Generation of $C_{10}H_4$ species in a low-temperature argon matrix: consecutive photolysis of 1,2;5,6-naphthalenetetracarboxylic dianhydride†

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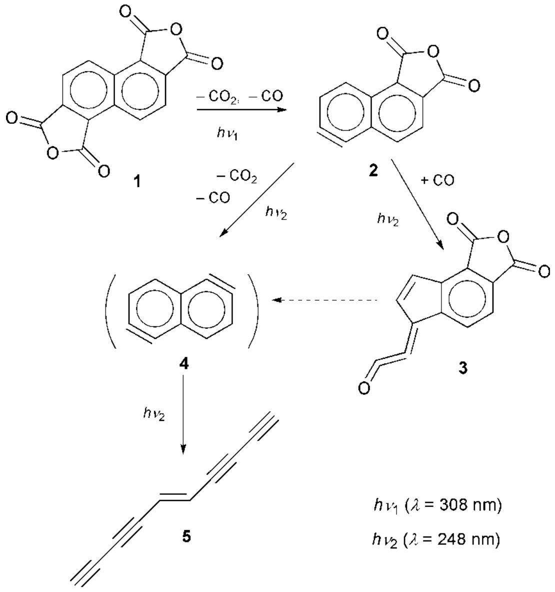
Received (in Cambridge, UK) 30th March 2000, Accepted 30th May 2000

1,2;5,6-Naphthalenetetracarboxylic dianhydride has been consecutively photolyzed in a low-temperature argon matrix by wavelength-selective irradiation; dec-5-ene-1,3,7,9-tetrayne, which is the second $C_{10}H_4$ isomer, was generated as the final product.

Benzdiyne and naphthdiyne, in which two triple bonds are contained within one aromatic system, are challenging reactive intermediates. Recently, we reported the direct observation of a benzdiyne derivative by photolysis of 1,4-bis(trifluoromethyl)-2,3;5,6-benzenetetracarboxylic anhydride in a low-temperature argon matrix, which was the first finding that a benzdiyne could be trapped by the matrix isolation method.[1] However, we were unable to confirm the generation of parent benzdiynes (C_6H_2) by the consecutive photolysis of the corresponding precursors.[2–4] In a series of experiments, we confirmed the generation of hexa-1,3,5-triyne, the most stable C_6H_2 isomer, as a final photoproduct. This final product was formed by the ring opening of the benzdiynes.[4] Ring-opening reactions resulting in the generation of an acetylenic compound have also been reported in the case of benzyne.[5] These findings suggested that arynes containing diyne species are good precursors for acetylenic compounds, which are difficult to prepare by normal synthetic methods.

These acetylenic compounds, oligoynes and the compounds with a cross-conjugated π-system, have attracted much attention in the past. For example, Diederich *et al.* have thoroughly investigated such compounds in a series of research on molecular and polymeric carbon allotropes,[6,7] reporting the synthetic preparation of tetraethnylethene,[8] which is the only isomer with a $C_{10}H_4$ molecular formula identified so far. The acetylenic compounds are of interest as a building block for novel carbon networks.

Here, we report the consecutive photolysis of 1,2;5,6-naphthalenetetracarboxylic dianhydride **1**[9] in a low-temperature argon matrix (Scheme 1). The photolysis, which used several lasers, was carried out in an attempt to generate naphth-1,5-diyne. A novel acetylenic compound with a cross-conjugated π-system was observed as the final product, as well as stepwise-produced reactive intermediates.



Scheme 1

Crystallites of **1** were vaporized at 145 °C and co-deposited with argon (99.9999%) onto a CsI or CaF_2 plate in a sample chamber whose pressure was kept at $< 10^{-5}$ Torr.[10] Precursor **1** was photolyzed using a XeCl excimer laser (308 nm, 5 Hz, *ca.* 10 mJ cm^{-2} $pulse^{-1}$). The photolysis was followed by FTIR and UV–VIS absorption spectroscopies. Upon irradiation, new IR bands ascribable to photogenerated species appeared, while the IR bands of **1** decreased. The appearance of IR bands arising from CO and CO_2 indicated that decarboxylation and decarbonylation of **1** were induced upon irradiation at 308 nm. This photolysis resulted in the generation of an intermediate having a naphthyne structure, **2**. Prolonged irradiation at 308 nm caused the formation of ketene species **3** by the addition of CO to **2**, which was confirmed by the appearance of the characteristic IR bands at 2082 and 2087 cm^{-1}.[11] The intermediates **2** and **3** were identified on the basis of their FTIR spectra being in good agreement with the theoretical IR spectra calculated by density functional theory (B3LYP/6-31G** level).[12] The obtained intermediate **2** was photolyzed upon irradiation at 248 nm (KrF excimer laser, 5 Hz, 8 mJ cm^{-2} $pulse^{-1}$). During the initial stage of irradiation, generation of **3** was the dominant process. However, upon prolonged irradiation, the generation of **3** was diminished and the generation of CO and CO_2 became the dominant process. Since the IR bands of **2** decreased upon irradiation, it was suggested that this process resulted in the formation of naphth-1,5-diyne ($C_{10}H_4$, **4**). However, IR bands ascribable to **4** were not observed. Upon irradiation, only two weak IR bands at 621 and 3323 cm^{-1} appeared, other than the increasing peaks of CO and CO_2. These weak bands were ascribable to the C–H bending and stretching modes of acetylenic compounds. Moreover, upon further irradiation at 248 nm, **3** was also photolyzed slowly. Even at this stage, increases in the IR bands of CO, CO_2 and the acetylenic species was still observed.

Taking into account benzyne[5] and benzdiynes,[2–4] it is plausible that acetylenic compounds may be generated by ring-opening of **4**. Certainly, the acetylenic C–H stretching band at 3323 cm^{-1} was observed at almost the same position as that of butadiyne (3324–6, 3340 cm^{-1}), hexatriyne (3324–7 cm^{-1}), or hex-1-ene-3,5-diyne (3324 cm^{-1}), which were formed by ring-opening reactions of benzyne[5] and/or benzdiynes[2–4] or the photo-decomposition of benzene.[13] It should be noted that several peaks were observed when several kinds of acetylenic compounds were formed simultaneously.[3,13] In our experiment, one C–H stretching peak accompanied by a shoulder on its higher wavenumber side was observed at 3323 cm^{-1} as shown in Fig. 1. Moreover, no peaks ascribable to other photo-

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† Electronic supplementary information (ESI) available: synthesis of **1**, theoretically estimated IR data for *cis*- and *trans*-dec-5-ene-1,3,7,9-tetrayne and details of TD-DFT calculations. See http://www.rsc.org/suppdata/cc/b0/b002555k/

DOI: 10.1039/b002555k

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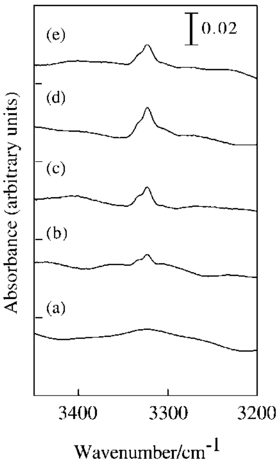

Fig. 1 FTIR spectra (C–H stretching band) upon photoirradiation of **1** with a KrF excimer laser: (a) before irradiation, (b) after 9000 pulses, (c) after 21000 pulses, (d) after 66000 pulses and (e) after 1800 pulse irradiation with the ArF excimer laser.

generated species were observed. Thus, the acetylenic $C_{10}H_4$ species was solely or dominantly generated: fragmentation of the $C_{10}H_4$ species can be excluded as a minor process. The species formed upon irradiation at 248 nm showed specific UV–VIS absorption bands as shown in Fig. 2. After irradiation by the XeCl excimer laser, absorption bands at 305, 296, 250 and 205 (broad) nm were observed. The bands at 250 and 205 nm were assigned to **2**, which was the major species existing upon irradiation at 308 nm and photolyzed upon irradiation at 248 nm. In contrast, the bands at 305 and 296 nm were assigned to **3**, since these bands also grew up in the initial irradiation at 248 nm. During this stage, increases in the bands at 372, 354, 338 and 305 nm were clearly observed, which were also assigned to **3**. Under prolonged irradiation, the absorption bands of **3** decreased slowly, and other bands emerged at 317, (296), 280, 213, 203 and 195 nm. These bands were assigned to the acetylenic $C_{10}H_4$ compound showing the C–H stretching band at 3323 cm^{-1}. Similar vibronic absorption bands have frequently been observed in acetylenic compounds.[14,15] As mentioned above, it was assumed that the acetylenic $C_{10}H_4$ compound was generated by ring-opening of **4**. Compound **4** has C_{2h} structure, in which two *o*-benzyne molecules are symmetrically fused. Considering that hex-1-ene-3,5-diyne was formed by ring-opening of benzyne,[5] we tentatively assigned the compound to dec-5-ene-1,3,7,9-tetrayne ($C_{10}H_4$, **5**), which has not been isolated before. This assignment was supported by the following discussions. The theoretical prediction shows two C–H bending bands (581 and 587 cm^{-1}) and one C–H stretching band (3354 cm^{-1}) with intensities >90 km mol^{-1}. On the other hand, the experimental results showed one C–H bending band (621 cm^{-1}) and one C–H stretching band (3323 cm^{-1}) with a shoulder as described above. Only one bending band would be ascribed to two neighboring bands and the appearance of the shoulder on the stretching band would be explained by matrix splitting.[16] Although tetraethynylethene, which is also a $C_{10}H_4$ species, would seem to be a possible candidate, it can be dismissed because it shows a quite different UV–VIS absorption spectrum.[8] The lowest transition band of the acetylenic $C_{10}H_4$ compound (317 nm) was seen in a longer wavelength region than that of hex-1-ene-3,5-diyne (275 nm in an Ne matrix).[5] This indicated that the π-conjugation system of the observed acetylenic compound was extended more than that of hex-1-ene-3,5-diyne. Electronic absorption spectra can be well described by time-dependent density functional theory (TD-DFT) calculations.[17] Transition energies and oscillator strengths of **5** calculated by the TD-DFT method are shown by bars in Fig. 2, which show favorable correspondences with the experimental result.[18] Thus, the observed acetylenic $C_{10}H_4$ compound was assigned to dec-5-ene-1,3,7,9-tetrayne.

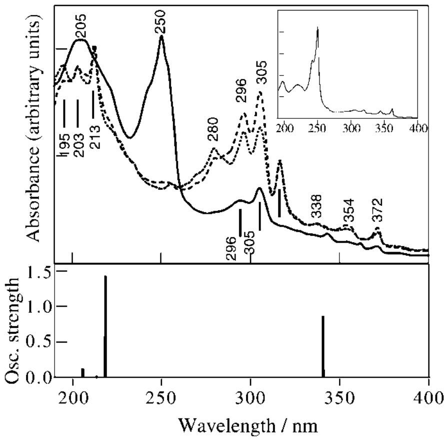

Fig. 2 (Top) UV spectra of the photolysis of **1** with a Nd : YAG laser (THG), XeCl and KrF excimer lasers in an argon matrix at 11 K: (——) after irradiation with Nd:YAG laser (THG) and XeCl excimer laser, (– – –) after successive irradiation with 3000 pulses and (····) 9000 pulses of the KrF excimer laser. Inset: UV spectra of **1** observed before irradiation in the argon matrix. (Bottom) transition energies and oscillator strengths of **5** calculated by the TD-DFT method.

In conclusion, the reactive intermediates **2** and **3** were identified on the basis of their FTIR spectra being in good agreement with calculated IR spectra. The aromatic $C_{10}H_4$ species, naphth-1,5-diyne, converted to a $C_{10}H_4$ species with acetylenic C–H moieties by ring-opening reactions. The acetylenic $C_{10}H_4$ species was dec-5-ene-1,3,7,9-tetrayne, the second $C_{10}H_4$ isomer, which has not previously been prepared.

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9 Compound **1** was synthesized from 2,6-dimethylnaphthalene following the literature procedure [Y. Dozen and S. Fujishima, *Yukigoseigaku*, 1972, **30**, 964 (Japanese)]. Details of the synthesis are provided as ESI†.

10 *Spectroscopic data* for **1** (Ar matrix, 11 K) UV–VIS λ/nm: 362, 355, 350, 329, 319, 306, 250, 242, 221, 198. FTIR ν/cm^{-1} 3094vw, 1862s, 1790vs, 1625w, 1389w, 1385w, 1292s, 1231w, 1175m, 1132m, 921vs, 869m, 790vw, 749m, 707w, 635w, 598w, 565m, 531w.

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16 In the results on DFT calculations for **5** (C_{2h} structure), another symmetrically forbidden C–H stretching mode (A_g 3354.6 cm^{-1}, 0 km mol^{-1}) was observed at higher wavenumber than that of the symmetrically allowed mode (B_u 3354.2 cm^{-1}, 341 km mol^{-1}). In the argon matrix, compound **5** may not be able to form an ideal symmetrical structure because it confined within a matrix cavity. In this case, the IR band corresponding to the A_g mode could be observed as a weak shoulder on the high wavenumber side of main C–H stretching band. As another possibility, we should consider the *trans*-confomer formed by *cis–trans* isomerization of the central C=C bond under photoirradiation (two acetylenic C–H stretching modes of the *trans*-conformer are predicted at higher wavenumbers: B_2 3355.2 cm^{-1}, 138 km mol^{-1}; A_1 3355.7 cm^{-1}, 120 km mol^{-1}).

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18 TD-DFT calculations were performed: see ESI.†