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Pulsed Nd:YAG Laser-induced Photoreaction of cis,cis-1,3-Cyclooctadiene at 266 nm: Selective Cycloaddition to cis-Bicyclo[4.2.0]oct-7-ene

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Figure S1. Molar absorption coefficient of *c,c-***1** (0.105 mM in pentane, 10 mm optical path length, blue line), and 266-nm nanopulsed Nd³⁺:YAG laser (red line). The molar absorption coefficient at 266 nm was 30.2 (L mol⁻¹cm⁻¹).



Figure S2. Molar amounts of product versus reaction time for the photoreaction of *c,c-1* in 0.1 mL of a pentane solution. The solid and dotted blue lines refer to **2** in the 37.5-mM ($^{\circ}$) and 150-mM ($^{\Delta}$) pentane solutions, respectively. The solid and dotted orange lines refer to *c,t-1* in the 37.5-mM ($^{\circ}$) and 150-mM($^{\wedge}$) pentane solutions, respectively.

The energy per 1 pulse was 7.0 mJ.

[#]: The numbers in the parenthesis show the real irradiation time calculated on the basis of the pulse flash time.

3. Calculation of the number of excited molecules

The conditions of the pulsed Nd:YAG laser used for the 266-nm irradiation are indicated below:

wavelength : $\lambda = 266$ nm laser power : W = 70 mJ/s frequency (number of pulse per 1 second): v = 10 Hz beam area : $s = 10 \text{ mm}\phi$

The photon number per 1 pulse (n) was calculated from the energy per 1 photon of 266 nm light. The Planck constant and the velocity of light are shown as h and c, respectively.

n =
$$\frac{\text{Energy per 1 pulse}}{\text{Energy per 1 photon for 266-nm light}} = \frac{W / v}{hc / \lambda}$$

The number of excited molecules per 1 h (N) was estimated from the equation below. I_0 and I_t are the intensities of the irradiated and transmitted beams, respectively, while N_0 and N_t are the photon number of the irradiated and transmitted laser light per 1 h, respectively. The absorbance (A) of *c*,*c*-1 in a 37.5 mM pentane solution was measured at 266 nm with a 1-mm optical path length cell. All the photons were irradiated on the solution and a single-photon excitation was assumed.

$$A = \log (I_0 / I_t) = \log (N_0 / N_t)$$

 $N_0 = (Photon number / pulse) \times (number of pulse / second) \times 3600$

=
$$n \times v \times 3600$$

N = N₀ - N_t = N₀ - $\frac{N_0}{10^A}$ = N₀ (1 - $\frac{1}{10^A}$)

Using the measured volume of A (0.436) in the above equation, the number of excited molecules per 1 h, N, was estimated to be 2.13×10^{20} .



Figure S3. Spectrum from a used high-pressure mercury lamp.