Photolysis of 1,2,3,4-Benzenetetracarboxylic Dianhydride in a Low-temperature Argon Matrix. Formation of C_6H_2 Reactive Intermediates

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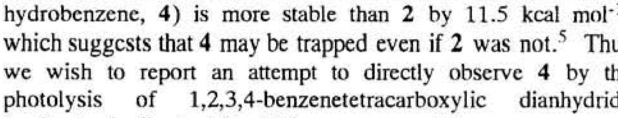
The photolysis of 1,2,3,4-benzenetetracarboxylic dianhydride in an argon matrix produced 1,3,5-hexatriyne *via* C_6H_2 reactive intermediates, similarly to the case of the photolysis of 1,2,4,5-benzenetetracarboxylic dianhydride. Formation of C_6H_2 reactive intermediates by elimination of CO_2 and CO was discussed.

Benzdiyne, tetradehydrobenzene, is one of challenging reactive intermediates from the viewpoint of direct observation, so that most studies of benzdiyne have been discussed in trapping experiments[1-3] and theoretical calculations.[4,5]

We have recently 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.[6] This was the first finding that a benzdiyne structure could be trapped by a matrix isolation method. On the other hand, in the photolysis of non-substituted 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride, **1**), 1,4-benzdiyne (1,2,4,5-tetradehydrobenzene, **2**) was not trapped in an argon matrix, although 1,3,5-hexatriyne (**3**), a C_6H_2 isomer of **2**, was confirmed as a final photoproduct.[7] An ab initio calculation has predicted that 1,3-benzdiyne (1,2,3,4-tetradehydrobenzene, **4**) is more stable than **2** by 11.5 kcal mol^{-1}, which suggests that **4** may be trapped even if **2** was not.[5] Thus we wish to report an attempt to directly observe **4** by the photolysis of 1,2,3,4-benzenetetracarboxylic dianhydride (mellophanic dianhydride, **5**) in an argon matrix.

Starting material **5** was synthesized from 1,2,3,4-tetramethylbenzene by the literature.[8,9] Matrix isolated samples of **5** in argon were prepared on CsI (for IR) and sapphire (for UV-vis) plates at 12 K. Photolyses of **5** were carried out by successive irradiation with XeCl (308 nm), KrF (248 nm), and ArF (193 nm) excimer lasers and followed by IR and UV-vis spectroscopies.

Irradiation of **5** with an XeCl laser gave IR bands at 1799 and 1810 cm^{-1} due to C=O stretching, together with the decrease of bands due to **5** (1800 and 1817 cm^{-1}) and the increase of bands due to carbon dioxide (2343 and 667 cm^{-1}) and carbon monoxide (2139 cm^{-1}) as shown in Figure 1(a)→(b). Compared with the photolysis of **1**, these C=O bands were assigned to benzyne **6**. On the other hand, benzocyclopropenone **7** as a precursor of **6** was not trapped, while its analog was trapped in the case of **1**.[7] Upon further irradiation the formed benzyne **6** did not decompose significantly.



Scheme 1.

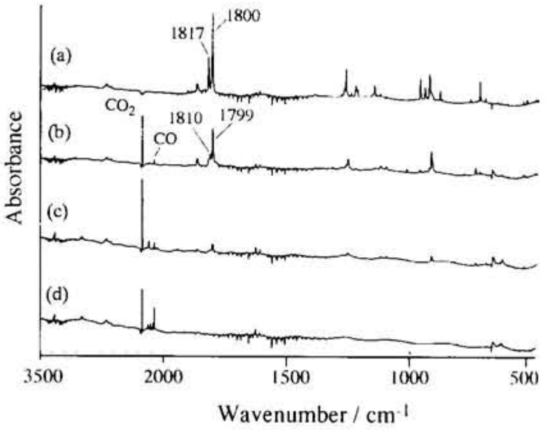


Figure 1. (a) IR spectra of matrix isolated **5** (argon, 12 K). (b) IR spectrum obtained after irradiation of **5** with 8000 pulses of XeCl laser. (c) IR spectrum after irradiation of (b) with 5000 pulses of KrF laser. (d) IR spectrum after irradiation of (c) with 10000 pulses of ArF laser.

Subsequent irradiation of the matrix with a KrF laser resulted in the decrease of the IR bands due to **6**, along with the further increase of CO_2 and CO. Simultaneously, new bands appeared at 3335, 3317, 2245, and 623 cm^{-1} (Figure 1(b)→(c)). Among these bands, the growth rate of 2245 cm^{-1} band was different from those of other bands. In other words, two kinds of species, one having the IR band at 2245 cm^{-1} and the other having the bands at 3335, 3317, and 623 cm^{-1}, were produced in this stage. The former species was assigned to tricarbon monooxide, C_3O, by the literature.[10,11] The observed intensity of 2245 cm^{-1} band was too weak whereas the absorption coefficient of C_3O should be very strong. Hence, it was presumed that the formation of C_3O was a minor pathway and the main reaction was the formation of unidentified species having the bands at 3335, 3317, and 623 cm^{-1}.

Continued irradiation of the matrix with an ArF laser after irradiation with the XeCl and KrF lasers resulted in the decrease of the IR bands due to the above-mentioned species and the appearance of new bands at 3324 and 628 cm^{-1} (Figure 1(c)→(d)). On the other hand, the UV-vis spectrum was measured under the same condition as carried out in the IR study. It showed an intense band at 223 nm (Figure 2(d)), which was assigned to **3** by the comparison with the results of matrix isolation of **3** formed from the photolysis of benzene[12] and the flash vacuum pyrolysis of **1**. From these results, we concluded that the photolysis of **5** produced **3** as a final photoproduct similarly to that of **1**.

Figure 3 shows IR spectral changes in the region of 3400-3200 cm^{-1} upon irradiation with the ArF laser. In both the photolyses of **1** and **5**, the peak at 3335 cm^{-1} decreased and the peak at 3317 cm^{-1} shifted to 3324 cm^{-1} as the number of laser pulses

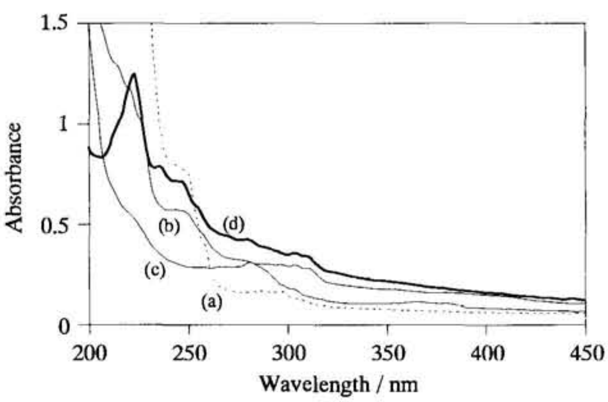


Figure 2. (a) UV-vis spectrum of matrix isolated **5** (argon, 12 K). (b) UV-vis spectrum obtained after irradiation of (a) with 10000 pulses of XeCl laser. (c) UV-vis spectrum obtained after irradiation of (b) with 15000 pulses of KrF laser. (d) UV-vis spectrum obtained after irradiation of (c) with 18000 pulses of ArF laser (bold line).

increased. The UV-vis spectra corresponding to this change show the formation of **3** from its precursor (Figure 2(c)→(d)). Therefore, the unidentified species having the IR bands at 3335, 3317, 623 cm^{-1} should be a precursor of **3**. In addition, the molecular formula of the precursor should be C_6H_2, because it was produced by the complete elimination of CO_2 and CO from **6**. The IR bands at 3335, 3317, 623 cm^{-1} due to the C_6H_2 species were ascribable to an acyclic compound having -C≡C-H moieties by the literatures.[13] This assignment was supported from the results of the photolysis of D-enriched **1**.[14] On the basis of the above-mentioned results, the structure of the unidentified C_6H_2 species would be narrowed down to the following: one is biradical **8** and the other is carbene **9** (Scheme 2). Although both the structures have a C=C moiety in addition to -C≡C-H assigned above, the IR band due to $\nu_{C=C}$ would hide in the region of H_2O bands around 1700-1500 cm^{-1}. With regard to the formation of **8** or **9**, a plausible mechanism is shown in Scheme 2, although we must clarify participation and reactivity of benzdiynes.

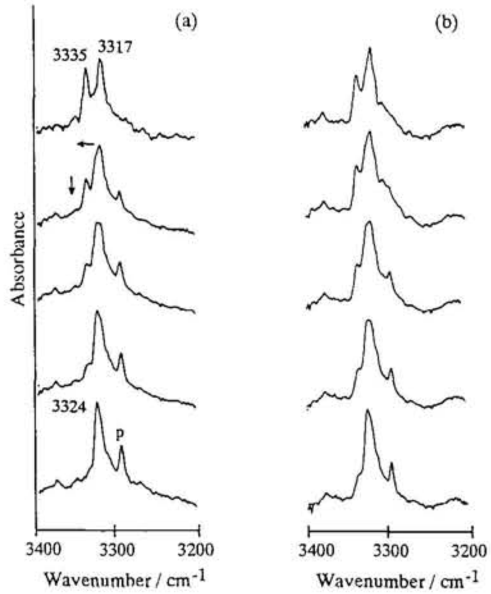
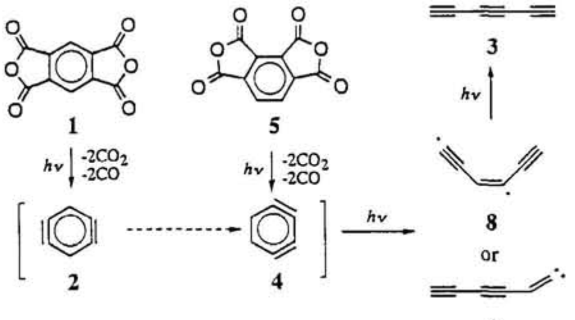


Figure 3. (a) IR spectra obtained after irradiation of **5** with 5000 pulses of KrF laser (top) and afer continued irradiation with 1000, 3000, 5000, 10000 pulses of ArF laser (to the bottom in order). (b) IR spectra obtained after irradiation of **1** with 10000 pulses of KrF laser (top) and afer continued irradiation with 2000, 7000, 10000, 20000 pulses of ArF laser (to the bottom in order). Mark p, see reference 15.



Scheme 2.

Consequently, although benzdiyne **4** could not be trapped similarly to **2**, this work will arouse further interest in photochemistry of C_6H_2 species including benzdiynes.

References and Notes

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14 Unpublished results.
15 The increasing band at 3294 cm^{-1}, marked p, would be assigned to the polymer of the photoproducts from the result of annealing experiments in which its intensity slightly increased, although the band at 3324 cm^{-1} was decreased.