

Direct Observation of Benzdiyne: Photolysis of 1,4-Bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride in an Argon Matrix

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Direct observation of *o*-benzyne (*o*-didehydrobenzene) has extensively been studied by IR,¹ UV–vis,² and NMR³ spectroscopies using a matrix isolation technique. On the other hand, although the existence of benzdiyne (tetrahydrobenzene, **1**) has been suggested in theoretical studies⁴ and from final products in organic reactions,⁵ the direct observation of **1** has not yet been reported. Recently, we reported an attempt to observe **1** in the photolysis of 1,2,4,5-benzenetetracarboxylic dianhydride (**2**) in an argon matrix.⁶ In that work, **1** was observed neither in the IR nor UV–vis spectra. However, the stepwise photo-reaction of **2** was revealed by selective irradiation using three kinds of excimer lasers. In the initial stage, the photolysis of **2** produced a benzyne derivative through a benzocycloproponone intermediate with stepwise elimination of CO₂ and CO. Subsequent photolysis caused cleavage of the aromatic ring to produce the acetylenic compounds, 1,3,5-hexatriyne and 1,3-butadiyne, as the main products and ketenes as minor products (Scheme 1).^{6,7}

The fact that **1** was not observed in the photolysis of **2** could be explained in terms of facile hydrogen migration in the electron-rich structure. In order to suppress the hydrogen migration, **1** was substituted with bulky groups. Moreover an electron-withdrawing substituent would stabilize the electronic state of **1**. Thus, we report the photolysis of 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (**3**)⁸ in an argon matrix.

The photolysis of **3** involving irradiation with three excimer lasers of XeCl (308 nm), KrF (248 nm), and ArF (193 nm) in an argon matrix at 12 K was followed by IR and UV–vis spectroscopies.

From the IR spectra it was found that the irradiation of **3** at 308 nm gave two carbonyl intermediates stepwise along with the elimination of CO₂ (2343 and 663 cm⁻¹) and CO (2143 cm⁻¹). The first intermediate with a carbonyl peak at 1858 cm⁻¹

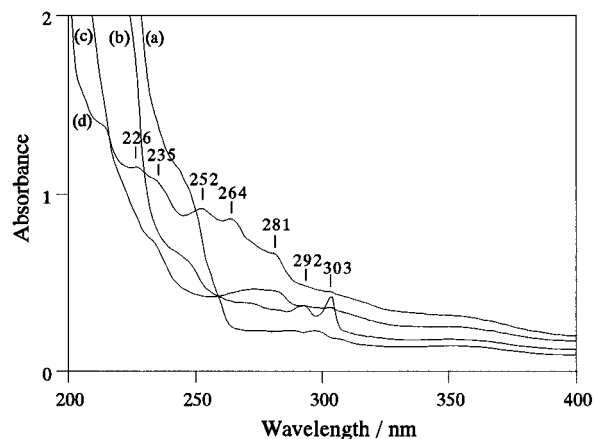
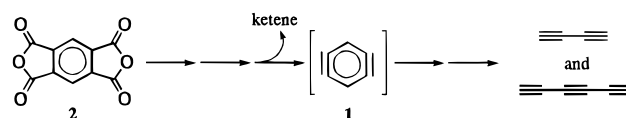
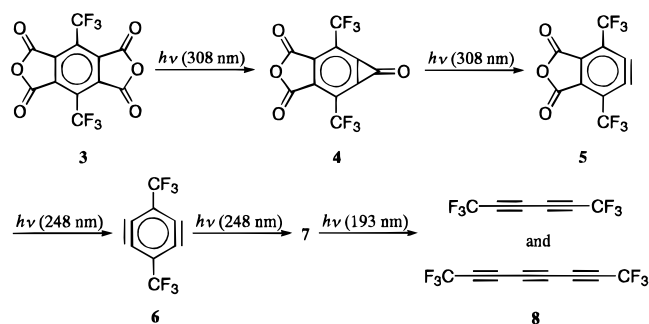


Figure 1. UV spectra obtained by the stepwise (XeCl → KrF → ArF) photolysis of **3** (argon matrix, 12 K): (a) before irradiation; (b) after irradiation with 15 000 pulses of XeCl laser (308 nm); (c) 15 000 pulses of KrF laser (248 nm); (d) 20 000 pulses of ArF laser (193 nm).

Scheme 1



Scheme 2



was tentatively assigned to benzocycloproponone (**4**), since this peak is in good agreement with those of typical cyclopropanones.^{6,9} The assignment for **4** was further supported by the UV–vis spectrum where the matrix containing **4** showed sharp peaks at 292 and 303 nm (Figure 1), which were quite similar to those (287 and 296 nm)⁶ of the benzocycloproponone derivative produced in the photolysis of **2**. The subsequently produced intermediate that had a strong absorption at 1807 cm⁻¹ was assigned to benzyne **5** by a trapping experiment as follows. After **5** was generated by the photolysis of **3** in an argon–furan (ca. 1000:3) matrix at 12 K, the argon was removed by gentle warming to room temperature. The residue was examined by GC–MS, which revealed the adduct of **5** with furan ($M^+ = 350$). As shown in Scheme 2, these results suggested that the photolysis of **3** proceeded stepwise in the initial stage similarly to that of **2** as reported previously.⁶

After most of **3** was converted to **5**, continued irradiation of the matrix sample at 248 nm resulted in a further increase in intensity of the IR peaks of CO₂ and CO along with the decrease of peaks due to **5**. Simultaneously, new bands which were not assigned to a carbonyl or ketene group appeared (Figure 2). Although these peaks did not appear discretely in the spectrum as the number of laser pulse increased, we could classify them

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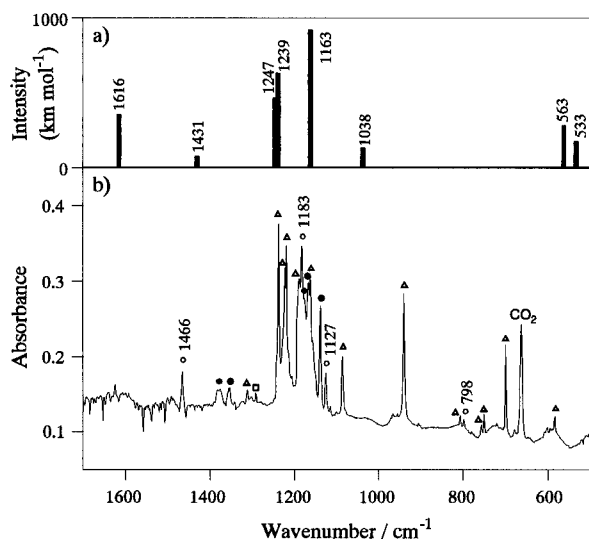


Figure 2. (a) Theoretical (RHF/6-31G*) IR spectrum of **6**. The frequencies were scaled by an arbitrary factor of 0.89. (b) IR spectra obtained by the photolysis of **3** with 2500 pulses of laser at 248 nm (argon matrix, 12 K); the peaks marked with \square , \triangle , \circ , and \bullet are due to photoproducts **4**, **5**, **6**, and **7**, respectively. Unmarked weak peaks are due to an impurity and starting material **3**.

Table 1. IR Frequencies (cm^{-1}) of **6–8** Observed by the Photolysis and Pyrolysis of **3**

6		7		8			
freq	int	assign ^a	freq ^a	int	freq ^a	int	assign ^b
1466	m	ring str	1377 (1379)	m	2212 (2211)	w	C≡C str
1183	s	} C–F str	1354 (1355)	m	1227 (1226)	s	} CF str
1127	m		1176 (1173)	s	1207 (1205)	s	
798	w	C–CF ₃ def	1169	s			
			1139 (1137)	s			

^a The values in parentheses are the pyrolysis results. ^b Tentative assignment. Str = stretch. Def = deformation.

into three species (**6–8**) by careful analysis of the peak intensities (Table 1). Irradiation of the matrix sample containing **6–8** at 193 nm gave a further increase of the peaks due to **8** while the peaks due to **6** and **7** decreased. On the other hand, when the starting material **3** was irradiated with 248 or 193 nm laser from the start, it was confirmed that **6–8** were produced *via* **5**, similar to the case of stepwise laser irradiation. These results showed that the irradiation wavelength controlled the product distribution without change in the reaction path from **3** to **8**. Therefore, our selective irradiation with three kinds of excimer lasers proved to be useful in the investigation of each intermediate produced in the consecutive photolysis of **3**.

To obtain additional support for the assignment of the final photoproducts of **3**, we carried out the flash vacuum pyrolysis of **3** at 1000 °C, since McNaughton and co-workers reported that pyrolysis of **2** at 1020 °C yielded ring opened products of **1**, 1,3,5-hexatriyne, 1,3-butadiyne, and acetylene as final products of **2**.¹⁰ The products of **3** deposited on a CsI plate at 12 K were analyzed by IR spectroscopy. The peaks due to **7** and **8** were observed, whereas the peaks due to **6** were not

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observed. On the other hand, the photolysis in the final stage was studied by UV–vis spectroscopy under the same conditions as those carried out in the above-mentioned IR study (Figure 1). Irradiation of **5** at 248 nm resulted in the appearance of a new broad band at 270–280 nm. These bands were assigned to **6** or **7** by comparison with results from the IR study. Subsequent irradiation of the matrix at 193 nm, which was responsible for the formation of **8** in the IR study, caused the appearance of new maxima at 226, 235, 252, 264, and 281 nm. The peaks at $\lambda < 250$ nm were in good agreement with those of 1,1,1,6,6,6-hexafluoro-2,4-hexadiyne,¹¹ and the peaks at $\lambda > 250$ nm suggested the formation of 1,1,1,8,8,8-hexafluoro-2,4,6-octatriyne, which is a longer conjugated compound.¹² The assignment to these acetylenic compounds was further supported by the observation of the C≡C stretching band at 2212 cm^{-1} in the IR spectra.¹¹ With regard to **7**, although we could not definitely identify it in this work, it should be a ring-opened compound, because it was produced by the pyrolysis at such a high temperature (1000 °C). Additionally, we could confirm that **7** was a precursor of **8**.

We interpret the formation of **6** in the following way. In the consecutive photolysis, the elimination of CO₂ and CO from **5** prevailed over the formation of carbonyl and ketene products. Therefore, the intermediate **6** formed from **5** should have the molecular formula C₆(CF₃)₂. Next, the peak 1466 cm^{-1} due to **6** may be ascribed to aromatic ring stretching, since the corresponding peak appears at 1451 cm^{-1} for benzyne.^{1a} This assignment was supported by ab initio calculations at the RHF/6-31G* level (RHF = restricted Hartree–Fock), which predicted that aromatic ring stretching of **6** should lie at 1616 and 1431 cm^{-1} (Figure 2).¹³ From these results, it should be noted that the intermediate **6** has a benzdiyne structure with two triple bonds. For *o*-benzyne,¹ it has been established that a very weak peak at 1846 cm^{-1} observed by Radziszewski^{1a} should be ascribed to the C≡C stretching, after many aggressive discussions over two decades since the first suggestion by Chapman.^{1b} For benzyne, however, we have not observed the corresponding peak. This result should not be a negative proof for assignment of benzyne, since the calculations predicted no definite peak for the C≡C stretching. Direct observation of the C≡C peaks will be a further challenging subject. In this work we could trap the benzdiyne derivative, 1,4-bis(trifluoromethyl)benzdiyne, and directly observe its IR spectrum by substitution of trifluoromethyl groups on benzyne.

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