

# Direct observation of 1,2-didehydronaphthalene in a low temperature argon matrix: consecutive photolysis of 1,2-naphthalenedicarboxylic anhydride

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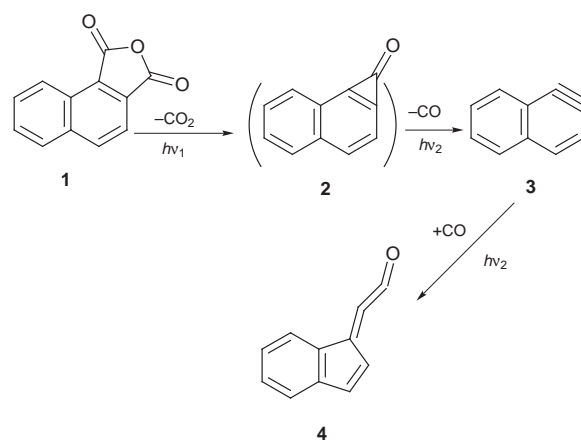
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1,2-Didehydronaphthalene (1-naphthyne) was produced in a low temperature argon matrix by wavelength-selective photolysis of 1,2-naphthalenedicarboxylic anhydride, which was confirmed by comparison of its FTIR spectrum with the theoretical IR spectrum calculated by density functional theory.

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. Among them, only the simplest member, *o*-benzyne, has been thoroughly characterized by its direct observation using matrix isolation spectroscopy.<sup>1</sup> Recently, its peculiar structure has been discussed on the basis of both experimental and theoretical results. The length of the triple bond in *o*-benzyne estimated by <sup>13</sup>C dipolar NMR<sup>2</sup> has shown that theoretical calculations, particularly calculations at the density functional theory (DFT) level, have provided reasonably accurate geometries of such an unstable species.<sup>3</sup> On the other hand, larger arynes, dehydrogenated polycyclic aromatic hydrocarbon molecules (PAHs), have scarcely been characterized by direct observation, although dehydrogenated and/or ionized PAHs have been recognized as important components of the interstellar medium.<sup>4</sup> Whereas some experimental results of ionized species are available,<sup>5</sup> little data on dehydrogenated PAHs have been presented: there is only one brief experimental report on 2-naphthyne.<sup>6</sup> Herein we wish to report the first direct observation of 1-naphthyne in a low temperature argon matrix. The FTIR spectrum of this compound is discussed on the basis of DFT calculation (B3LYP/6-31G\*\* level).<sup>7</sup>

1,2-Naphthalenedicarboxylic anhydride **1** was photolyzed in an argon matrix at 11 K. During the experiment, the pressure in a sample chamber was kept under 10<sup>-5</sup> Torr. Crystallites of **1** were vaporized at 50 °C and co-deposited with argon (99.9999%) onto a CsI plate.<sup>8</sup> It has been reported that the efficiency of photo-decomposition of anhydrides decreases as the pressure of a buffer gas increases in the gas phase and approaches zero in a condensed medium.<sup>9</sup> Therefore, a high intensity light is necessary to photolyze the anhydride in a cryogenic matrix.<sup>10</sup> Moreover, the choice of an appropriate wavelength for photolysis is quite important in order to suppress the multiple reactions proceeding simultaneously. Since the lowest transition band of matrix-isolated **1** observed was at 356 nm in its UV-VIS absorption, we used the third harmonic pulse of Nd:YAG laser (355 nm, 10 Hz, 4 mJ cm<sup>-2</sup> pulse<sup>-1</sup>) to photolyze **1**. The photolysis was followed by FTIR spectroscopy. Irradiation at 355 nm led to the diminution of the intensities of all the IR bands of **1** and concomitant growth of new IR bands ascribable to the first intermediate **2**<sup>11</sup> and CO<sub>2</sub> (2343 and 666 cm<sup>-1</sup>). No IR band due to CO appeared in this photolysis. Thus it was confirmed that selective decarboxylation of **1** resulted in the formation of a C<sub>10</sub>H<sub>6</sub>-CO species **2**. Naphtho[*a*]cyclopropanone (in parentheses in Scheme 1) is a possible structure for **2** by analogy with the photolysis of phthalic anhydride.<sup>1a</sup> Indeed, the observed FTIR bands, except the C=O stretching bands, were in good agreement with the calculated vibrational bands of naphtho[*a*]cyclopropanone.<sup>11</sup> Meanwhile, four bands ascribed to this mode were observed at



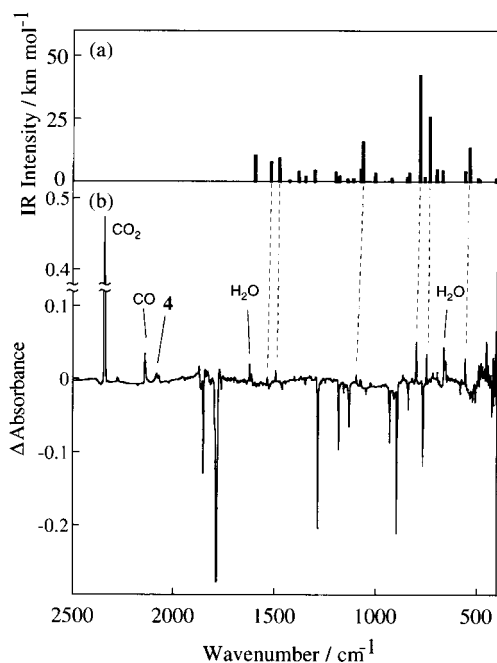
1832, 1843, 1856 and 1873 cm<sup>-1</sup>, although only one band was predicted theoretically for the C=O stretching mode. Such complex IR bands have often been observed for ketenes in cryogenic matrices.<sup>12</sup> Thus, we tentatively assigned **2** to naphtho[*a*]cyclopropanone. This compound was stable under prolonged irradiation at 355 nm.

To photolyze **2**, a high-pressure mercury lamp (500 W) was used through a 20 cm water filter and a UV-cut off glass filter (> 290 nm) since the UV absorption edge of **2** was observed at 320 nm in the matrix. In contrast to the photolysis of **1**, compound **2** was photolyzed in a rather short time upon irradiation. New bands due to the second intermediate **3** (Table 1) and CO (2142 cm<sup>-1</sup>) appeared, while the IR bands of **2** disappeared upon irradiation. In particular, since the band of CO

**Table 1** Observed FTIR data for **3** in an argon matrix and calculated data for 1-naphthyne

Observed for <b>3</b>		Calculated for 1-naphthyne	
$\tilde{\nu}/\text{cm}^{-1}$	Integrated intensity <sup>a</sup> (relative value)	$\tilde{\nu}^b/\text{cm}^{-1}$	IR intensity km mol <sup>-1</sup>
452.2	43	390.4	70
558.4	22	538.4	14
—	—	701.6	5
749.3	37	736.3	26
799.4	42*	786.4	42
1072.3	11	1066.7	16
1077.2	8	1076.6	5
1494.7	11	1494.7	9
1537.2	6	1521.1	8
—	—	1600.1	11
—	—	3065.6	10
3028.0, 3048.3,	38	3078.3	22
3088.8	—	3088.1	16
—	—	3092.3	21

<sup>a</sup> For comparison with calculated values, integrated intensities were normalized based on the value marked by an asterisk. <sup>b</sup> Scaled by 0.9614.<sup>14</sup>



**Fig. 1** (a) Theoretical IR spectrum of 1-naphthynes calculated at the B3LYP/6-31G\*\* level. Frequencies have been scaled by a factor of 0.9614.<sup>14</sup> (b) Difference FTIR spectrum before and after irradiation of **1** with 95000 pulses of THG of Nd:YAG laser followed by 1.5 min with a high-pressure mercury lamp (>290nm). Positive peaks correspond to **3** and negative peaks to **1**.

appeared with diminution of all the C=O stretching bands of **2**, it was revealed that a C<sub>10</sub>H<sub>6</sub> species was formed by decarbonylation of **2**. The observed IR spectrum was compared with the theoretical IR spectrum of 1-naphthynes calculated at B3LYP/6-31G\*\* level.<sup>13</sup> As shown in Fig. 1, all the predicted bands with intensities > 5 km mol<sup>-1</sup> (listed in Table 1), except those at 701.6 and 1600 cm<sup>-1</sup>, were observed in the experimental spectrum. The latter two bands could not be identified probably because of overlap with those of CO<sub>2</sub> and H<sub>2</sub>O produced by the inevitable small leakage in the apparatus. Frequency deviations for all the bands except that observed at 452 cm<sup>-1</sup> were within 20 cm<sup>-1</sup>. These deviations are reasonably small at the computational level.<sup>13</sup> On the other hand, the relatively large deviation (62 cm<sup>-1</sup> underestimated) for the band at 452 cm<sup>-1</sup> can be explained as follows. The band is due to the ring deformation mode containing angular motions of the C–C≡C moiety. In the vibrational analysis of *o*-benzynes at the same computational level, the frequency of the corresponding mode was underestimated by 83 cm<sup>-1</sup> from the observed frequency.<sup>1a</sup> Therefore, this deviation appears to be peculiar to the triple bond in arynes at the computational level. Moreover, no other IR bands ascribed to by-products formed by ring opening<sup>15</sup> or ring deformation<sup>16</sup> were observed. Thus, we conclude that the obtained C<sub>10</sub>H<sub>6</sub> species can be assigned to 1-naphthynes.

Incidentally, in view of the keen debate concerning *o*-benzynes,<sup>1</sup> we should comment on the stretching mode of the C–C triple bond in **3**. For 1-naphthynes, the frequency and intensity of this mode were predicted as 1988 cm<sup>-1</sup> and 0.0983 km mol<sup>-1</sup>, respectively. Although we could observe all the bands with predicted intensity > 5 km mol<sup>-1</sup>, the observation of the C≡C stretching band of 1-naphthynes was not possible under our experimental conditions.

By prolonged irradiation (>290 nm) of **3**, new IR bands slowly appeared at 2084 and 2072 cm<sup>-1</sup>. These bands could be ascribed to benzocyclopentadienyldeneketene **4** according to the literature.<sup>1a</sup> This result shows that **3** reacts easily with CO to form **4** upon the irradiation. This reaction also occurred upon irradiation using the fourth harmonic pulse of the Nd:YAG laser (266 nm, 10 Hz, 3 mJ cm<sup>-2</sup> pulse<sup>-1</sup>). By contrast, 2-naphthynes<sup>17</sup> did not form the corresponding ketene upon irradiation

at 266 nm. These results indicate differences in reactivity of the two naphthynes. The characteristics of the triple bond in arynes should be responsible for their reactivity. In the calculated geometries of these naphthynes, the lengths of triple bonds in these naphthynes were apparently different; 1.241 and 1.260 Å for 1- and 2-naphthynes, respectively.

In conclusion, we successfully produced 1-naphthynes by wavelength-selective photolysis of **1** in a low temperature argon matrix. Observed differences in reactivity of the two naphthynes is of interest from the viewpoint of their reactivity–structure profile. Further detailed study is in progress.

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## Notes and references

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- 1** (Ar matrix, 11K) UV-VIS ( $\lambda$ /nm): 356, 349, 339, 333, 324, 319, 311, 306, 250, 248, 243, 211. FTIR ( $\tilde{\nu}$ /cm<sup>-1</sup>): 3098vw, 3068vw, 1852m, 1787s, 1461w, 1348w, 1286s, 1182m, 1158w, 1131m, 931m, 896s, 839m, 767m, 747w, 582w, 507w.
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- The quantum yield of the photolysis of **1** isolated in the argon matrix was estimated as ca. 10<sup>-4</sup>.
- 2** (Ar matrix, 11 K) UV-VIS ( $\lambda$ /nm): 316, 309, 303, 296, 290, 278, 268, 238s, 231, 225. Observed FTIR bands ( $\tilde{\nu}$ /cm<sup>-1</sup>) and theoretically-predicted frequencies (cm<sup>-1</sup>) and intensity (km mol<sup>-1</sup>) in parentheses: 3047vw, 2074vw, 3084vw (3069, 7; 3080, 16; 3089, 15; 3092, 12), 1832m, 1842m, 1856m, 1872m, (1875, 915; C=Ostr), — (1604, 22), 1579vw (1570, 37), 1568vw (1552, 14), 1510w (1495, 37), 1448vw (1428, 8), 1329vw (1326, 6), — (1316, 8), — (1092, 9), — (967, 6), 820w (809, 39), 774w (763, 8), 748w (737, 20), 645w (664, 25), — (594, 20), 493w (488, 10).
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- 2-Naphthynes was directly formed from 2,3-naphthalenedicarboxylic anhydride upon irradiation at 266 nm and showed a similar FTIR spectrum to that reported.<sup>6</sup>