

BEHAVIORS OF THE TRIPLET MOLECULE IN NEAT LIQUID OF
NAPHTHALENE DERIVATIVES AT ROOM TEMPERATURE

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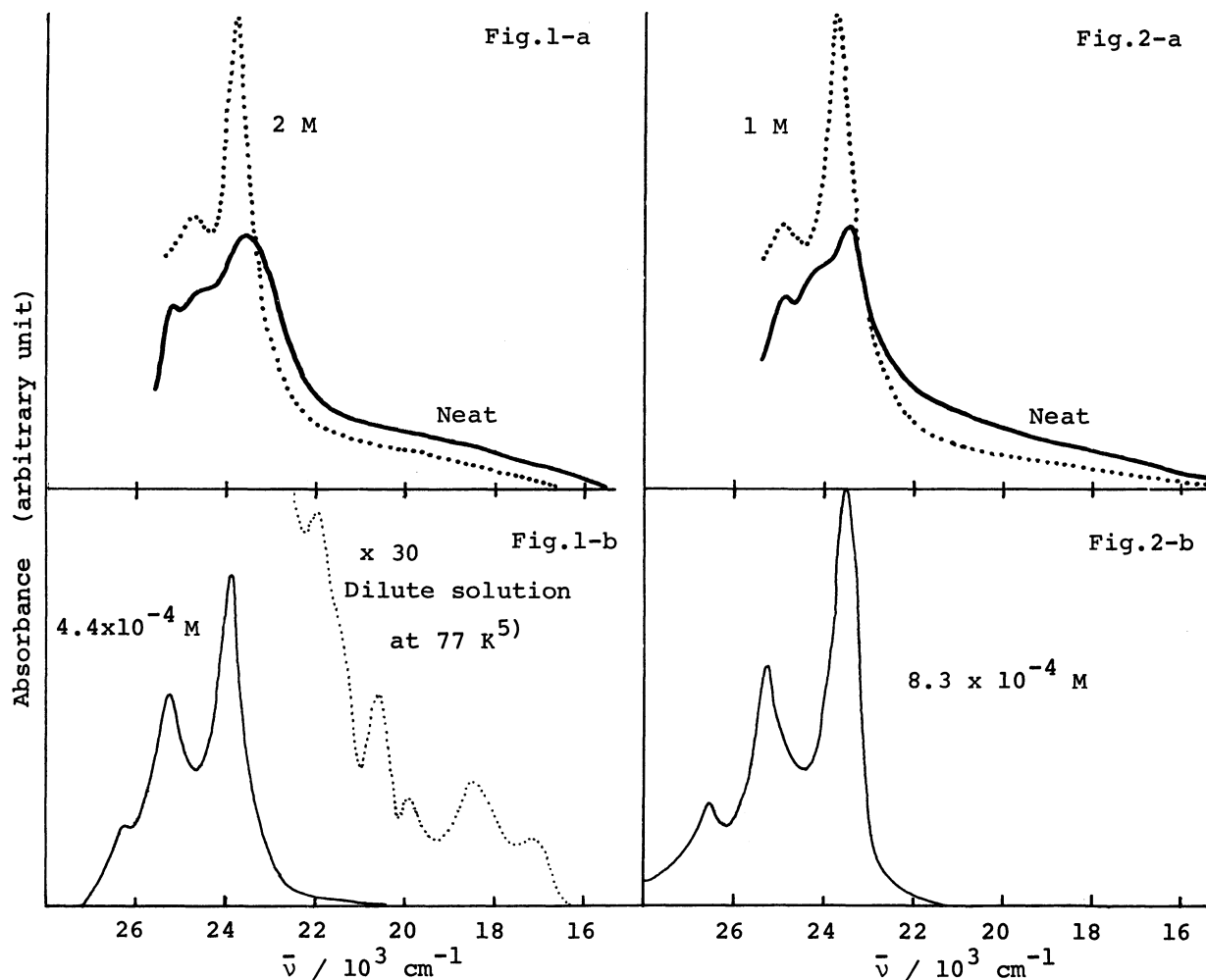
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Triplet excited species in neat liquids of 1-methylnaphthalene and 1-chloronaphthalene were investigated by means of flash photolysis. The triplet excited dimers are assumed on the bases of analysis of T-T absorption spectra. A rapid T-T energy transfer from 1-chloronaphthalene to trans-stilbene indicates a triplet excitation migration.

While the symmetry forbidden bands of neat benzene is almost the same as those in the dilute solution,¹⁾ the neat liquid emits both the molecular fluorescence and the excimer fluorescence²⁾ in contrast to the crystal with the molecular fluorescence.³⁾ In the neat benzene, the excitation energy may be exchanged among the several molecules being close with each other.⁴⁾ We tried to investigate the triplet excited species in neat 1-methylnaphthalene and 1-chloronaphthalene by means of flash photolysis. The two flash lamps (FP-4 of Xenon Co.) were operated with 10~15 kV and capacitance of 0.2~4 μ F and had the duration of 2.5~10 μ s. The sample cells had an inner diameter of 0.35, 0.40, 0.45 or 1.0 cm and a length of 10 cm. When the neat liquids are irradiated by the flash, the light absorption is completed in the thin layer close to the cell wall. It is, therefore, difficult to make an accurate measurement of the transient absorption of the excited species. In order to avoid this difficulty, benzophenone of $8 \sim 10 \times 10^{-3}$ M was added as an triplet sensitizer to make the triplet states of the molecules in question. By this means, uniform concentrations of the triplet states were established through over the samples. 1-methylnaphthalene was purified by means of column chromatography on alumina and 1-chloronaphthalene by means of distillation under reduced pressure.

Fig.1-a shows the transient absorption spectrum observed at 30 μ s after flashing the neat 1-methylnaphthalene. The absorption spectrum consists of two bands, one band (B-I) in the near u.v. region and the other broad band (B-II) in the visible region.

On the other hand, the T-T absorption spectrum in a dilute hexane solution consists of a strong and well resolved band in the u.v. region and a very weak tail in the visible region (Fig.1-b). The visible band is one-hundredth in intensity of the u.v. band in methanol and ethanol according to Meyer et al.⁵⁾ As 1-methylnaphthalene was diluted with isooctane keeping the triplet production constant, B-I was increased in intensity, but B-II was decreased to fading out at the solution of 10^{-1} M (see Fig.1-a). The dependence of B-II intensity on the concentration of 1-methylnaphthalene ($[N]$) is shown in Fig.3, where $A(480)$ is the transient absorbance at 480 nm, denoting the production of the triplet excimer and $A^\circ(420)$ is the transient absorbance at 420 nm of the 10^{-1} M solution, denoting the total production of the triplet species. The linear relationship in Fig.3 indicates an existence of the triplet excimer which is in equilibrium with the molecular triplet. The triplet excimer formation constant is obtained to be 0.15 M^{-1} at 292 K from the slope and the intercept. This value is a little smaller than the formation constant of the singlet excimer (0.80 M^{-1} at 293 K ⁶⁾);



this is reasonable, because the excimer formation is brought out by only coulomb exchange interaction in the triplet state but by both coulomb exchange and molecular exciton interactions in the singlet excited state. The existence of the rapid equilibrium was supported by the simultaneous decay of B-I and B-II (the first order decay constant is $4 \times 10^4 \text{ s}^{-1}$ for the neat 1-methylnaphthalene).

Also in the case of 1-chloronaphthalene, the similar observation was made.

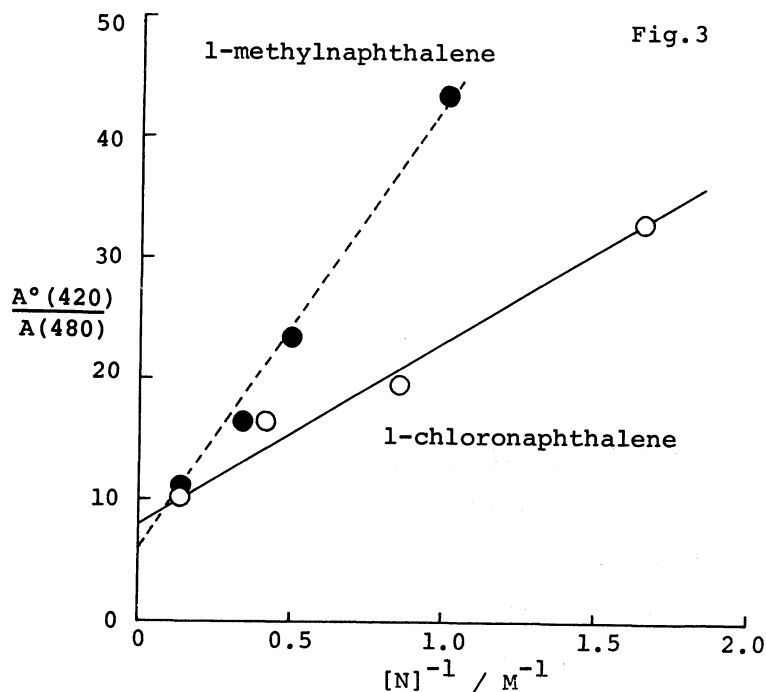


Fig.3 to be 0.55 M^{-1} at 295 K.

It is improbable that the new bands are attributed to some impurity molecule of the triplet multiplicity, since the lifetimes of B-II and B-II' agreed with those of B-I and B-I' respectively in any condition. The explanations that the visible band is due to an anion or cation radical of a naphthalene derivative or a kety radical of benzophenone are excluded by the disagreement between the absorption spectra of B-II and those of the radicals.^{7,8)} It is also improbable that B-II and B-II' are attributed to the triplet state of some molecular complex between the naphthalene derivative and benzophenone, because pulse radiolyses of neat 1-methylnaphthalene⁹⁾ and neat 1-chloronaphthalene¹⁰⁾ in the absence of benzophenone produced transient species with the same spectra as shown in Fig.1-a and Fig.2-a.

It is not likely that the symmetry forbidden band of the triplet molecule may be strengthened in the neat liquid by the effect of the localized field of the neighbouring molecules (so-called solvent effect), because the intensity of the lowest symmetry

Fig.2-a shows a transient absorption spectrum of neat 1-chloronaphthalene in which the broad bands (B-II') in the visible region is one-fourth in intensity of that of the band (B-I') in the u.v. region, where one well-resolved absorption band in the u.v. region was observed in the dilute isooctane solution (see Fig.2-b).

The same first order decay constants ($5.0 \times 10^4 \text{ s}^{-1}$) were measured for both bands. From the dilution effect on the intensity of B-II' with isooctane, the triplet excimer formation constant is calculated from

forbidden band of benzene is independent of the concentration, the dilute solution or the neat liquid. It is more probable that the symmetry forbidden transition (${}^3B_{2u}^+$ ${}^3A_{1g}^+$ in naphthalene¹¹⁾) in the dilute solutions becomes allowed as a result of the excimer formation, which was proposed by several authors^{12,13)} on the basis of the measurement of phosphorescence spectra of naphthalene and its derivative.

The triplet excitation migration in the neat liquid was supported by the fact that the rate constant ($6.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) of T-T energy transfer between 1-chloronaphthalene and trans-stilbene ($0.125 \times 10^{-6} \text{ M}$) was three times as large as that of the diffusion controlled reaction in 1-chloronaphthalene ($1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ at 301 K).

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