Synthesis and Photolysis of Biphenylenetetracarboxylic Dianhydride in Low-temperature Neon Matrixes

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Biphenylenetetracarboxylic dianhydride was synthesized by dimerization of benzynedicarboxylic anhydride generated quantitatively by laser photolysis in low-temperature matrixes. Synthesized dianhydride was used as a precursor of matrix photolysis. It was isolated in a neon matrix and photolyzed to form biphenylynedicarboxylic anhydride, a novel aryne species.

Benzynes have attracted great interest because of their ability to participate in a wide variety of organic reaction and their peculiar chemical structures containing a strained triple bond.[1,2] It is known that benzyne undergoes a cycloaddition with itself to form biphenylene or triphenylene.[1,3] Generation of these compounds was also confirmed for benzynes isolated in low-temperature matrixes.[4] They were generally found in product mixtures and supported the intermediacy of benzyne. In our early work aiming to generate benzdiynes, the generation of dimerized product of benzyne intermediate **1** was indicated.[5] Later, we could confirm that **1** can be quantitatevely prepared from 1,2,4,5-benzenetetracarboxylic 1,2:4,5-dianhydride (**2**) by laser photolysis in low-temperature matrixes.[6] This quantitative formation would enhance the generation of specific product from the matrix-isolated intermediate and enables us to apply it to other experiments. In this work, dimerization of matrix-isolated **1** and matrix-photolysis of the obtained product were examined.

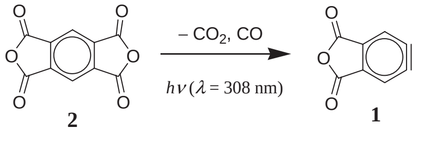
To form **1**, dianhydride **2** isolated in a neon matrix[7] was photolyzed upon 308-nm irradiation as previously reported[6] (Scheme 1).

Neon matrixes containing **2** were prepared as followed: **2** was sublimed at 92 °C, and co-deposited with neon onto a calcium fluoride substrate at 6.7 K. Then, matrix-isolated **2** was completely photolyzed into **1** upon 308-nm irradiation (XeCl excimer laser, 5 Hz, 3 mJ·cm^{-2}·pulse^{-1}, 45 min). Quantitative generation of **1** was confirmed by FTIR spectra as observed in the previous work.[6] This cycle of matrix preparation and photolysis was repeated for 7 times.

After these processes, temperature of matrix was gradually raised to 9.8 K, and then it kept at 9.8 K for more than 15 h. In general, the matrix-isolated species in neon matrixes can diffuse slowly at this temperature.[8] Simultaneously, neon was slowly removed from the matrix, that was indicated by the chamber pressure increasing from 10^{-5} to 10^{-2} Pa. When matrix temperature was raised to over 10.0 K without annealing at 9.8 K, matrix was explosively sublimed at around 10.0 K, and almost nothing remained on the cold substrate. This situation can be avoided by the annealing process at 9.8 K. The IR spectrum observed at the end of the annealing showed little difference from that observed before annealing, indicating that dimerization did not occur in this stage. After the annealing at 9.8 K, temperature of the matrix was raised carefully. Sublimation of neon also started around 10.0 K. But it was not so explosive. After the sublimation, temperature of the substrate was allowed to warm up to rt. As a result, white precipitate remained on the substrate. This precipitate was dissolved into acetone and transferred into sample holder used in the next matrix experiment. Above preparation processes were done twice: 0.25 and 0.17 mg of precipitate was transferred, respectively. For these experiments, 7.99 mg of **2** was used: it was estimated from the mass reduction of sample holder containing **2**. A major product was assigned to **3** (Scheme 2) as discussed later. Assuming that all produced precipitate was **3** and that the sublimed **2** was fully used for the reaction, crude yield of **3** was estimated to be 7.9%.

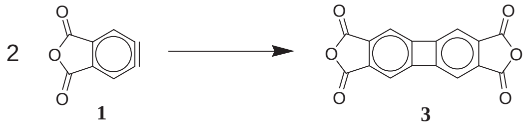
Obtained precipitate was used in the successive matrix photolysis experiment without further purification. First, a matrix was prepared by sample sublimation at 150 °C with co-deposition with neon for 30 min. Observed IR spectrum showed IR bands ascribed to H_2O and CO_2 as well as weak IR bands including C=O bands: the intensities of these IR bands were less than 0.01, indicating that there are no major compounds sublimed under 150 °C. Then, temperature for sublimation was raised to 180 and 200 °C. At the temperature, preparation of matrix was continued for 8 h. During this preparation, several IR bands including C=O band at 1802 cm^{-1} continuously increased. The IR spectrum observed after the 8 h preparation is shown in Figure 1 with calculated IR spectrum of **3**.

Given the early results,[5] **3** would be the most promising product. Meanwhile, other possible products are triphenylene derivative, and biphenyl derivative. The calculated IR spectra of these species are shown in the Supporting Information.[14] As shown in Figure 1, many observed IR bands (marked with open circle) showed agreement with calculated ones of **3**. While some IR bands are not seen in the calculated IR spectrum, indicating the existence of impurity. The IR bands marked with solid circle disappeared upon short irradiation at 308 nm (5 Hz, 3.0 mJ·pulse^{-1}, 15 min).[10] In this short photolysis, other IR bands remained unchanged. The remained species could be photolyzed



2 1

Scheme 1.



1 3

Scheme 2.

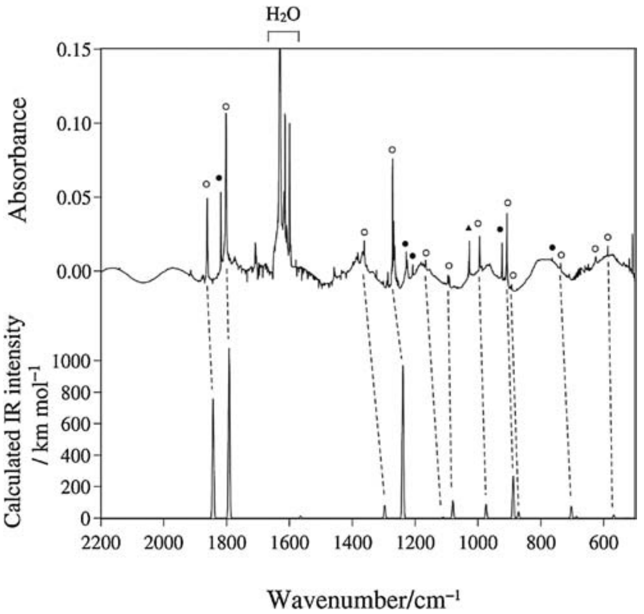


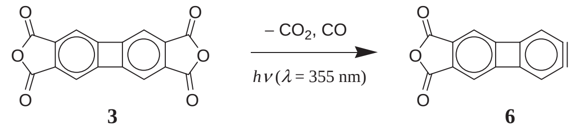
Figure 1. Observed IR spectrum (top) and theoretical IR spectrum of **3** (bottom) calculated at the B3LYP/6-31G* level. Calculated wavenumbers were scaled by 0.9614.[9]

upon irradiation at 355 nm (third harmonic generation (THG) pulses of Nd:YAG laser, 10 Hz, 3.4 mJ·pulse^{-1}). The IR bands marked with open circle (Figure 1) slowly decreased upon the irradiation. An IR band at 1028 $\mathrm{cm^{-1}}$ (marked with close triangle), which did not decrease upon 355-nm irradiation, was ascribed to impurity.

UV–vis absorption spectrum of the matrix (shown in Supporting Information)[14] showed the similar shape with those of other dianhydrides, **2**,[5,6] 2,3,6,7-naphthalenetetracarboxylic 2,3:6,7-dianhydride (**4**),[11] and 2,3,6,7-anthrathenetetracarboxylic 2,3:6,7-dianhydride (**5**). It was composed of intense absorption band at around 260 nm with weak absorption bands with vibronic structures at longer wavelength (324–370 nm). Little change was observed upon short irradiation at 308 nm and these bands decreased upon 355-nm irradiation, indicating these absorption bands should be assigned to the species showing IR bands marked with open circle. The lowest transition band was observed at 370 nm. The corresponding bands were observed at 309, 361, and 406 nm for **2**, **4**, and **5**, respectively. Given that the lowest transition band shift to longer wavelength reflecting the expansion of π-system, the lowest transition at 370 nm indicates that the compound showing the absorption has π-system with a size between naphthalene and anthracene. Results of time-dependent (TD) DFT calculation indicated that triphenylene derivative, and biphenyl derivative should show different UV–vis absorption bands as discussed in the Supporting Information.[14] Therefore, the observed UV–vis absorption spectrum strongly supports the assignment of **3**.

Upon 355-nm photolysis of **3**, several product IR bands appeared. Given the results on photolyses of other dianhydrides,[6,11] biphenylynedicarboxylic anhydride **6** would be the most promising photoproduct (Scheme 3).

It was supported by the appearance of CO band at 2141 $\mathrm{cm^{-1}}$. New C=O band appeared at 1796 $\mathrm{cm^{-1}}$ and increased with irradiation. Calculated results on **6** suggested that C=O IR band of **6** located at the slightly smaller wavenumber (1788 $\mathrm{cm^{-1}}$) than that of **3** (1792 $\mathrm{cm^{-1}}$). Calculated IR spectra indicated that **3** and **6** shows major IR bands at almost same wavenumbers. From the IR spectrum observed after 10-h irradiation, contribution of **3** was removed by weighted subtraction.[12] Then, the IR bands ascribable to photoproducts could be observed. These IR bands showed good correspondence with the calculated IR bands of **6** at the B3LYP/6-31G* level.[13] Thus, a major product of 355-nm photolysis of **3** was assigned to **6**, which should be a novel aryne species. It was confirmed that the IR bands ascribed to **6** decreased upon 266-nm irradiation. The study on the photolysis is still continuing.



Scheme 3.

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References and Notes

1 H. Heaney, *Chem. Rev.* **1962**, *62*, 81.
2 W. Sander, *Acc. Chem. Res.* **1999**, *32*, 669; H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem., Int. Ed.* **2003**, *42*, 502.
3 E. K. Fields, S. Meyerson, *Chem. Commun. (London)* **1965**, 474; R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, R. K. Solly, *Chem. Commun. (London)* **1966**, 407.
4 J. Kolc, *Tetrahedron Lett.* **1972**, *13*, 5321; O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, G. Orr, *J. Am. Chem. Soc.* **1973**, *95*, 6134; J. G. Radziszewski, B. A. Hess, Jr., R. Zahradnik, *J. Am. Chem. Soc.* **1992**, *114*, 52.
5 M. Moriyama, T. Sato, T. Uchimaru, A. Yabe, *Phys. Chem. Chem. Phys.* **1999**, *1*, 2267.
6 T. Sato, S. Arulmozhiraja, H. Niino, S. Sasaki, T. Matsuura, A. Yabe, *J. Am. Chem. Soc.* **2002**, *124*, 4512.
7 Neon matrixes at 6.7 K was employed because thick matrix can be prepared easily without the lost of transparency or peeling off.
8 I. R. Dunkin, in *Matrix-Isolation Technique A Practical Approach*, ed. by L. M. Harwood and C. J. Moody, Oxford University Press, New York, **1998**, p. 100.
9 A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.
10 IR bands ascribed to the product of this photolysis were appeared at 947, 920, 918, and 595 $\mathrm{cm^{-1}}$ with quite low absorbance (<0.005).
11 T. Sato, H. Niino, A. Yabe, *J. Photochem. Photobiol., A* **2001**, *145*, 3.
12 The contribution of **3** was completely removed by subtracting the baseline-corrected spectra of **3** (observed before photolysis) scaled with a factor of 0.31.
13 Observed and calculated IR bands of **6** at the B3LYP/6-31G* level. Calculated wavenumbers ($\mathrm{cm^{-1}}$) were scaled by 0.9614 and in parentheses: 608 (587), 740 (706), 837 (824), 909 (888), 974 (974), 1001, 1005 (1000), 1078 (1062), 1156 (1101), 1270 (1244), 1796 (1788), 1861 (1843).
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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