



# Photochemistry of cyclopentadiene isolated in low-temperature argon matrices

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## Abstract

The photochemistry of cyclopentadiene isolated in low-temperature argon matrices was studied by means of IR and UV/VIS spectroscopy. Bicyclo[2.1.0]pent-2-ene was formed by the irradiation of matrix-isolated cyclopentadiene using a super-high-pressure mercury lamp. When the matrix-isolated cyclopentadiene was irradiated with shorter wavelength using a low-pressure mercury lamp, further reactions of bicyclo[2.1.0]pent-2-ene were found to produce allylacetylene and vinylallene. While the photochemistry of cyclopentadiene to form bicyclo[2.1.0]pent-2-ene is known in a solution system, the production of allylacetylene and vinylallene in a matrix-isolated system has never been previously reported. The assignments of the species and the determination of the reaction mechanisms were performed using molecular orbital calculations.

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**Keywords:** Cyclopentadiene; Photochemistry; Matrix-isolation; Infrared spectroscopy; Molecular orbital calculation

## 1. Introduction

Cyclopentadiene (Cpd) is commonly used as a diene-donor in the Diels–Alder reaction [1]. It is also known as a ligand which coordinates to metal atoms in the form of cyclopentadienyl anion (Cp). It is well known that ferrocene, which has two Cp ligands, coordinates to iron atoms; the delocalized electrons in the five-membered ring of Cp bonds to the center iron metal in  $\eta^5$ . However, in the case of  $\text{HgCp}_2$ ,  $\eta^1$  bonding takes place with diene character, wherein an electron is localized in one of the carbon atoms in the five-membered ring of Cp. The differences in such bonding character are observed as differences in the infrared spectra [2]. The structure and electronic state of Cp correlate to the bonding nature of Cp with the center metal. It is therefore important to investigate electronic structure and photochemistry of Cpd in order to understand the photochemistry of metal complexes with Cp, which could be used to synthesize novel compounds.

The photochemistry of Cpd in solution systems has been described previously. Bicyclo[2.1.0]pent-2-ene (BCP) is formed by UV irradiation of Cpd in ethanol at 0 °C [3,4].

Cpd, with sensitizers such as acetophenone, was irradiated with a UV lamp to produce *endo*- and *exo*-dicyclopentadiene and *trans*-(3,0,3,0)-tricyclo-2,8-decadiene in approximately a 1:1:1 ratio [1].

Matrix isolation is a technique for trapping a highly reactive atom or unstable molecule, radical, or ion in inert solid such as low-temperature Ar. Using this technique, it is possible to study photochemical reactions of the sample without the intervening effects of solvents. The reaction of iron atoms with Cpd in an argon matrix [5] and hydrogen-bonded complexes of Cpd with the strong bases [6] have been reported using the matrix isolation technique. Moreover, unstable species have been reported; cyclopentadienyl radical and cyclopentadienyl anion were produced by pyrolysis of bis(cyclopentadienyl)nickel in argon matrix [7], and a radical cation of Cpd was produced by X-ray irradiation of Cpd in a matrix [8]. However, to the best of our knowledge, the photoisomerization of matrix-isolated Cpd is yet to be reported.

In the present study, the photochemistry of Cpd isolated in a low-temperature argon matrix was studied using a super-high-pressure mercury lamp (SHPML) and a low-pressure mercury lamp (LPML), and the reactivity and electronic properties of photochemical products of Cpd were investigated.

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## 2. Experimental

Cpd was prepared by cracking the dimer, dicyclopentadiene, (Kanto Chemical Co., Inc. more than 97% purity) and further purified by freeze-thaw cycles at 77 K. The preparation of the pure Cpd was confirmed by Fourier transform infrared spectroscopy (FTIR). Argon (Nippon Sanso, more than 99.9995%) was used without further purification as the matrix gas.

Matrix samples were condensed on a cold substrate (CsI or CaF<sub>2</sub>) that had been cooled down to 18 K by a closed-cycle helium refrigerator (Iwatani Cryo Techno, Cryo Mini D510). The temperature of Cpd in the glass tube was kept at 273 K by a crushed-ice bath, and Cpd vapor was introduced onto the cold substrate through a needle valve. The amount of deposited Cpd was estimated by weighing the glass tube before and after the vaporization. The matrix gas, Ar, was introduced in a controlled manner with a fine needle valve. The amount of argon matrix gas was estimated by

monitoring the pressure change in the gas-line before and after introduction of the gas.

Infrared spectra were recorded with an FTIR spectrometer (Perkin Elmer, System 1720x). UV/VIS spectra were recorded by a Shimadzu MPS-2000 spectrometer. For infrared spectra measurements, CsI and KBr were employed as the cold substrate and optical window, respectively. For measurement of UV/VIS spectra, CaF<sub>2</sub> and quartz were employed as the cold substrate and external windows, respectively.

The excitation sources were a super-high-pressure mercury lamp (SHPML) (USHIO, USH-500D) and a low-pressure mercury lamp (LPML). For the irradiation using SHPML ( $200 \text{ nm} < \lambda < 800 \text{ nm}$ , 17.5 mW), the infrared region in the light was filtered out by a water filter to prevent heating of the sample. The wavelength was controlled by an optical glass filter. The LPML with strong bright lines at 184.9 and 253.7 nm was located in the vacuum chamber to irradiate the sample directly without loss of UV-light.

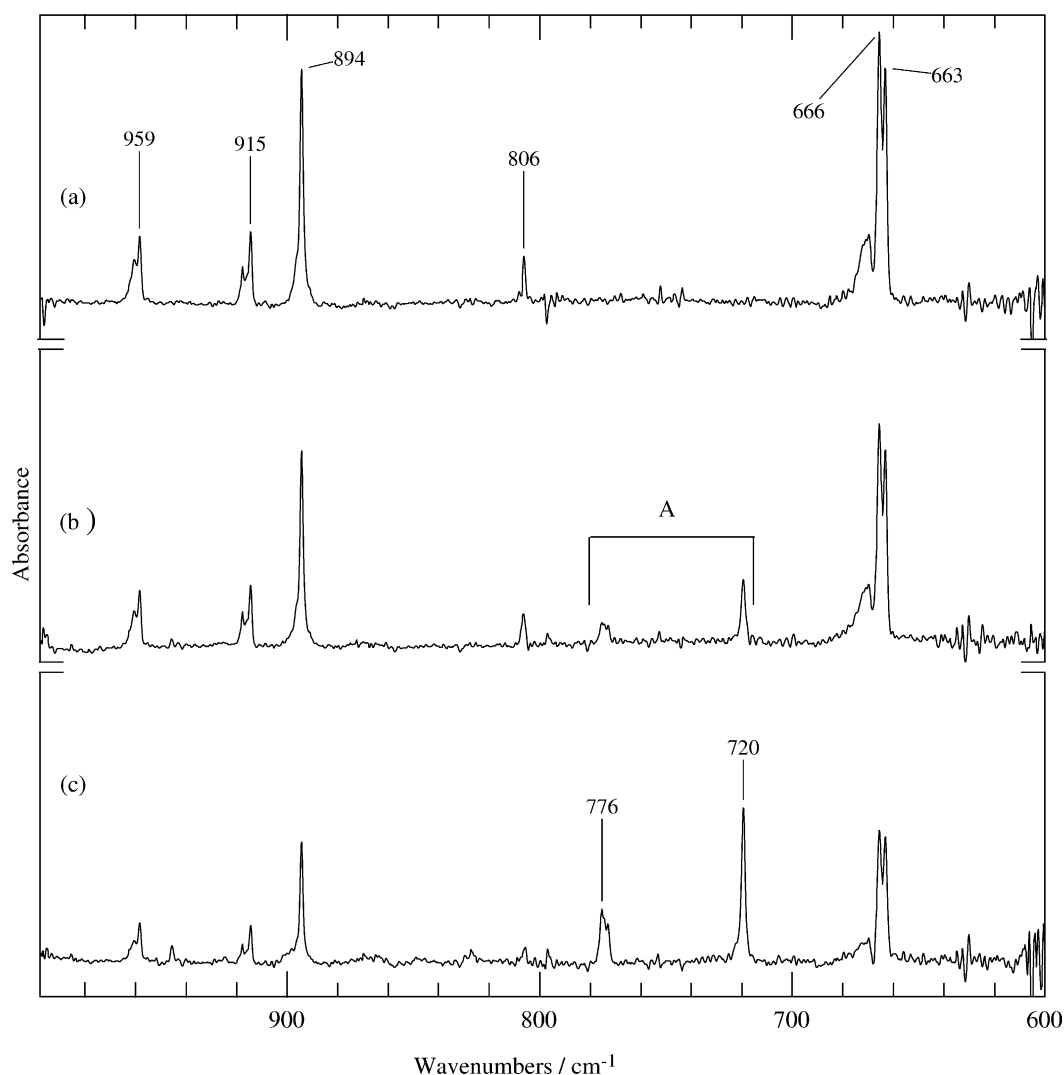


Fig. 1. Infrared Spectra of Cpd isolated in solid Ar matrices (18 K). (a) Cpd/Ar = 1/25, (b) Irradiated with SHPML for 10 min, (c) Irradiated with SHPML for 180 min.

### 3. Results

#### 3.1. Infrared spectra

Infrared spectra of Cpd isolated in the solid argon matrix (molar ratio: Cpd/Ar = 1/25) are shown in Fig. 1. Similar experiments with other mixture ratios (Cpd/Ar = 1/1000–1/25) were also performed, and the same IR spectra were obtained. In this wave-number region, vibrations of CH and ring deformation of Cpd are expected. The ring stretching and CH bending are observed at 959 cm<sup>-1</sup>, and CH<sub>2</sub> rocking is observed at 894 cm<sup>-1</sup>. The absorptions at 666 and 663 cm<sup>-1</sup> are assigned to CH in-plane bending. Other observed peaks and their assignments are summarized in Table 1 [5].

On irradiation using SHPML (200 nm < λ < 280 nm), absorption bands of Cpd decreased and new bands appeared at 776 and 720 cm<sup>-1</sup> (Fig. 1(b)). The species represented by the new bands is denoted as photochemical species A. Though dicyclopentadiene may be formed by photo-aggregation in a matrix, the corresponding absorptions at 755, 727, 720 cm<sup>-1</sup> were not observed in this experiment. Therefore it was concluded that species A was not dicyclopentadiene. Further irradiation using SHPML (180 min) increased the intensity of species A bands (Fig. 1(c)), and no other absorption was observed. In order to see the effects of annealing, the temperature of the sample was increased to 30 K and maintained at this temperature for 60 min; No spectral change was observed indicating that species A was stable at 30 K.

When the Cpd in the matrix was irradiated with longer-wavelength radiation (λ > 280 nm) using a SHPML light filtered by an optical short-cut filter (UV-28), no photochemical reaction was observed. Therefore, this indicates that only light in the region of 200 nm < λ < 280 nm can promote the photoreaction of Cpd isolated in a matrix to produce species A.

The IR spectrum of Cpd isolated in the solid argon matrix, Cpd/Ar = 1/50, is shown in Fig. 2(a). When the matrix sample was irradiated by LPML light, the absorption of Cpd decreased and the bands of species A at 776 and 720 cm<sup>-1</sup> appeared, as in the case of irradiation by SHPML (Fig. 2(b)). But further irradiation (180 min) resulted in the formation of other bands at 641, 849, 1953, and 3333 cm<sup>-1</sup> at the expense of the Cpd and species A (Fig. 2(c)). The absorption at 849 cm<sup>-1</sup> is assigned to C–H out-of-plane deformation of an allene group, the absorption at 1953 cm<sup>-1</sup> is assigned to C = C = C stretching of an allene group, the absorption at 641 cm<sup>-1</sup> is assigned to C–H out-of-plane deformation, and 3333 cm<sup>-1</sup> is assigned to C–H stretching of C≡CH ethynyl group. Therefore the new species produced by irradiation by LPML contains ethynyl (species B) or allene (species C) groups (Fig. 2(c)). No spectral change was observed on annealing at 30 K, indicating that the new species B and C were stable. The species A, B, and C are assigned to bicyclo[2.1.0]pent-2-ene (BCP),

Table 1  
Observed frequencies (cm<sup>-1</sup>) for Cpd and reaction products

Cyclopentadiene (Cpd)	Assignment	SHPML (BCP)	LPML	Assignment
3122 } 3113 } 3101 } 3087 } 3083 } 3058 } 3050 }	CH stretching		3333	CH stretching (allylacetylene)
2910 } 2906 } 2899 } 2894 } 2891 }	CH <sub>2</sub> stretching	3087 3070 3046 3022 2985		
1573 1383 1370 1294	C=C stretching CH <sub>2</sub> scissoring C–H bending C–H bending + ring stretching	1286 1284	1953 1648	C=C=C stretching (vinylallene) C=C stretching (allylacetylene)
1240 1091	C–H bending + ring stretching CH <sub>2</sub> wagging	1175 1087 1060 1013	991	CH <sub>2</sub> allylrocking (allylacetylene)
961 } 959 } 918 } 914 } 894 }	ring stretching + C–H bending Ring CH <sub>2</sub> rocking	946	902 } 899 }	=CH <sub>2</sub> (vinylallene)
		869	849	C=C=CH <sub>2</sub> (vinylallene)
806	ring bending	776 774 773 720		
666 } 663 }	C–H bending		641 } 629 }	C≡CH (allylacetylene)

allylacetylene, and vinylallene, respectively. The assignments are confirmed by their chemical behavior and molecular orbital calculations as described later.

The intensities of absorbance in infrared spectra were checked by varying the irradiation time. SHPML irradiation increased the production of species A (BCP) at the cost of Cpd. LPML irradiation initially increased species A (BCP) at the cost of Cpd. However, prolonged LPML irradiation (30 to 60 min) increased species B (allylacetylene) and C (vinylallene) at the cost of Cpd and species A (BCP). Since the production of species B (allylacetylene) and C (vinylallene) was observed only after the formation of species A (BCP) and the increase of species B (allylacetylene) and C (vinylallene) accompanies the consumption of species A (BCP), it was demonstrated that the new species B

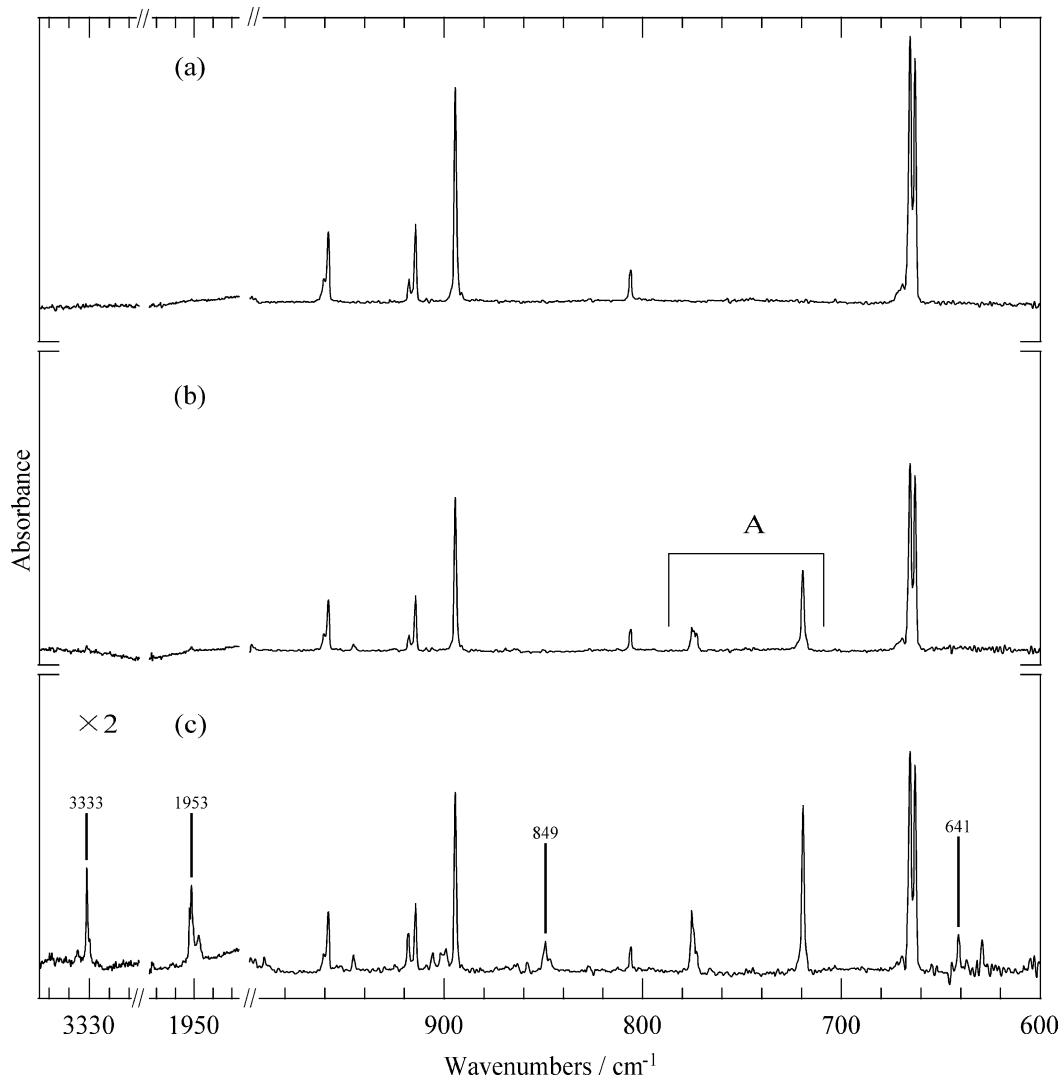


Fig. 2. Infrared spectra of Cpd isolated in solid Ar matrices (18 K). (a) Cpd/Ar = 1/50, (b) Irradiated with LPML for 10 min, (c) Irradiated with LPML for 180 min.

(allylacetylene) and C (vinylallene) arose only from species A (BCP) on irradiation by short wavelengths.

### 3.2. UV/VIS spectra

Cpd isolated in a solid argon matrix (18 K) was irradiated using SHPML (Fig. 3(a)) and LPML (Fig. 3(b)), and UV/VIS spectra were observed by varying the irradiation time. On irradiation using SHPML, the bands at 237 nm ( $\pi-\pi^*$  transition of Cpd) decreased: Cpd may decrease to form species A (BCP) that is not observed in this spectral region. On irradiation using LPML, the absorption at 237 nm decreased up to 30 min, and then new bands at 226 nm appeared by further irradiation up to 180 min. The new bands at 226 nm is assigned to the  $\pi-\pi^*$  transition of the allene group. As the increase of species C (vinylallene) was observed after the decrease

of Cpd, species C (vinylallene) are not produced directly from Cpd. It was shown that species C (vinylallene) are produced via intermediates, which may be species A (BCP).

### 3.3. Molecular orbital calculations

Molecular orbital calculations were performed in order to confirm the assignments. The Gaussian98 [9] software program with B3LYP/6-311 + G\* basis sets was employed to estimate the structures of photochemical species A, B, and C. We performed the geometry optimization and frequency analysis for Cpd and bicyclo[2.1.0]pent-2-ene (BCP), as well as the various species which are expected to be produced on irradiation: dicyclopentadiene, its isomers, and species containing allene and ethynyl groups.

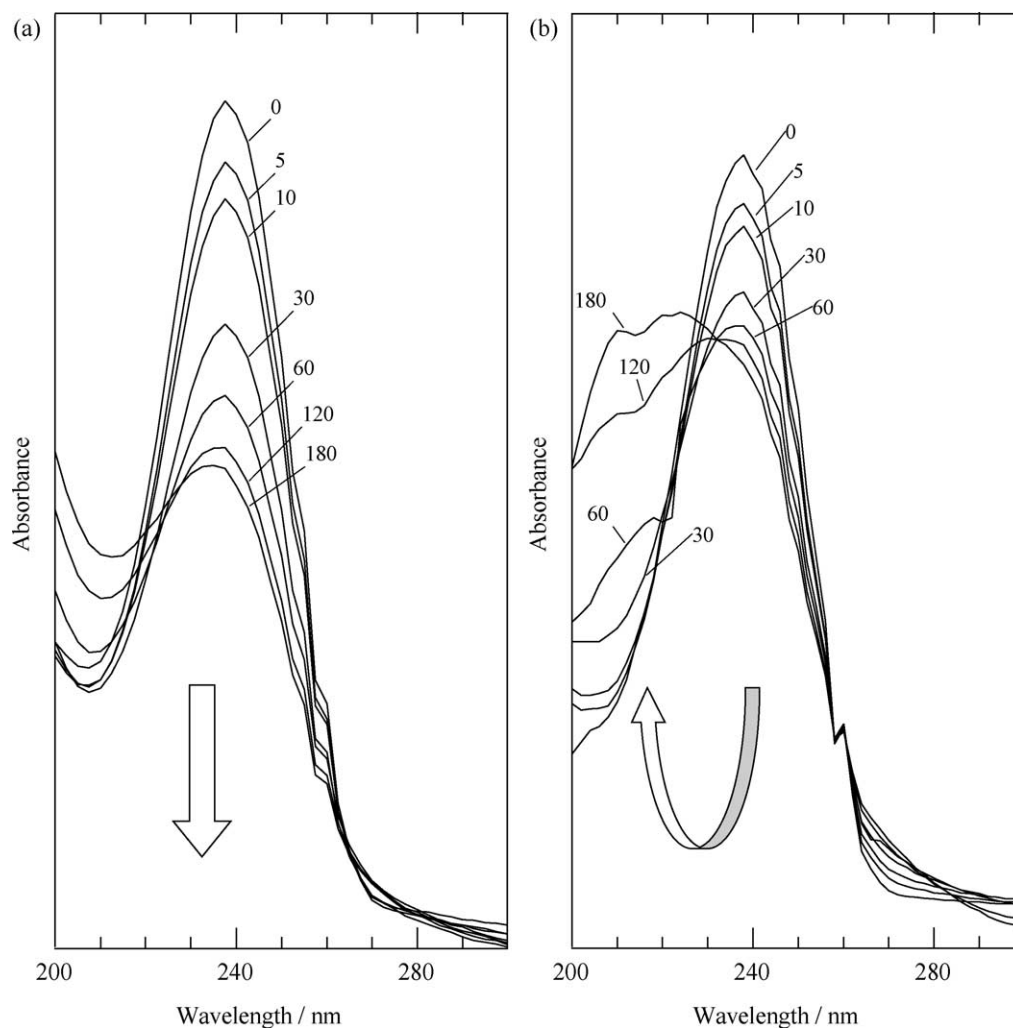


Fig. 3. UV/VIS spectra of Cpd isolated in solid Ar matrices (18 K). (a) is irradiated using SHPML, (b) is irradiated using LPML. Irradiation times (min) are indicated in the figures.

Frequency analysis of BCP is in agreement with observed IR absorption peaks of species A. Species B, containing the ethynyl group, is assigned to allylacetylene ( $\text{CH}\equiv\text{CCH}_2\text{CH}=\text{CH}_2$ ), and the species C containing the allene group is assigned to vinylallene (penta-1,2,4-triene:  $\text{CH}_2=\text{C}=\text{CHCH}=\text{CH}_2$ ) from comparison of observed IR spectra with calculated frequencies. The optimized geometries and energy differences based on the ground states are summarized in Fig. 4. All the photochemical products have higher potential energies than that of Cpd. Allylacetylene and vinylallene have *cis* and *trans* isomers for each species. When the ground state energies were compared, the *trans* form isomer of vinylallene is 2.836 kcal/mol more stable than the *cis* isomer, and the *cis* isomer of allylacetylene is 0.145 kcal/mol more stable than the *trans* isomer. Calculated frequencies for the optimized species using B3LYP/6-311 + G\* are listed in Table 2, and the scaling factor was estimated to be 0.98. The calculated frequencies and their intensities are in

agreement with experimentally observed infrared spectra (Fig. 5). The assignments are summarized in Table 1.

#### 4. Discussion

For the photochemical products with ethynyl group (species B) and allene group (species C) produced by irradiation using LPML, methylacetylene ( $\text{CH}_3\text{C}\equiv\text{CH}$ ) and allene ( $\text{CH}_2=\text{C}=\text{CH}_2$ ) are also candidates. Infrared spectra of these compounds in low-temperature matrices have already been reported including hydrogen discharge photolysis of methylacetylene or allene [10], and vacuum-ultraviolet photolysis of propylene to produce methylacetylene and allene [11]. It was reported that methylacetylene has absorptions at 3330 and 628  $\text{cm}^{-1}$ , and allene has absorptions at 1954 and 838  $\text{cm}^{-1}$ , which are very similar to our experimental results. However the reaction of Cpd to produce methylacetylene or allene should be accompanied

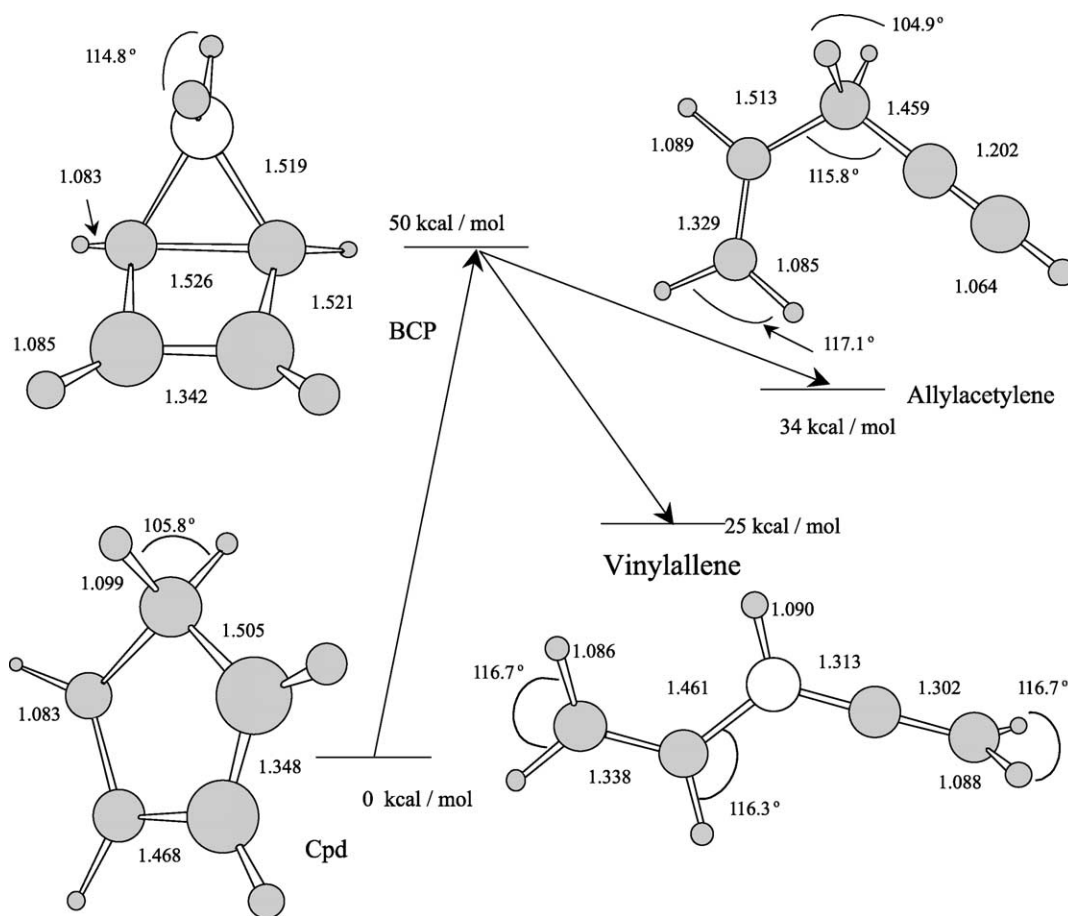


Fig. 4. Optimized geometries and energy differences based on the ground state using B3LYP/6-311 + G\*.

by the formation of acetylene ( $3300$  and  $735\text{ cm}^{-1}$ ), the bands for which were not observed in our experiments. Therefore it was concluded that the species B and C observed in this experiments cannot be methylacetylene nor allene.

Species B and C are produced simultaneously and therefore one could suspect the presence of ethynyl group and allene group in one molecule. Ethynylallene (Penta-3,4-dien-1-yne:  $\text{CH}\equiv\text{CCH}=\text{C}=\text{CH}_2$ ) has ethynyl group and allene group in the same molecule, and infrared spectra have been measured in  $\text{CS}_2$  [12], or in gas-phase [13], which have absorptions at  $3333$ ,  $1950$ ,  $853\text{ cm}^{-1}$ . These bands are very close to those in our experimental results. But the band at  $899\text{ cm}^{-1}$  was observed in the infrared spectrum of matrix isolated Cpd irradiated with LPML for 180 min (Fig. 2(c)), which was assigned to  $=\text{CH}_2$  out-of-plane deformation. Therefore, it was concluded that ethynylallene was not a product in our experiment.

Infrared spectra of allylacetylene or vinylallene isolated in a low-temperature matrix have never been reported. We therefore performed molecular orbital calculations using Gaussian98 software in order to estimate their IR spectra in an isolated system. While infrared spectra of the species isolated in low-temperature matrices have never been reported, the spectra in conventional conditions have indeed been previously reported. The results of the calculations are

in agreement with experimental data. Infrared spectra of vinylallene in the vapor phase, in solution, as well as in the solid state [14,15] have been reported to have bands of  $\nu\text{H}_2\text{C}=\text{C}=\text{CH}_2$  stretching ( $1940\text{ cm}^{-1}$ ),  $=\text{CH}_2$  out-of-plane deformation ( $895\text{ cm}^{-1}$ ), and  $\text{C}=\text{C}=\text{CH}_2$  out-of-plane deformation ( $845\text{ cm}^{-1}$ ). These bands are compatible with the absorption bands in Fig. 2(c). The absorptions of allylacetylene were observed at  $\nu\text{C}\equiv\text{CH}$  stretching ( $3330\text{ cm}^{-1}$ ),  $\nu\text{-HC}=\text{CH}_2$  stretching ( $1640\text{ cm}^{-1}$ ),  $\nu\text{-HC}=\text{CH}_2$  out-of-plane deformation ( $990\text{ cm}^{-1}$ ),  $=\text{CH}_2$  out-of-plane deformation ( $920\text{ cm}^{-1}$ ) [15]. In the UV/VIS spectrum (Fig. 3), increase of the bands at  $226\text{ nm}$  was observed after LPML irradiation. As vinylallene in ethanol is reported to have bands of  $\pi\text{-}\pi^*$  transition at  $228\text{ nm}$  [15], the production of vinylallene in our experiment is also supported by UV/VIS spectra.

Thermal decomposition of Cpd has been studied earlier using the shock tube technique [16], and the tube flow reactor method [17]. The main products of the decomposition were acetylene, ethylene, benzene, allene, propylene, methane, and 1-3butadiene. Two pathways of thermal decomposition of Cpd have been proposed:

- Cpd forms cyclopentadienyl radical by fission of the CH bond, and then decomposition of cyclopentadienyl

Table 2  
Calculated frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{kM/mol}$ ) using B3LYP/6-311 + G \*

Cpd		BCP		Vinylallene ( <i>trans</i> )		Allylacetylene ( <i>cis</i> )	
Frequencies <sup>a</sup>	Intensity	Frequencies <sup>a</sup>	Intensity	Frequencies <sup>a</sup>	Intensity	Frequencies <sup>a</sup>	Intensity
3154.92	2.82	3134.20	5.16	3156.3	16.4465	3392.18	52.795
3148.42	26.43	3125.76	59.20	3110.26	2.9974	3157.68	13.5206
3130.60	17.96	3117.81	24.20	3088.91	7.5522	3081.05	11.3308
3120.54	3.65	3111.63	3.80	3070.5	10.9297	3069.03	18.4524
2973.68	9.82	3098.98	8.43	3052.34	3.0263	2960.05	7.5186
2953.98	11.97	3027.08	39.78	3043.45	11.4507	2946.02	17.9337
1602.76	0.01	1564.70	9.20	1988.34	76.9024	2175.36	4.3668
1518.56	1.03	1454.98	2.91	1646.39	19.8359	1677.16	16.5331
1400.61	13.37	1287.12	23.28	1462.38	4.391	1448.57	13.7051
1375.32	13.02	1267.04	1.07	1422.83	0.4498	1421.74	3.8407
1294.04	1.03	1200.16	0.10	1315.11	3.8339	1335.68	3.9938
1249.60	2.35	1179.02	0.98	1291.37	3.9074	1305.53	0.2905
1115.69	0.00	1087.78	1.88	1168.29	4.0994	1227.99	1.1322
1109.73	0.32	1062.41	4.46	1093.22	1.5926	1077.27	4.8987
1092.52	2.67	1023.15	0.24	1007.96	19.0634	1003.65	21.3287
993.62	0.20	1016.25	8.49	1001.73	8.3367	950.127	1.4886
952.63	16.47	1013.61	1.87	904.776	61.0571	944.47	4.8481
927.18	0.57	943.10	4.02	904.069	2.8697	924.897	45.9302
926.04	0.00	924.51	4.55	885.787	0.1922	849.442	0.1352
906.94	11.51	866.14	7.72	856.85	59.6454	635.872	56.586
901.59	33.23	833.30	2.66	715.454	6.2726	611.802	55.4518
803.42	6.02	814.80	1.10	557.763	10.1225	603.655	1.9361
801.14	0.01	784.87	0.13	497.667	7.5142	554.619	16.1693
692.38	0.00	765.86	36.89	394.71	6.4463	371.977	3.0547
664.68	93.98	718.24	77.59	345.761	5.6485	322.322	9.1108
510.38	0.00	443.51	1.02	163.483	0.8107	158.399	0.7538
341.20	7.76	413.15	8.05	126.368	0.8565	146.018	0.0479

<sup>a</sup> The scaling factor 0.98 applied.

radical occurs [18,19]. Cyclopentadienyl radical isolated in a low-temperature matrix has been previously reported [7], and its molecular orbital calculations have been performed [18]. However, no corresponding absorption bands were observed in our experiments.

- (ii) Cpd forms carbene intermediate by proton shift, and then acetylene plus propylene or allene are produced. In the process of forming acetylene, allylacetylen

and vinylallene are proposed as the intermediate species [19]. However, in this study, it was shown that BCP exists as an intermediate product to form allylacetylene and vinylallene.

There have been no previous reports indicating that allylacetylene and vinylallene are produced from Cpd via BCP. In order to examine this photochemical reaction

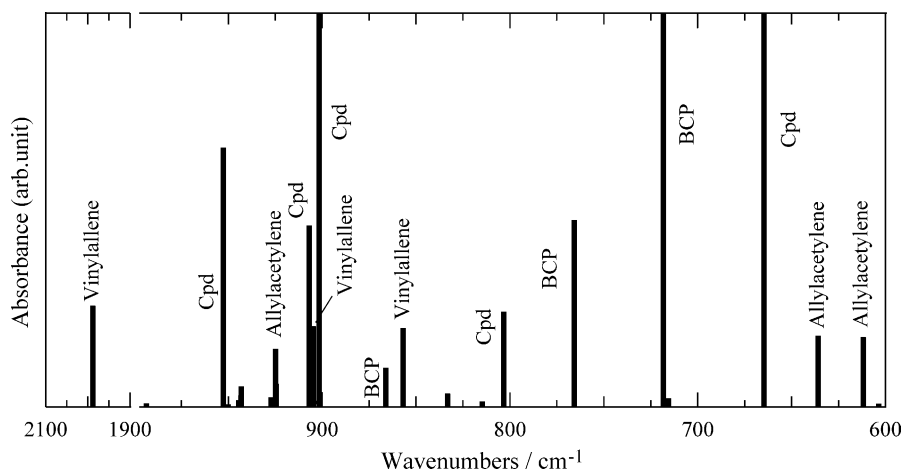


Fig. 5. Calculated frequencies using B3LYP/6-311 + G \* and the scaling factor 0.98 applied.

Table 3  
Calculated of electronic spectra (nm) and oscillator strength (f) using ZINDO

State	Cpd		BCP		Vinylallene		Allylacetylene	
	$\lambda/\text{nm}$	f	$\lambda/\text{nm}$	f	$\lambda/\text{nm}$	f	$\lambda/\text{nm}$	f
1	238.27	0.2229	233.64	0.1087	287.61	0.0000	276.50	0.0000
2	198.61	0.0392	203.67	0.0139	270.64	0.0000	248.26	0.0002
3	193.94	0.0006	186.84	0.0364	232.79	1.2631	248.17	0.0002
4	192.11	0.0000	175.96	0.1132	204.33	0.0039	180.54	0.0001
5	157.59	0.9126	163.47	0.0087	188.08	0.0178	178.36	0.0162

mechanism, we performed electronic states calculations using ZINDO in Gaussian98 and INDO/S in MOS-F ver. 4.2C [20]. The structure employed in the calculation is the optimized structure using B3LYP/6-311 + G\*. The calculated electronic spectra are summarized in Table 3. The bands at 237 nm observed in UV/VIS spectra that corresponds to  $\pi-\pi^*$  transition of Cpd are in agreement with the results of these calculations. Moreover, the calculations show that allylacetylene has no strong UV/VIS absorption, which correlates with our experimental results.

BCP is calculated to have three bands at 234 nm ( $f = 0.1087$ ), 204 nm ( $f = 0.0139$ ) and 187 nm ( $f = 0.0364$ ) above  $\lambda > 180$  nm region. The band at 234 nm is compatible with the 232 nm ( $\epsilon_{\text{max}} = 1000$ ) band in UV/VIS absorption spectra of BCP in ethanol [4]. The photoreaction of BCP to form allylacetylene and vinylallene was only observed by irradiation using LPML, which has a shorter wavelength, and absorption of BCP at 187 nm may promote the reaction. The difference atomic charge between the ground and the excited states (state 3;

$\lambda = 187$  nm) of BCP using INDO/S calculations is shown in Fig. 6. By the transition from the ground to the excited state, the electron is localized at the three-membered ring, especially on the carbon at  $\text{CH}_2$ . Consequently, BCP could decompose from the three-membered ring by UV irradiation.

## 5. Conclusions

Matrix isolated cyclopentadiene (Cpd) forms bicyclo[2.1.0]pent-2-ene (BCP) on irradiation with a super-high-pressure mercury lamp (SHPLM) ( $200 \text{ nm} < \lambda < 280 \text{ nm}$ ). Irradiation with a low-pressure mercury lamp (LPML) promotes subsequent reaction of BCP to produce allylacetylene and vinylallene. The assignments were made with the aid of molecular orbital calculations, and the calculated results are in good agreement with observed IR spectra and UV/VIS spectra. The reaction of BCP to form allylacetylene and vinylallene is promoted by the three-membered ring opening of BCP which corresponds to absorption at 187 nm. This is the first reported photochemical reaction of BCP in low-temperature matrices.

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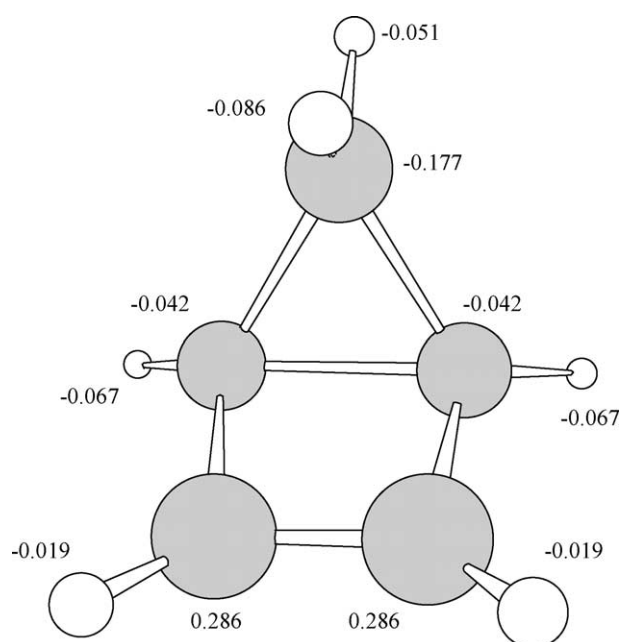


Fig. 6. Calculated structure of BCP (B3LYP/6-311 + G\*) and difference atomic charge between the ground state and the state3 (INDO/S).



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