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PHOTOPHYSICAL PROCESSES OF TRIPTYCENE IN CYCLOHEXANE

FUAT BAYRAKÇEKEN, LEMAN SAĞAT*, ABDULLAH ÇAVUŞ

Spectroscopy Lab. Department of Engineering Physics, Ankara University, 06100 Tandoğan, Ankara, Turkey

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ABSTRACT

Phosphorescence, triplet lifetime and T-T absorption spectra of triptycene in cyclohexane are studied by flash photolysis at room temperature and at 77 K. The results are compared with the findings of photolysis experiments of triptycene in different solvents.

INTRODUCTION

Triptycene (tribenzobarrelene) has been given much attention since the first synthesis by Barlett, owing to its rigid cage structure. A considerable number of studies have been carried out about electronic spectra of triptycene and its derivatives. On the basis of appreciable spectral difference between triptycene and triphenylmethane in absorption maxima as well as in extinction coefficient, Bartlett and Lewis ascribed the difference to the presence of intramolecular charge transfer (cross-ring interaction) in triptycene (Bartlett, Lewis 1950).

On the other hand Wilcox, and Craig calculated the UV spectrum of triptycene (Wilcox 1960) and a few ring-substituted triptycenes (Wilcox 1961) and concluded that the spectra of these compounds could be regarded as the superpositions of the three benzenoid chromophores.

Photochemical isomerization of triptycene was studied by (Walsh 1969 and Turro and his co-workers Tobin, Friedman, Hamilton 1969). They found that triptycene produces a single yellow isomer (λmax, 249, 345 nm., log$\in$, 4.26, 3.89) upon direct irradiation in dilute ether or acetone solution. This product was neither the anticipated semibull-

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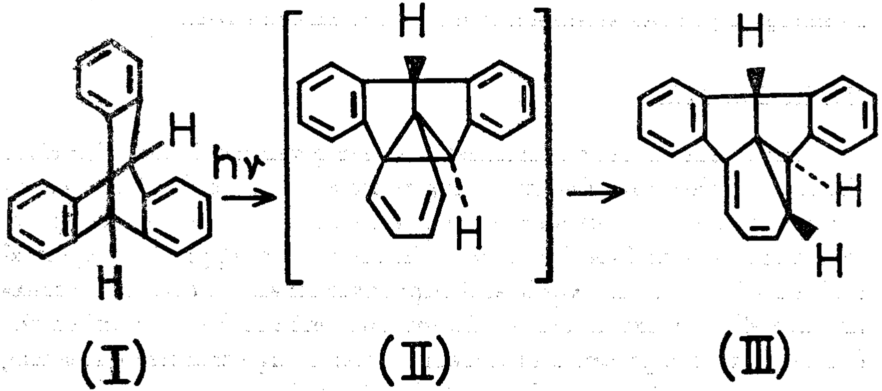
* Faculty of Engineering, Yıldız University, Kocaeli, Turkey.

valene nor a cyclooctatraene derivative. This result contrasted with previous results on the photochemistry of barrelene and its benzoderivatives which yield a mixture of semibullvalenes and cyclooctatraenes when irradiated. Formation of (III) was interpreted by Walsh and Turro in terms of formation of the semibullvalene (II) which then undergoes a sigmatropic rearrangement to the more stable (III). The conversion of (I) to (III) was thought to be a very fast triplet rearrangement. However, it was also pointed out that since formation of (III) was also observed in photolyses at 77 K, unless the rate of this rearrangement prossessed a remarkably large temperature coefficient, it appeared unlikely that the reaction occurs from T_1 (Turro 1969).

The excited-state reactions of triptycenes are also studied by (Iwamura and Yoshimura 1974). They suggest that a carbene mechanism takes place for the photolytic rearrangement of (I) to (III).



Photochemical studies of triptycene by flash photolysis reveal that the excited triptycene formed in the primary step subsequently undergo a variety of processes, triplet formation, isomerization, etc. Irradiation of triptycene (I) results in the smooth formation ($\varnothing=0.3$) of one product (III).

EXPERIMENTAL

Triptycene was purified by repeated recrystallization, all other chemicals used were analytical reagent grade. Phosphorescence spectrum and intensities were measured on a Hitachi Perkin-Elmer, MPF-2A spectrofluorimeter, and triplet-triplet absorption experiments were carried out using a flash photolysis apparatus described previously (Watkins, Bayrakçeken 1980).

RESULTS AND DISCUSSION

The photoconversion of (I) to (III) is a fast triplet rearrangement. In photolysis experiments there is no possibility to observe the formation of triplet triptycene. Since phosphorescence and delayed fluorescence of triptycene are observable we may write the following: (Here ^1M represents triptycene in its ground electronic state).

$$^1M + h\nu_1 \rightarrow {}^1M^* \rightarrow {}^3M^*$$

$$^3M^* \rightarrow {}^1M + h\nu_2 \quad \text{(phosphorescence)}$$

$$^3M^* + h\nu_3 \rightarrow {}^3M^{**} \quad \text{(T-T absorption)}$$

$$^3M^* \rightarrow \text{photoproduct (I to II)}$$

Figure 1. shows one-photon absorption spectra of (I) and (III), figure 2. shows excitation spectrum of (I), figure 3. shows phosphorescene spectrum of (I) at 77 K and figure 4 shows T-T absorption spectrum of (I) in cyclohexane at room temperature. The spectrum of figure 4, shows that triptycene triplets are stable at room temperature. This conclusion is reinforced by the appearance of delayed fluorescence. The lowest excited singlet state of triptycene is regenerated by triplet-triplet annihilation for p-type delayed fluorescence experiments. Due to the noisy signals, decay time for p-type delayed fluorescence is not reported here. But estimated decay times were in agreement with the triplet lifetime. 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 or a photoproduct.

The formation of photoproduct (III), phosphorescence emissions from triplet state, collisional radiationless decays from triplet state, and triplet-triplet annihilation decreased the triplet triptycene concentration, therefore triplet-triplet absorption is weakly observed at room temperature. Triplet lifetime in cyclohexane is measured at 420 nm., and found to be 196 microsecond. The concentrations of the samples were 2.5×10^{-4} M, for all the experiments.

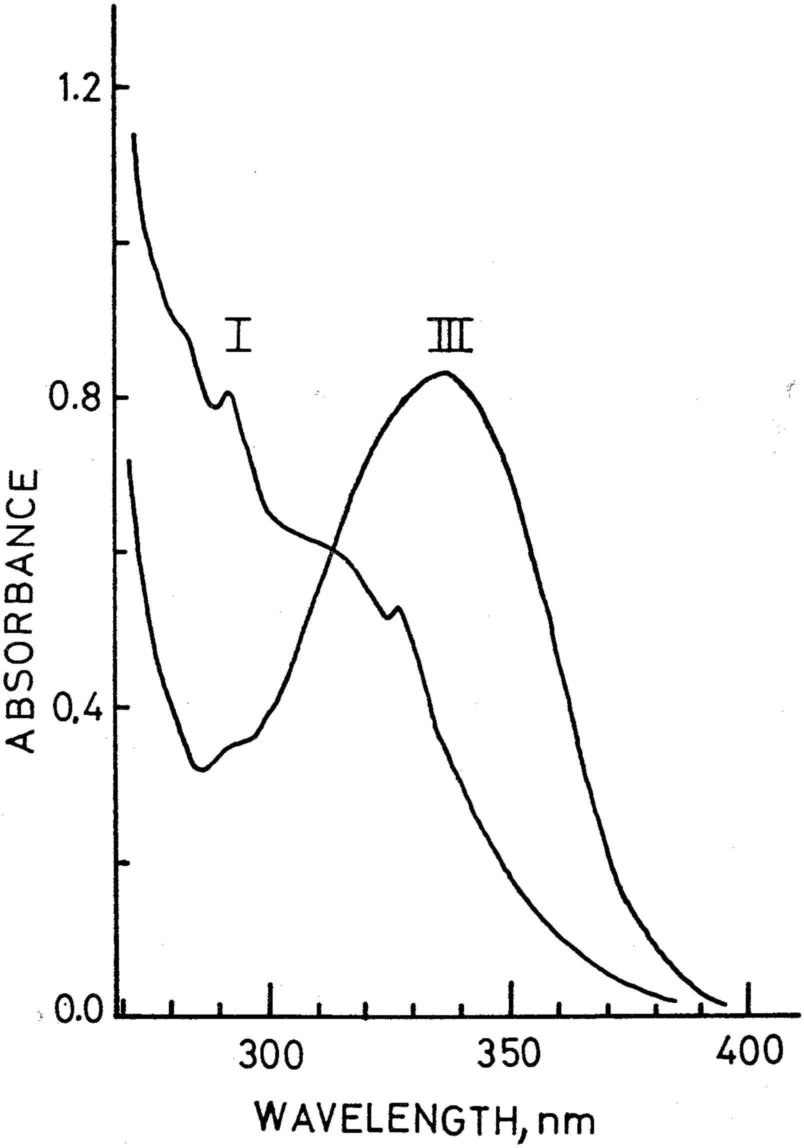


FIG. 1. Absorption spectra of triptycene and photoproduct in cyclohexane at room temperature.

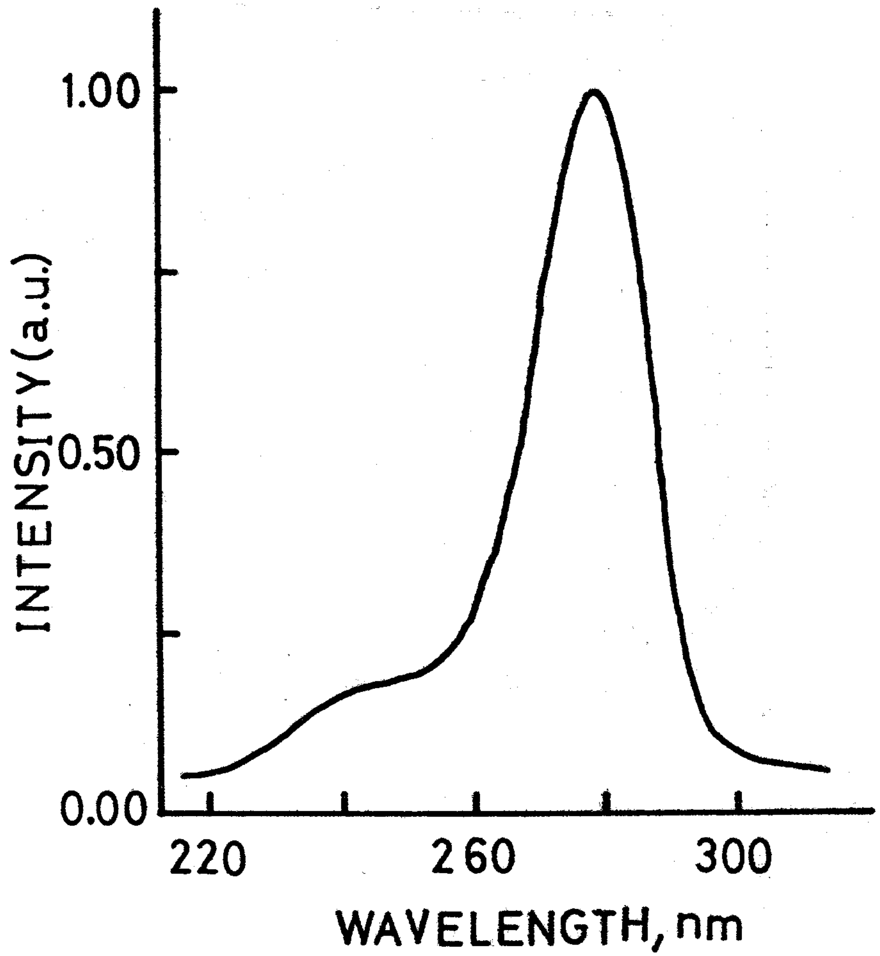


FIG. 2. Excitation spectrum of triptycene in cyclohexane at room tempearture, λem = 280 nm.

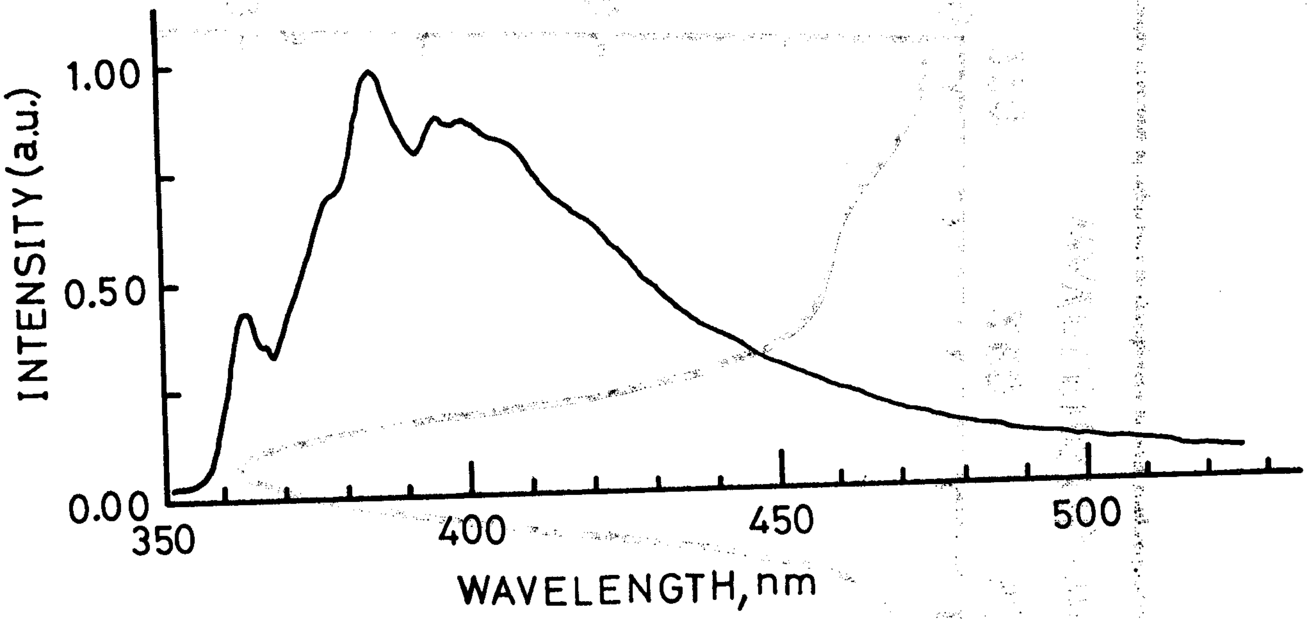


FIG. 3. Phosphorescence spectrum of triptycene in cyclohexane at 77 K, λex = 280 nm.

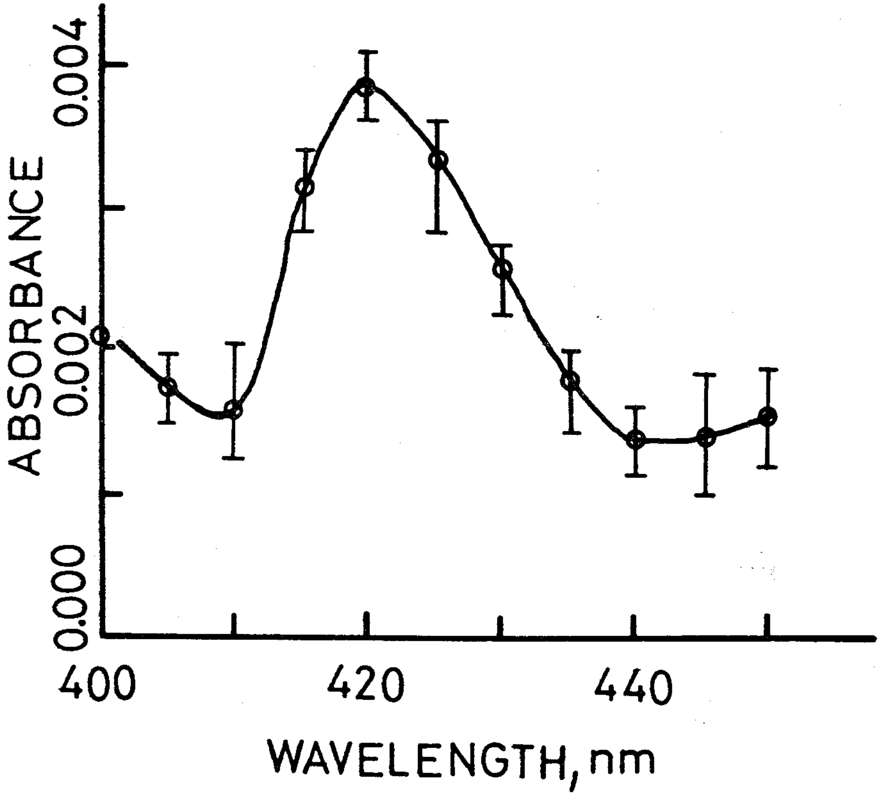


FIG. 4. T—T absorption spectrum of triptycene in cyclohexane at room temperature.

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