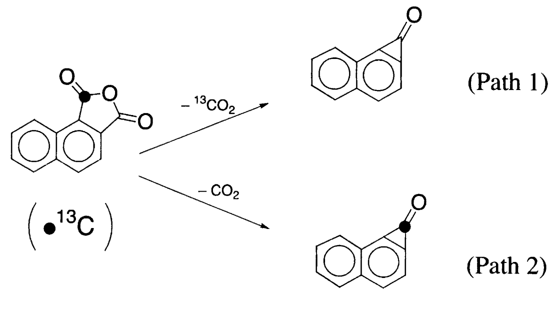


Fig. 3. Changes in molar ratio of **1** (circle), **4** (square), and **5** (triangle) in an argon matrix during the irradiation at 355 nm. Solid lines are the results of fitting of each molar ratio with Eqs. (1)–(3).



Scheme 3.

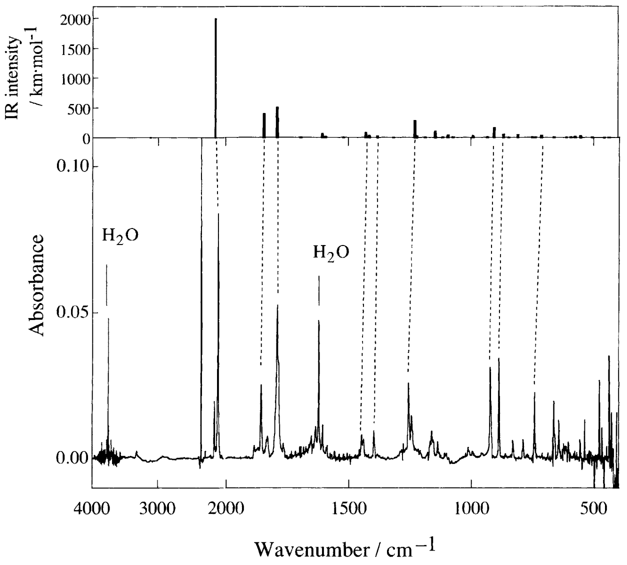


Fig. 4. The observed and calculated IR spectra of **6**.

As a result, two intermediates (**4** and **5**) coexisted in the matrix upon irradiation at 355 nm, and the intermediate **4** was converted to **5** upon irradiation at 308 nm. IR spectrum corresponding to pure **4** could be obtained by the removal of the contribution of **5** from the spectra observed upon photolysis at 355 nm. Thus obtained IR spectrum was in good agreement with the calculated spectrum of **4** as shown in Fig. 2(b). If we assume that the formation of other intermediates can be negligible, we can estimate molar ratio of **1**, **4**, and **5** in the matrix during the irradiation as shown in Fig. 3. The ratio of **5** to **4** increased gradually during the photolysis. However, the dynamic behavior of theses species could not be described by normal consecutive reaction scheme (Scheme 2(a)). The dynamic behavior of formation of **4** and **5** can be well described using the reaction scheme in Scheme 2(b). The rate equations describing the reaction scheme are as follows:

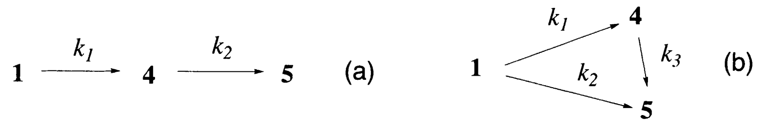
$$[\mathbf{1}] = [\mathbf{1}]_0 \exp\{-(k_1 + k_2)t\} \tag{1}$$

$$[\mathbf{4}] = \frac{k_1[\mathbf{1}]_0}{k_3 - (k_1 + k_2)}[\exp\{-(k_1 + k_2)t\} - \exp(-k_3 t)] \tag{2}$$

$$[\mathbf{5}] = [\mathbf{1}]_0 - [\mathbf{1}] - [\mathbf{4}] \tag{3}$$

The changes of the molar ratio of **1**, **4**, and **5** were fitted with Eqs. (1), (2), and (3), respectively. The rate constants k_1, k_2, and k_3 were estimated as 9.0×10^{-3}, 1.7×10^{-2}, and 1.5×10^{-4} min^{-1}, respectively, from the curves in Fig. 3. Here, the branching ratio of k_1/k_2 is 0.53. In the case of the isotopically labeled **3**, the branching in decarboxlylation was indicated as shown in Scheme 3: the ratio of ${}^{13}CO_2/CO_2$ was estimated as 0.42 [14]. In this case, the decarboxylation forming ${}^{13}CO_2$ would become slower due to the heavy-atom effect, which decreases the ratio of ${}^{13}CO_2/CO_2$. Therefore, it would be possible that the branching observed in photolysis of **1** is originated in the branching of decarboxylation. The formed **5** still has small absorbance at 355 nm due to the aryne moiety. This absorbance should contribute to the slow decarbonylation of **4**, that is, k_3.

As in the case of 1-naphthyne [13], prolonged irradiation at 308 nm caused the formation of ketene species **6** by addition of CO to **5**. The formation of ketene species was enhanced by initial irradiation at 266 or 248 nm. IR spectrum corresponding to pure ketene was extracted from the spectra as shown in Fig. 4, which showed good agreement with the calculated one for **6**.



Scheme 2.

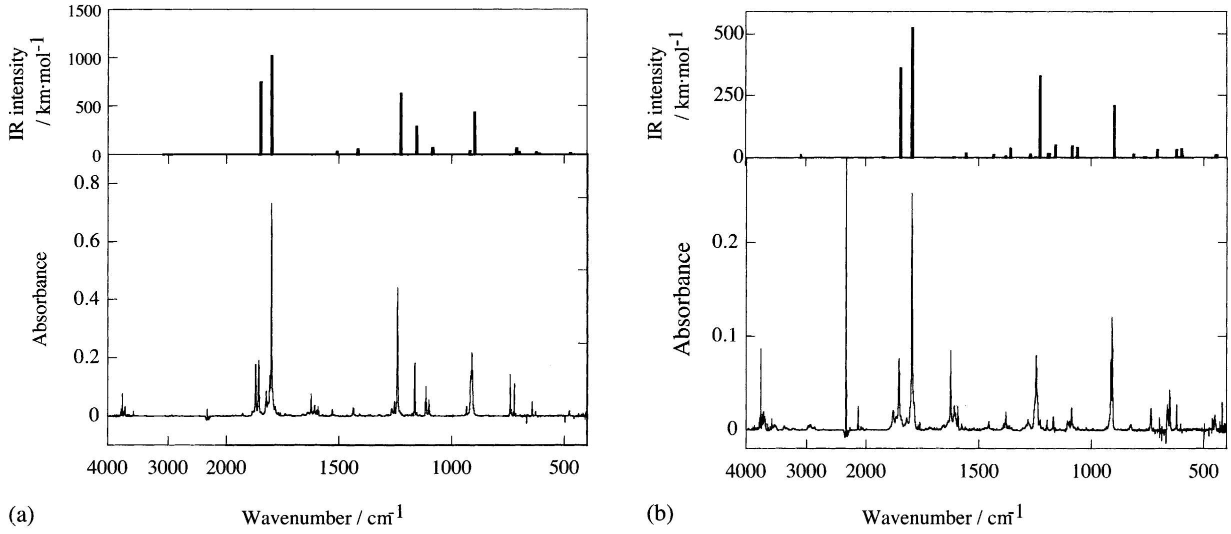


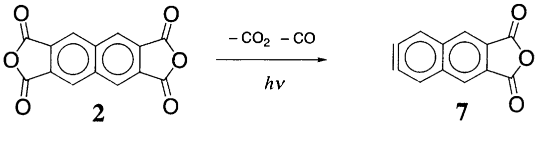
Fig. 5. The observed and calculated IR spectra of **2** (a) and **7** (b).

3.2. Naphthyne intermediate from 2,3,6,7-naphthalenetetracarboxylic dianhydride

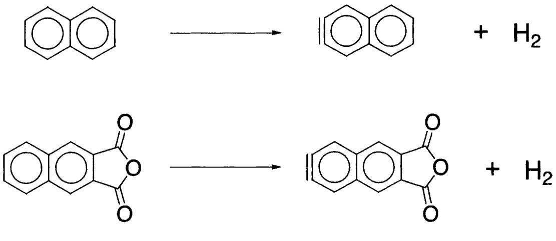
Crystallines of **2** was vaporized at 175°C and co-deposited with argon onto a cold substrate. Fig. 5(a) shows the IR spectrum of matrix-isolated **2**. In contrast to **1**, the naphthyne intermediate **7** was directly formed from **2** upon irradiation at 355 nm (Scheme 4). The further irradiation at 308 nm caused no change in the spectra. The formation of the intermediate containing cyclopropanone moiety could not be observed, similarly with the case of 2,3-naphthalenedicarboxylic anhydride [14]. The FT-IR spectra observed after this irradiation showed good agreement with the calculated one as shown in Fig. 5(b).

3.3. Computational investigations of naphthynes: geometries and energies

The geometries of naphthyne intermediates optimized at the B3LYP/6-31G** level are depicted in Fig. 6 together with those of naphthynes and naphthdiynes. The triple bond length of *o*-benzyne estimated as 1.251 Å at the same level showed good correspondence with the experimental result [7]. The bond lengths of the corresponding triple bonds in **5** and **7** are estimated as 1.241 and 1.259 Å, respectively. These values are almost the same as those of 1- and 2-naphthynes. In naphthynes, the geometries reflect the changes in their electronic structures induced by the fusion of an additional benzene nucleus with *o*-benzyne [14]: in 1-naphthyne, the triple bond is more highly localized compared to that in *o*-benzyne, on the other hand, in 2-naphthyne, the cumulenic character becomes dominant. If the electron density of in-plane π-bond is reduced by the electron withdrawing nature of an anhydride group, the length of triple bonds should be increased. However, such effect was not observed. The electronic fluctuation induced by anhydride group should be rather small. The energy differences for the dehydrogenation (Scheme 5) estimated at the B3LYP/6-31G** level are listed in Table 1. Slightly higher destabilization induced by anhydride group was observed for **7**. This destabilization should originate in steric effect: the bond length (1.416 Å) between the two adjacent C atoms to which



Scheme 4.



Scheme 5.

Table 1
Energy differences for dehydrogenation[a]

Compounds	ΔE (kcal mol^{-1})
5	94.26
7	97.25
1-Naphthyne	93.74
2-Naphthyne	96.22

[a] These values were estimated from the energies at the B3LYP/6-31G** level corrected by zero point energies at the same level (without scaling).

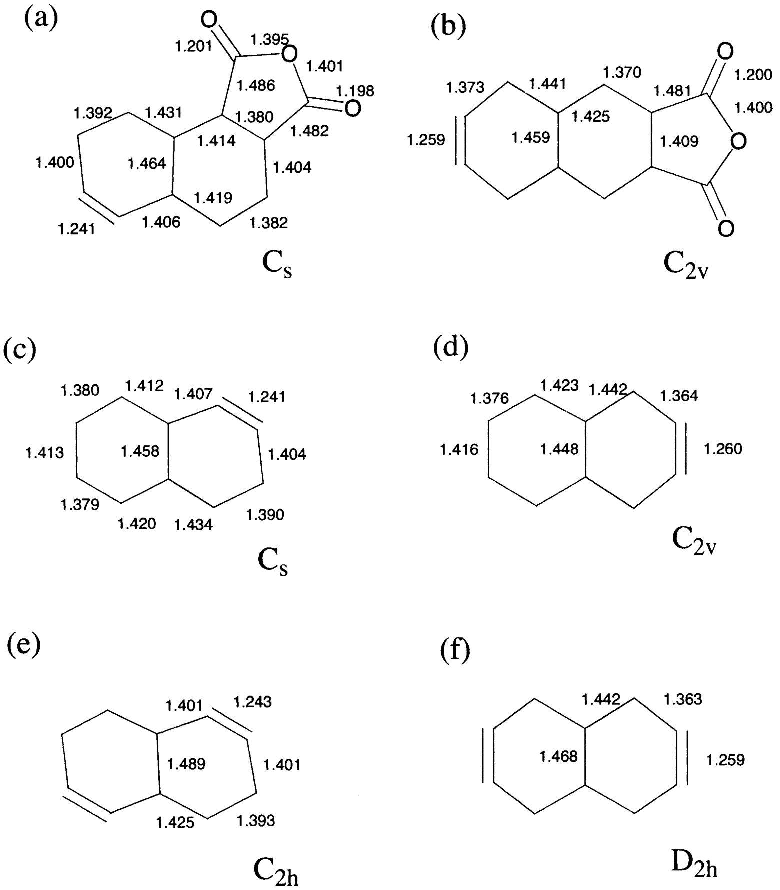


Fig. 6. The geometries of: (a) **5**; (b) **7**; (c) 1-naphthyne; (d) 2-naphthyne; (e) 1,5-naphthdiyne; (f) 2,6-naphthdiyne optimized at B3LYP/6-31G** level. Bond lengths are given in Å.

anhydride moiety attached is shortened by the existence of 2,3-anhydride moiety compared with the corresponding bond length in 2-naphthyne (1.409 Å), whereas it shows little change in 1,2-anhydride system: 1.379 and 1.380 Å for **5** and 1-naphthyne, respectively.

3.4. Photolyses of naphthyne intermediates

Obtained intermediate **5** could be photolyzed upon irradiation at 266 nm (FHG of Nd:YAG laser) or 248 nm (KrF excimer laser). Fig. 7(a) shows the difference in IR spectrum

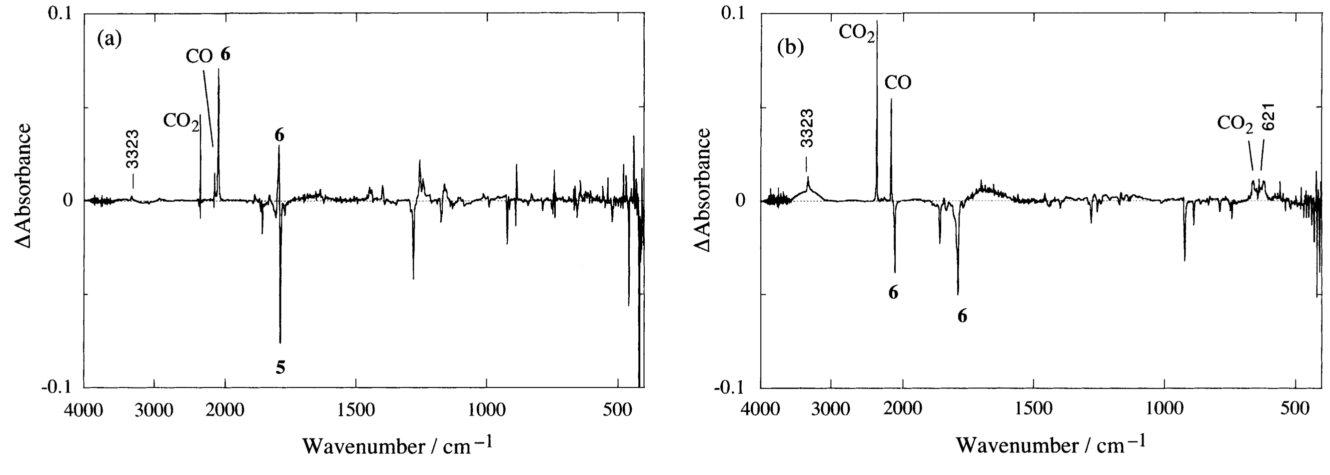
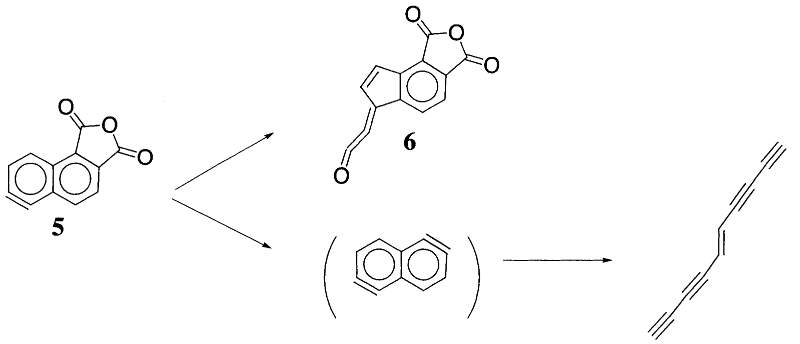


Fig. 7. The difference IR spectra for the photolysis of **5** with FHG of Nd:YAG laser (λ = 266 nm): (a) difference between before and after initial 24 000 shots; (b) difference between before and after successive 276 000 shots.



Scheme 6.

between before and after initial irradiation (initial 24 000 shots) by using FHG of Nd:YAG laser. In the spectrum, the positive and negative peaks corresponded to **6** and **5**, respectively. The positive peaks revealed that the generation of **6** was the dominant process in this stage. Although CO should be consumed by the reaction with **5** to form **6**, the peaks of CO and CO_2 are also positive in this stage. Moreover, the intensity of negative peak due to C=O asymmetric stretching mode of **5** is larger than that of positive peak due to the corresponding mode of **6**. These results reveal the existence of an additional process, that is, decarboxylation and decarbonylation of **5**. This process became dominant upon the prolonged photo-irradiation as shown in the difference IR spectrum of successive 276 000 shots (Fig. 7(b)). This process should result in the formation of $C_{10}H_4$ species. However, we could not observe any IR band ascribable to 1,5-naphthdiyne probably because of low concentration and low IR intensity. With the aid of the UV–Vis spectra and TD-DFT calculations, we assigned the final compound to deca-5-ene-1,3,7,9-tetrayne (Scheme 6) [28].

The photolysis of 2-naphthyne intermediate **7** was also executed. Upon irradiation at 266 or 248 nm, the intermediate **7** can be photolyzed. Several new IR bands increased together with that of CO and CO_2 upon the irradiation, while IR bands of **7** decreased. The difference IR spectrum between before and after irradiation with a KrF excimer laser is shown in Fig. 8. Although the IR band at 2086 cm^{-1} was ascribable to ketene species, this ketene did not contain the anhydride moiety. Moreover, the IR bands appeared at 2235 cm^{-1}, which was not observed in photolysis of **1**, would be ascribed to C_3O [18]. However, the formation of these species should be minor processes because their absorption coefficients are generally rather large. In this stage, the increasing band at 3317 cm^{-1} was also observed, which revealed the formation of acetylenic species as in the case of **1**. However, the IR band of the corresponding bending mode was not observed around 620 cm^{-1}. In this photolysis, an acetylenic compound would be formed by the ring cleavage of 2,6-naphthdiyne, although we could not assign this species (Scheme 7). The four peaks observed at 737, 853,

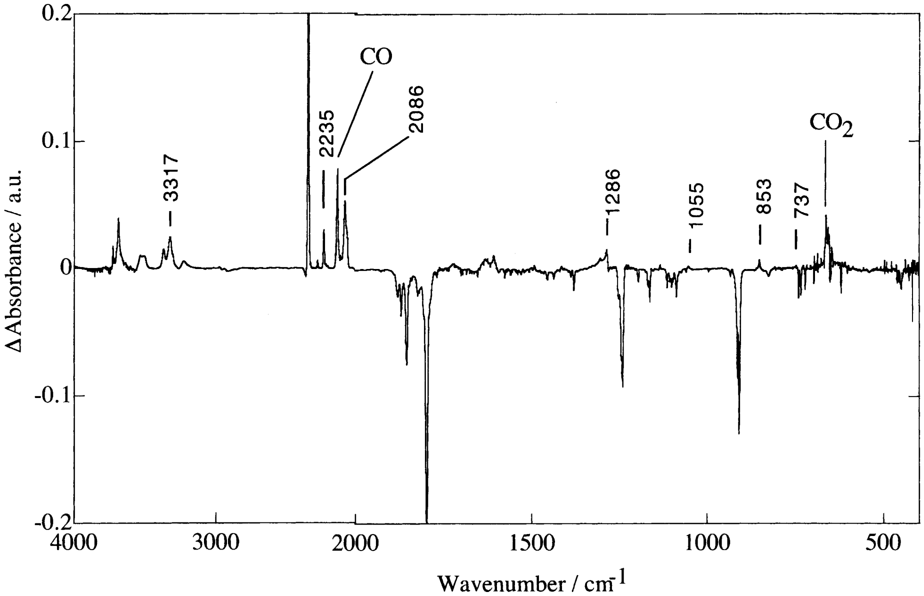
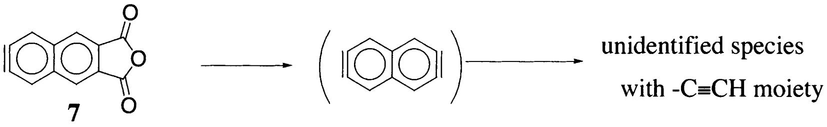


Fig. 8. The difference IR spectra for the photolysis of **7**: difference between before and after irradiation with a KrF excimer laser (λ = 248 nm).



Scheme 7.

1055, and 1286 cm^{-1} were ascribed to skeletal vibrations of the photoproduct on the basis of the dynamic behavior in their intensities during the irradiation. However, we could not find out an appropriate compound for the intermediate showing the theoretical IR bands at these positions.

4. Conclusion

The photolyses of **1** and **2** in argon matrices at cryogenic temperature were studied by IR and UV–Vis spectroscopies. The photolyses were initiated by decarboxylation and decarbonylation of **1** and **2**. In the initial stage of the photolyses, the intermediates **4** and **5** from **1** and the intermediate **7** from **2** were identified, which was confirmed on the basis of good agreement between the observed and the calculated IR spectra. On the other hand, the photolyses of thus obtained naphthyne intermediates **5** and **7** were done upon irradiation at shorter wavelength (266 or 248 nm). In these photolyses, decarboxylation and decarbonylation were revealed from the increase in the absorption of CO and CO_2. However, we could not detect naphthdiynes probably because of their low concentrations and low IR intensities. In the case of **1**, the final product was assigned to novel $C_{10}H_4$ species, deca-5-ene-1,3,7,9-tetrayne, which should be formed by ring cleavage of 1,5-naphthdiyne. Our attempts to observe naphthdiynes aroused new interests in chemistry of $C_{10}H_4$ species. However, further challenging studies, for instance, using more appropriate precursors and more sensitive spectroscopic methods, will be required to confirm the existence of naphthdiynes.

References

[1] J.G. Radziszewsky, B.A. Hess Jr., R. Zahradnik, J. Am. Chem. Soc. 114 (1992) 52.
[2] C. Wentrup, R. Blanch, H. Briehl, G. Gross, J. Am. Chem. Soc. 110 (1988) 1874.
[3] R.F.C. Brown, N.R. Browne, K.J. Coulston, L.B. Danen, F.W. Eastwood, M.J. Irvine, A.D.E. Pullin, Tetrahedron Lett. 27 (1986) 1075.
[4] I.R. Dunkin, J.G. MacDonald, J. Chem. Soc., Chem. Commun. (1979) 772.
[5] O.L. Chapman, C.-C. Chang, J. Kolc, N.R. Rosenquist, H. Tomioka, J. Am. Chem. Soc. 97 (1975) 6586.
[6] O.L. Chapman, K. Mattes, C.L. McIntosh, J. Pacansky, J. Am. Chem. Soc. 95 (1973) 6134.
[7] A.M. Orendt, J.C. Facelli, C., J.G. Radziszewski, W.J. Horton, D.M. Grant, J. Michl, J. Am. Chem. Soc. 118 (1996) 846.
[8] H.J. Jiao, P.V. Schleyer, B.R. Beno, K.N. Houk, R. Warmuth, Angew. Chem. Int. Ed. Engl. 36 (1998) 2761.
[9] J. Moursounidis, D. Wege, Aust. J. Chem. 41 (1988) 235.
[10] K. Jung, M. Koreeda, J. Org. Chem. 54 (1989) 5667.
[11] E. Pauzat, D. Talbi, Y. Ellinger, Astron. Astrophys. 293 (1995) 263.
[12] E. Pauzat, D. Talbi, Y. Ellinger, Astron. Astrophys. 319 (1997) 318.
[13] T. Sato, M. Moriyama, H. Niino, A. Yabe, Chem. Commun. (1999) 1089.
[14] T. Sato, H. Niino, A. Yabe, J. Phys. Chem. A 105 (2001) 7790.
[15] M. Moriyama, T. Ohana, A. Yabe, J. Am. Chem. Soc. 119 (1997) 10229.
[16] M. Moriyama, T. Ohana, A. Yabe, Chem. Lett. (1995) 557.
[17] M. Moriyama, A. Yabe, Chem. Lett. (1998) 337.
[18] M. Moriyama, T. Sato, T. Uchimaru, A. Yabe, Phys. Chem. Chem. Phys. 1 (1999) 2267.
[19] C.S. LeHoullier, G.W. Gribble, J. Org. Chem. 48 (1983) 1682.
[20] G.W. Gribble, R.B. Perni, K.D. Onan, J. Org. Chem. 50 (1985) 2934.
[21] R.T. Arnold, R.W. Liggett, J. Am. Chem. Soc. 64 (1942) 2875.
[22] L. Friedman, H. Shechter, J. Org. Chem. 26 (1961) 2522.
[23] Y. Dozen, S. Fujishima, Yukigoseigaku 30 (1972) 964 (Japanese).
[24] D.W. Boykin, B. Nowak-Wydra, A.L. Baumstark, J. Heterocyclic. Chem. 28 (1991) 609.
[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh, PA, 1998.
[26] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[27] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[28] T. Sato, H. Niino, A. Yabe, Chem. Commun. (2000) 1205.