

Laser-Induced Excited-State Properties of 5*H*-Dibenzo[*a,d*]cyclohepten-5-one in Solution

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Relatively little is known concerning the photophysical properties of the molecule 5*H*-dibenzo[*a,d*]cyclohepten-5-one, which corresponds, at least in its structure, to 5*H*-dibenzo[*a,d*]cyclohepten-5-ol, 5*H*-dibenzo[*a,d*]cycloheptenes, and the *cis*-isomer of stilbene. Only a few previous studies of 5*H*-dibenzo[*a,d*]cycloheptene have been carried out.¹⁻⁴ Also, the crystal structure of its derivative, 5*H*-dibenzo[*a,d*]cyclohepten-5-ol, has been studied.^{5,6} A study of the crystal structure of the title compound showed that the benzyl groups accept hydrogen bonds from a hydroxy and an ethynyl group, one to each face of the ring. The bond donated by the hydroxy group has an unusual geometry, and is directed almost linearly at a "C" atom with "H-C"=2.36 Å. All operations were performed in an atmosphere of dry argon using vacuum techniques. NMR and IR spectra were recorded and crystallographic data were characterized.^{7,10}

All of the analytical data support the adsorption mechanism and corroborate the theoretical predictions that $(4n+2)\pi$ electron aromaticity can be induced in 5*H*-dibenzo[*a,d*]cyclohepten-5-one. A comparison of the sorption of Dibenzo[*a,d*]tropone and 5*H*-dibenzo[*a,d*]cyclohepten-5-one by montmorillonite clearly demonstrates the importance of π interactions in the interlamellar space. π interactions between adsorbed cationic dyes and the oxygen planes of montmorillonite have been reported.^{7,11} A photoreaction, the photoketonization of 5*H*-dibenzo[*a,d*]cyclohepten-5-one in aqueous solution, was reported, the mechanism of which was believed to involve an initial ionization of the C-H proton at the 5-position in S_1 , to generate a dibenzosuberonyl carbanion intermediate.¹² The work reported here was undertaken with the aim of determining the values of a number of photophysical parameters which are of significance to the photochemistry of the excited singlet and triplet states.

Experimental

5*H*-Dibenzo[*a,d*]cyclohepten-5-one was of Aldrich reagent grade, and was used as received. All other chemicals used were also of reagent grade. 5*H*-Dibenzo[*a,d*]cyclohepten-5-one, at a concentration of 2×10^{-5} M, was in cyclohexane, ethanol, methanol and benzene, at room temperature.

The absorption spectra were recorded using a Cary-219 spectrophotometer, and the emission spectra were recorded using a Perkin-Elmer (MPF-2A) spectrophotometer. The singlet and triplet transient phenomena were excited with a laser-flash photolysis set-up consisting of a Q-switched and mode-locked Nd:YAG laser system and a dye-laser system. A kinetic-absorption spectrophotometer with a nanosecond response was Bausch & Lomb, UV-visible high intensity monochromator and RCA 4840 photomultiplier. A Tektronix 7912 digitizer and LSI-11 microprocessor unit controlled the experiments and processed the data at the initial stage. The data from LSI-11 were finally transferred to a time-shared PDP11/55 computer system for storage and further analysis.

The flash-photolysis experiments were carried out under different conditions. 1×0.2 cm² quartz cells were used with the absorbed light passing along a 0.2 cm path length. The exciting laser beam intersected the cell at angles ranging from 20° - 90°, and the flash duration time was 3.0 ± 0.1 ns. FT-IR spectra of the title compound were recorded using a Mattson 1000 FT-IR spectrometer; the resolution was 4 cm⁻¹.

Deoxygenating experiments were made in high-vacuum systems by repeated pump-and-thaw cycles, and the background pressure on the line was 10 to -7 Torr.

Results and Discussion

The one photon absorption and emission spectra, prompt fluorescence and p-type delayed fluorescence

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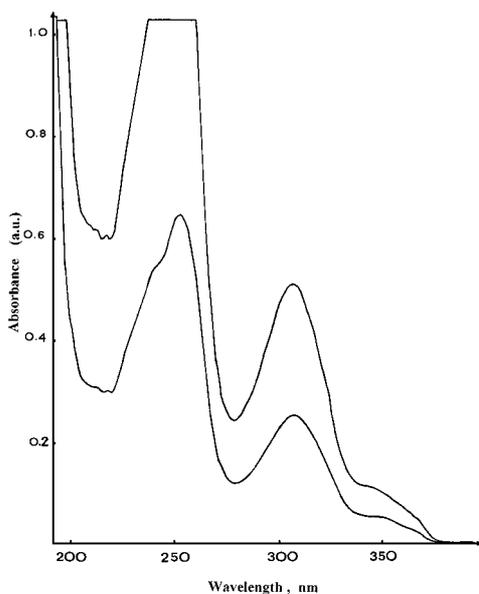


Fig. 1 One-photon absorption spectrum of 5H-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature.

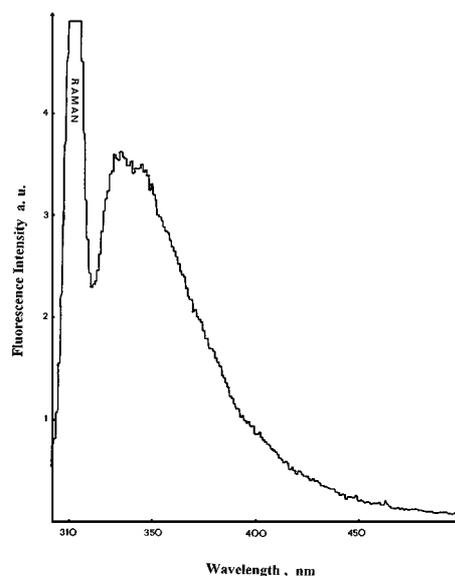


Fig. 2 Raman emission and prompt fluorescence spectra of 5H-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature.

decays, triplet-triplet absorption spectrum and triplet decays in different conditions are reported here. The identity of the delayed fluorescence and prompt fluorescence spectra excludes the possibility of the triplet state spectra observed being due to an impurity with a low-lying triplet state. Figures 1 and 2 show the one-photon absorption, Raman emission and prompt fluorescence spectra of 5H-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature, respectively. The peaks correspond to the $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions. The shape of the fluorescence spectrum is similar to the fluorescence spectrum of 5H-dibenzo[*a,d*]cycloheptene and 5H-dibenzo[*a,d*]cyclohepten-5-ol. The fluorescence spectrum of 5H-dibenzo[*a,d*]cyclohepten-5-one shows very intense Raman emission at around 310 nm. The Raman emission line is overlapped with the fluorescence emission, because the shape of the fluorescence below 320 nm is not clear. The T-T absorption spectra of 5H-dibenzo[*a,d*]cyclohepten-5-one and 5H-dibenzo[*a,d*]cycloheptene are similar. The only difference is a shift in the peak location by about 10 nm. The molecular weight of 5H-dibenzo[*a,d*]cyclohepten-5-one is greater than that of 5H-dibenzo[*a,d*]cycloheptene. The fluorescence spectra are also similar. The only difference is the Raman emission. This Raman emission is not observed for 5H-dibenzo[*a,d*]cycloheptene.

Because the Raman emission band is inside the absorption band ($S_0 \rightarrow S_1$), this emission is called Resonance Raman emission. The intensity of the Raman emission decreases rapidly along with an increase in the wavelength, as can be seen in Fig. 2. Raman scattering involves transitions to a lower energy state from a populated higher energy state. A quantum theory of the spectroscopic process should, therefore, treat the radiation and molecule together as a complete system, and explore how energy may be transferred

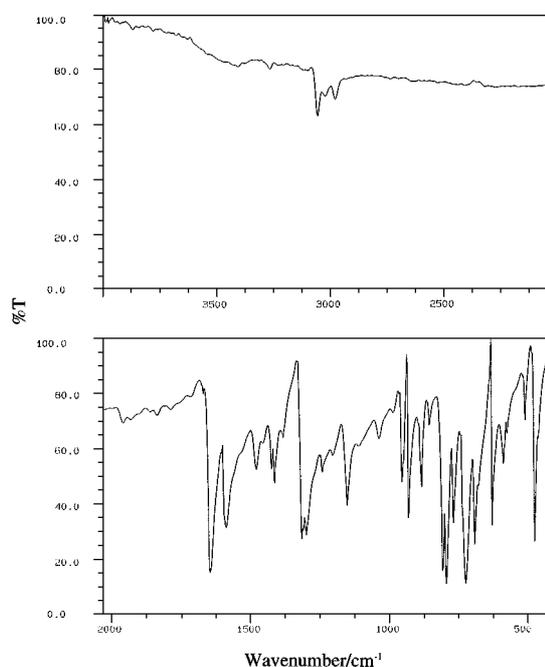


Fig. 3 FT-IR spectra of 5H-dibenzo[*a,d*]cyclohepten-5-one. (a) FT-IR spectra of the title compound between 4000 - 2000 cm^{-1} . (b) FT-IR spectra of the title compound between 2000 - 500 cm^{-1} .

between the radiation and the molecule as a result of their interaction. If a scattering system has an absorption band close to the excitation frequency, resonance Raman scattering results. The intensity of the resonance Raman scattering is usually many orders of magnitude greater than that of the prompt fluorescence. The decay of S_1 is influenced by the presence of oxy-

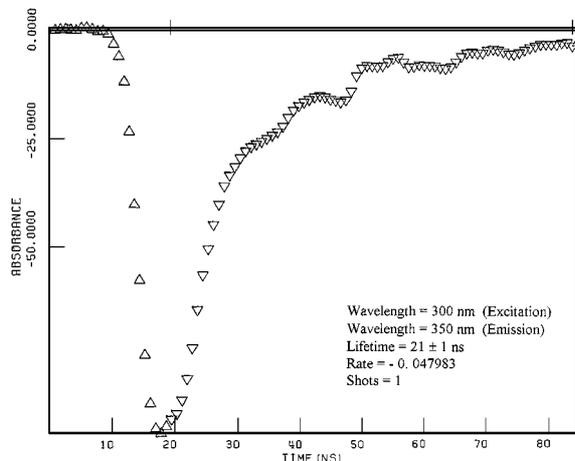


Fig. 4 Prompt fluorescence decay of *5H*-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature.

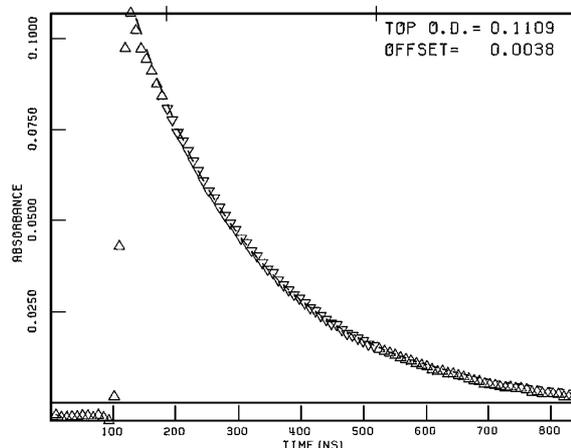


Fig. 6 Triplet decay of *5H*-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature.

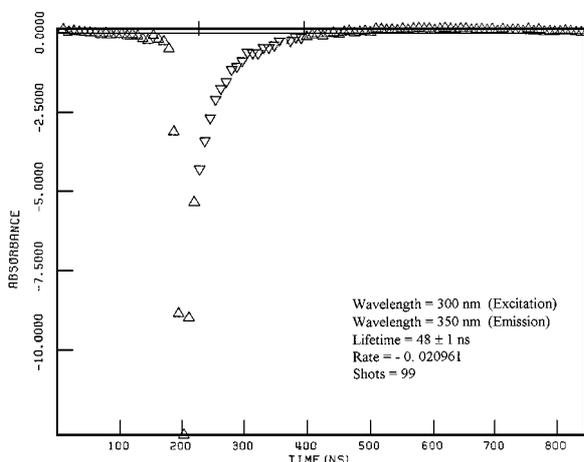


Fig. 5 P-type delayed fluorescence decay of *5H*-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature.

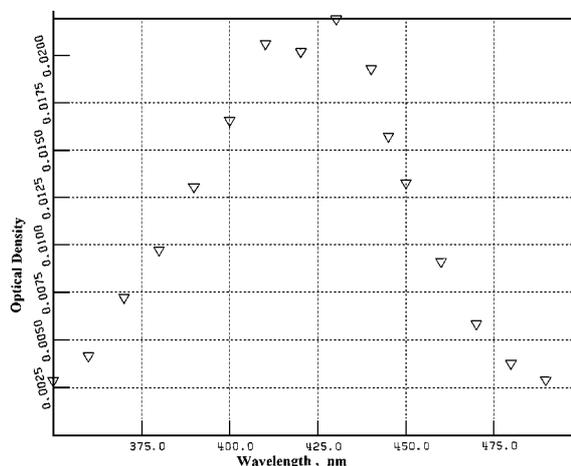


Fig. 7 Triplet-triplet absorption spectrum of *5H*-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature.

gen, but the decays for oxygen-free systems and the systems with oxygen in the presence of air were small and within the experimental error; for this reason it is not mentioned in the text. If the experiments were performed with oxygen-saturated solutions, a decay difference should be seen. The experimental difficulties do not permit us to carry out experiments with oxygen-saturated solutions. When we pump the optical energy, especially in the UV region, singlet oxygen is formed and an explosion in the tube is observed. In the future, experiments with oxygen will be carried out with extra care.

Figures 3 (a) and (b) show the FT-IR spectra of *5H*-dibenzo[*a,d*]cyclohepten-5-one between 4000 - 2000 cm^{-1} and 2000 - 400 cm^{-1} , respectively. Figure 3(b) shows many IR lines, which are almost equally spaced. We show the FT-IR spectra of the ground state of *5H*-dibenzo[*a,d*]cyclohepten-5-one in Fig. 3, because the highest vibrational energy level is closer to the lowest

energy value of the T_1 state. Unlike the molecule *5H*-dibenzo[*a,d*]cycloheptene, *5H*-dibenzo[*a,d*]cyclohepten-5-one does not phosphoresce. The energy gap is large enough only for IR decay from T_1 to S_0 to be observed. Therefore, multiphoton excitation is possible. Figures 4 and 5 show prompt and p-type delayed fluorescence decays in cyclohexane at room temperature; the decay times were determined to be 21 ± 1 ns and 48 ± 1 ns for prompt and delayed fluorescences, respectively. The other types of delayed fluorescence were tested, but unfortunately due to the very low emission signals, none of them were detectable. Figure 6 shows the triplet decay of *5H*-dibenzo[*a,d*]cyclohepten-5-one at 430 nm; the decay time was determined to be 199 ± 1 ns in the presence of air. Figure 7 shows the triplet-triplet absorption spectrum of *5H*-dibenzo[*a,d*]cyclohepten-5-one in cyclohexane at room temperature. Similar studies using an analogue may have wide application as a method for analyzing photochemical and

Table 1 Photophysical parameters of 5*H*-dibenzo[*a,d*]cyclohepten-5-one in different solutions and different conditions

Solution	Condition	T-T peak/ nm	Decay of S ₁ / ns	Decay of T ₁ / ns
Cyclohexane	vacuum degassed	430	21±1	5790±5
	argon-saturated			980±5
	air-diffused			199±5
Ethanol	vacuum degassed	425	12±1	8032±5
	argon-saturated			890±5
	air-diffused			216±5
Methanol	vacuum degassed	425	13±1	7095±5
	argon-saturated			740±5
	air-diffused			196±5
Benzene	vacuum degassed	440	17±1	6910±5
	argon-saturated			650±5
	air-diffused			252±5
Hexane	air-diffused	430	18±1	166±5

photophysical reactions. Table 1 lists photophysical parameters of the title compound in different solutions and under different conditions.¹³

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