

Notes

Ultraviolet Photolysis of 1,6-Methano[10]annulene Generates the Singlet Methylene

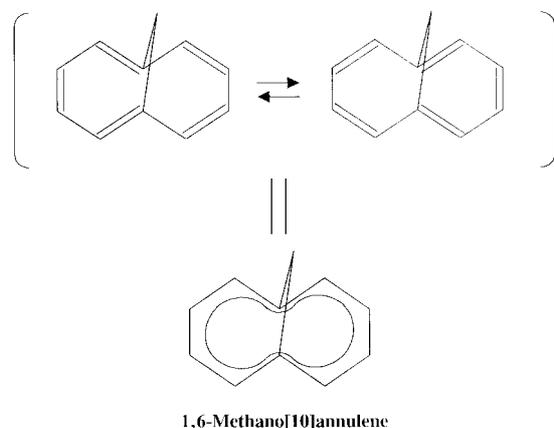
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Of various [10]-annulenes, all-*cis* and mono-*trans* isomers exist in nonplanar conformation and show non-aromatic characteristics.¹ Di-*trans*-[10]annulene is also expected to be non-planar due to the steric hindrance of two inner hydrogen atoms and has never been synthesized. On the other hand, 1,6-methano, 1,6-epoxy-, and 1,6-imino-[10]annulenes, in which the 10-membered rings are forced to form an approximately planar conformation by replacement of 1,6-positioned hydrogen atoms by CH₂, O or NH groups, respectively, are found to show aromaticity.²⁻⁸ Among these three 1,6-bridged[10]annulenes, 1,6-methano[10]annulene stands out because it is stable and synthesizable in quantity.²



Due to its unique characteristics, 1,6-methano- and the similar type of the molecule have been subject to intense investigation on diverse aspects of structural, chemical, and spectroscopic properties. Especially, a series of spectroscopic studies on 1,6-methano[10]annulene has been performed by the Salvi's group, revealing the molecular and electronic structures of the molecule.⁹⁻¹² According to their study, 1,6-methano[10]annulene [MA] has a relatively weak absorption band starting around 400 nm and a much stronger one near 300 nm.⁹ The Salvi's group also reported that the MA molecules emit fluorescence when they are excited to

the lower electronic state.¹⁰

In contrast to the prosperity of the spectroscopic studies on the 1,6-methano- and other 1,6-bridged[10]annulenes, no photochemical study on the molecules excited in the ultraviolet wavelength region has been reported. Identification of the fragments from the photolysis of the bridged annulene compounds would provide insights on the potential energy surfaces of the electronically excited states involved in the dissociation and many other relaxation processes. In this note, we report the experimental study on UV photochemistry of MA. The singlet methylene has been spectroscopically identified as a primary product of the photolysis. This observation suggests that the various kinds of singlet carbenes could be generated in solution by photolyzing appropriate 1,6-bridged[10]annulene compounds.

Experimental Section

The experimental setup used in this work has been described in detail elsewhere^{13,14} and thus only the brief description is given below. The photolysis was performed for the cooled sample in a supersonic jet. The liquid 1,6-methano[10]annulene was placed inside a pulse valve which was kept at 90 °C. The vaporized sample was mixed with He of 1 atm and expanded into a vacuum chamber through a 0.5 mm diameter nozzle orifice. The photolysis laser light was generated in a KD*P crystal by second-harmonic generation of the visible output of a pulsed dye laser (Lambda Physik SCANmate 2) pumped with a Q-switched Nd:YAG laser (Spectra-Physics GCR-11). The UV beam was separated from the fundamental with two dichroic mirrors and crossed the supersonic jet at 30 mm downstream from the nozzle. The pulse energy of the photolysis laser was 2-3 mJ/pulse and the beam size was ~3 mm in diameter at the interaction zone. About 50 nsec later, the probe laser pulse (~0.1 mJ/pulse), which was generated by the second dye laser (Lambda Physik SCANmate 2) also pumped with a Q-switched Nd:YAG laser (Spectra-Physics GCR-150), counterpropagated the photolysis laser beam. The probe laser wavelength was scanned through the $\tilde{b}-\tilde{a}$ transition of the singlet methylene $^1\text{CH}_2$ ($\tilde{a}^1\text{A}_1$)¹⁵ while monitoring the red fluorescence from the electronically excited methylenes with a photo-

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multiplier tube (Hamamatsu R928). The intensity of the fluorescence was measured with a gated integrator (SRS SR250) and stored in a PC with the corresponding wavelength of the probe laser. In some experiments where the contribution of the multiphoton excitation was checked, the energy of the probe laser was decreased by a factor of 5-10 and the fluorescence intensity was measured by the single photon counting technique using a gated photon counter (SRS SR400). The gate width was set to be 20 msec and the photons were counted for 50 laser shots for each wavelength position.

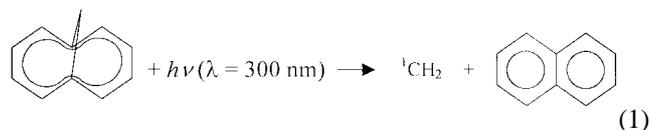
The 1,6-methano[10]annulene sample was prepared according to the procedure described by Vogel and Roth² and its purity was checked with mass spectrometry and gas chromatography.

Results and Discussion

Figure 1 shows the spectrum obtained by measuring the fluorescence intensity while scanning the probe laser wavelength with the photolysis laser fixed at 307 nm. The peaks in the spectrum appeared only when both of the photolysis and probe lasers were on and spatially overlapped. Based on frequencies of the peaks observed,¹⁵ the carrier of the fluorescence excitation spectrum is attributed to the $\tilde{b} \leftarrow \tilde{a}$ transition of the methylene in its singlet ground (\tilde{a}) state without any ambiguity. The red wavelength and long lifetime of the fluorescence also support this assignment.¹⁶ By referring to the transition-frequency table of the $\tilde{b} - \tilde{a}$ transition of methylene published by Petek *et al.*,¹⁵ each peak was assigned to the corresponding rovibronic transition and some of those assignments are shown in Figure 1.

The intensities of several peaks were measured with varying the energy of the photolysis laser pulse and showed a linear dependence on the energies of the photolysis laser pulses, confirming that the singlet methylene observed in this work is a primary photolysis product of MA excited by

one-photon absorption as below.



The other possible channel of MA to yield the methylene fragment is the multiphoton absorption due to the photolysis and probe laser photons and subsequent dissociations. However, since the lifetime of the electronically excited MA at ~ 300 nm is known to be a few ps or less⁹ and the time delay between the photolysis and probe laser pulses was fixed at 50 ns, the possibility that the electronically excited MA absorbs one or more photon(s) of the probe laser and generates the singlet methylene can be easily ruled out.

The fluorescence intensity of the methylene from MA was measured as a function of the photolysis wavelength. As the wavelength of the photolysis laser is decreased from 307 nm to 290 nm, the intensity of the fluorescence did not change noticeably. However, the fluorescence intensity decreases significantly with increasing the photolysis wavelength from 307 nm, and becomes too weak to be measured over 320 nm. This variation of the methylene yield with the excitation wavelength does follow the UV absorption spectrum of the S_2-S_0 transition of MA.⁹ When the excitation laser frequency was tuned to several strong bands of the S_1-S_0 transition covering from 398 nm to 340 nm, no fluorescence signal was observed, indicating that only the MA excited to the S_2 state generates the methylene. This observation is consistent with the previous report that the MA excited to the S_1 state emit strong fluorescence,¹⁰ which means no dissociation at the excitation energy.

Observation of the ${}^1\text{CH}_2$ ($\tilde{a} \text{}^1\text{A}_1$) in the UV photolysis of MA suggests that various singlet carbenes can be generated by UV photolysis of appropriate substituted 1,6-methano[10]annulenes in solution. The carbenes belong to an important group of reactive intermediates useful in organic syntheses and have usually been generated by photolyses or thermolyses of diazirines or ketenes.¹⁷ Although the diazirines and ketenes have been used as the sources of carbenes for a long time, they have some shortcomings. The diazirines are well known to be explosive,¹⁸ requiring extremely careful handling, and the ketenes have relatively weak absorption bands in UV.¹⁹ As mentioned above, MAs have strong absorption bands around 300 nm and thus can be effectively photolyzed to generate the corresponding carbenes. In addition, they are also quite stable.² Hence the MAs may replace diazirines or ketenes for generation of carbenes. Furthermore, the other product from the 1,6-bridged[10]annulene photolyses is naphthalene, which is relatively inert in organic syntheses.

Interestingly, we noticed a non-negligible amount of fluorescence without the probe laser beam. The non-resonant fluorescence exists for all photolysis wavelengths in this work and appears in Figure 1 as a DC level background. The red wavelength and long decay lifetime of the fluorescence

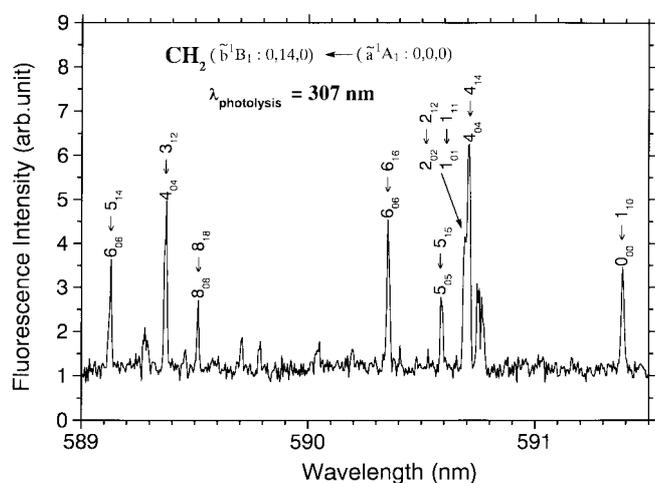


Figure 1. A portion of laser-induced fluorescence spectrum of the ${}^1\text{CH}_2$ ($\tilde{a} \text{}^1\text{A}_1$) products produced in the ultraviolet photolysis of the gaseous 1,6-methano[10]annulene in a supersonic jet. The rovibronic assignments are given on top of each peak.

indicate that the fluorescence comes from the electronically excited $^1\text{CH}_2$ ($\tilde{\text{b}}^1\text{B}_1$)¹⁶ and its intensity shows a quadratic dependence on the photolysis laser pulse energy. These facts indicate that the non-resonant fluorescence comes from the electronically excited $^1\text{CH}_2$ ($\tilde{\text{b}}^1\text{B}_1$), which is produced by fragmentation of the highly excited MA molecules by two-photon absorption of the photolysis laser light. This observation suggests that the electronically excited carbenes, which are known to be more reactive than those in the $\tilde{\text{a}}$ state, may be generated by two-photon excitation of MAs.

Our suggestion of use of the substituted 1,6-bridged[10]-annulenes as a source of carbenes may be practiced in an organic chemistry laboratory.

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