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Studies on the Electronic Spectra of Anethole Trithione

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The absorption and emission spectra of anethole trithione in various solvents were studied. In methylcyclohexane, an (n→π^*) absorption band was clearly observed in the longer wavelength region. It was postulated that anethole trithione emits fluorescence from the $S_2(^1(\pi, \pi^*))$ state on the basis of the positions of its maxima and excitation spectra. Judging from the solvent effect on the phosphorescence spectra and the lifetimes, the phosphorescence was assigned as (π^*→n). The intensity ratio of fluorescence and phosphorescence was larger in methylcyclohexane than in MeOH. This phenomenon is explained using energy level diagrams.

Keywords——anethole trithione; absorption spectra at room temperature; emission spectra at 77 K; (n→π^*) absorption band; (S_2→S_0)fluorescence; (π^*→n)phosphorescence

It is known that aromatic thioketones exhibit interesting photochemical behavior[2] because the energy gap between the lowest $^1(n,\pi^*)$ and the next higher $^1(\pi,\pi^*)$ states is very large.[3] Therefore, the electronic spectra of these compounds are of particular interest in connection with the photochemical reactions. However, no detailed studies on the electronic spectra of anethole trithione, which has been used as a cholagogue, have been reported. In this paper, the absorption and emission spectra of this compound in various solvents are reported.

Experimental

Material——Anethole trithione was generously supplied by Nippon Shinyaku Co., Ltd., and was purified by repeated recrystallization from EtOH before use, mp 110—111° (lit. 110°).[4] No trace of impurity was detected by thin-layer chromatography on silica gel (solvent: *n*-hexane–ethylacetate (9:1)).

Solvents——MeOH was purified according to the method described in the literature.[5] Other solvents used (methylcyclohexane, benzene, and iso-BuOH) were of commercial spectrograde.

Measurements——The absorption spectra at room temperature were measured with a Hitachi 200-20 spectrophotometer. The emission spectra at 77 K were measured with a Hitachi MPF-2A fluorescence spectrophotometer with a phosphorescence attachment. The fluorescence and total emission spectra, and the phosphorescence spectra were measured without and with a rotating-shutter phosphoroscope, respectively. The emission spectra were not corrected for the response characteristic of the instrument. The phosphorescence lifetimes were determined using a Iwatsu DM-305 digital memory and SS-5111 synchroscope. Unless otherwise noted, monochromatic light (430 nm) was used for excitation. All solvents were checked for emission deriving from impurities.

Results and Discussion

Absorption Spectra

Fig. 1 shows the absorption spectra of anethole trithione in methylcyclohexane, benzene, iso-BuOH, and MeOH solutions at room temperature. The positions and molar extinction

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[1] Location: *Yamashiro-cho, Tokushima 770, Japan.*

[2] H. Gotthardt, *Chem. Ber.*, **105**, 2008 (1972); P. de Mayo and H. Shizuka, *Mol. Photochem.*, **5**, 339 (1973).

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[4] B. Böttcher and A. Lüttringhaus, *Ann.*, **557**, 89 (1947).

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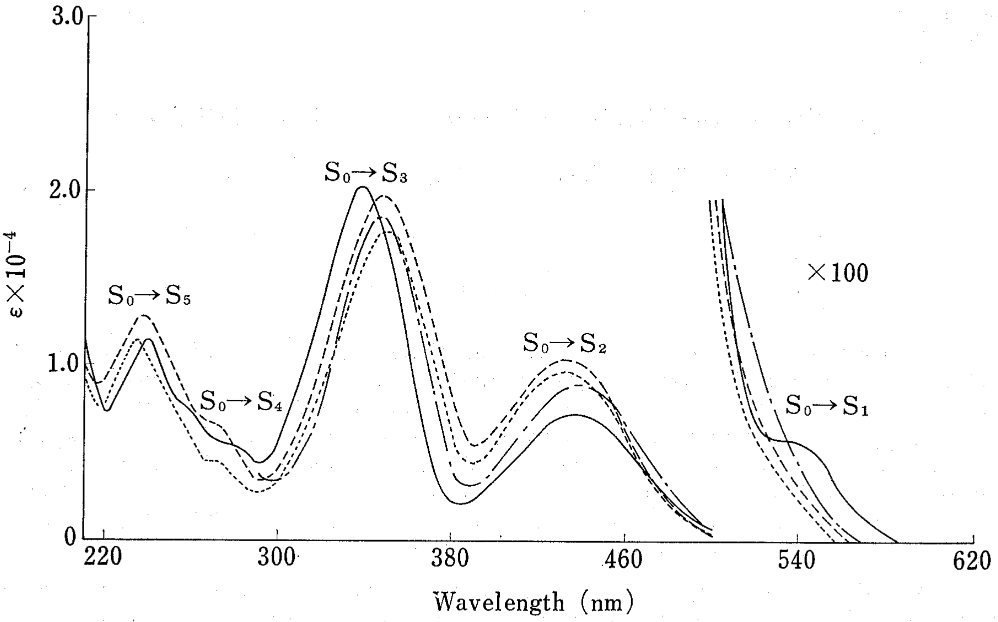

Fig. 1. Absorption Spectra of Anethole Trithione in Various Solvents at Room Temperature

——: methylcyclohexane. —·—: benzene. — —: iso-BuOH. ------: MeOH.

Table I. Absorption Spectral Data for Anethole Trithione at Room Temperature

Solvent	λ_{max}, nm (ε)				
	($S_0 \rightarrow S_1$)	($S_0 \rightarrow S_2$)	($S_0 \rightarrow S_3$)	($S_0 \rightarrow S_4$)	($S_0 \rightarrow S_5$)
Methylcyclohexane	540 (56)	438 (7350)	338 (20200)	280 (5430)^s	238 (11770)
Benzene		437 (8920)	347 (18400)		
iso-Butanol		434 (10460)	348 (19600)	274 (5930)^s	236 (12730)
Methanol		433 (9830)	349 (17500)	270 (5830)^s	234 (11250)

s: shoulder.

coefficients (ε) of the absorption maxima (λ_{max}) are listed in Table I. It can be seen that anethole trithione has five broad absorption bands in solutions. These bands are located at around 540 ($S_0 \rightarrow S_1$), 440—430 ($S_0 \rightarrow S_2$), 350—340 ($S_0 \rightarrow S_3$), 280—270 ($S_0 \rightarrow S_4$), 240—235 nm ($S_0 \rightarrow S_5$). The position of λ_{max} of the ($S_0 \rightarrow S_1$) band was clear in methylcyclohexane solution, but it was not clear in other solvents. As may be seen in Fig. 1, however, this band appears to show a blue shift with increasing polarity of the solvent. In addition, the ε value in methylcyclohexane solution was 56. Accordingly, it is considered that the ($S_0 \rightarrow S_1$) band arises from $n \rightarrow \pi^*$ transition. On the other hand, the other absorption bands may be assigned as ($\pi \rightarrow \pi^*$) bands on the basis of the ε values. Among these ($\pi \rightarrow \pi^*$) bands, the ($S_0 \rightarrow S_3$) band shows a red shift with increasing polarity of the solvent, but the ($S_0 \rightarrow S_2$), ($S_0 \rightarrow S_4$), and ($S_0 \rightarrow S_5$) bands show a blue shift. In general, a ($\pi \rightarrow \pi^*$) band shows a red shift due to the solvent effect,[6] so this observation is noteworthy. However, such a blue shift of a ($\pi \rightarrow \pi^*$) band has been reported for several compounds.[7]

Emission Spectra

The fluorescence of anethole trithione could not be detected at room temperature, but was observed at around 495 nm at 77 K. Fig. 2 shows the fluorescence, phosphorescence, and

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6) A. Kuboyama, *Bunko Kenkyu*, **20**, 14 (1971).

7) T. Nakabayashi, *Yakugaku Zasshi*, **74**, 901 (1954); H. Matsumoto and Y. Ohkura, *Chem. Pharm. Bull.*, **26**, 3433 (1978).

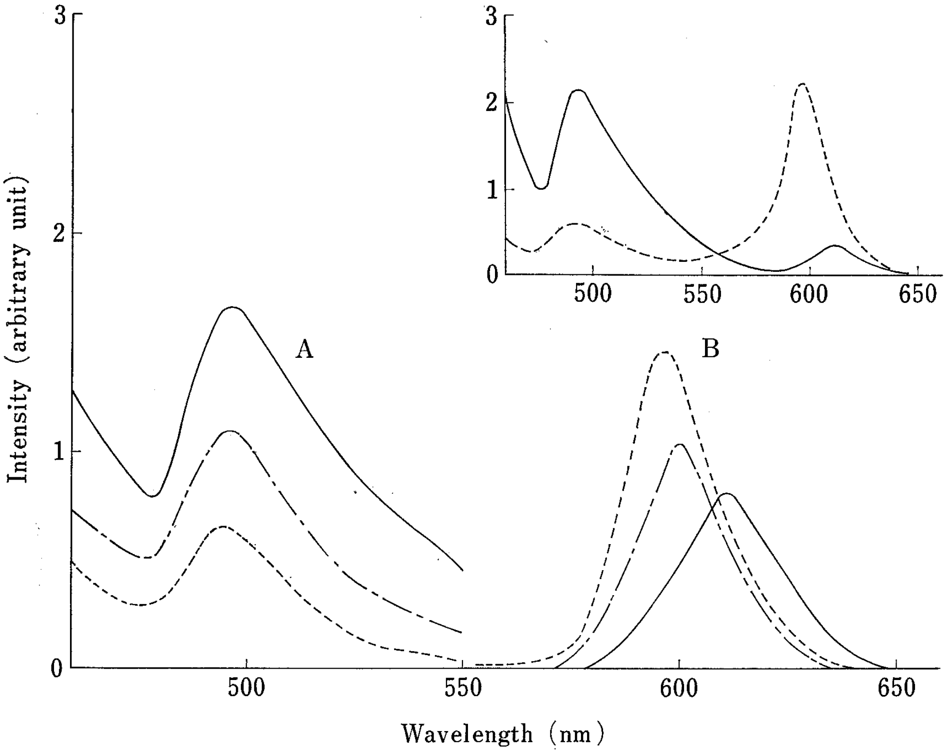

Fig. 2. Emission Spectra of Anethole Trithione in Various Solvents at 77 K

——: methylcyclohexane. —·—: iso-BuOH. ----: MeOH.
A: fluorescence. B: phosphorescence.
Concentration: 2.5×10^{-4} M for fluorescence, 1.0×10^{-3} M for phosphorescence.
Insert: total emission spectra; concentration, 2.5×10^{-4} M.

Table II. Emission Spectral Data for Anethole Trithione at 77 K

Solvent	$\lambda_{\max}^{f}$ (nm)	$\lambda_{\max}^{p}$ (nm)	$\tau^{a)}$ (msec)
Methylcyclohexane	496	610	
iso-Butanol	494	600	1.6
Methanol	494	597	2.0

a) Phosphorescence lifetime.

total emission spectra in various solvents at 77 K. The emission spectral data are summarized in Table II. The positions of the fluorescence maxima ($\lambda_{\max}^{f}$) seem to show little change with different solvents. It appears that the fluorescence is located between the $\lambda_{\max}$ of the ($S_0 \rightarrow S_1$) and ($S_0 \rightarrow S_2$) bands (Figs. 1 and 2). This is clear in methylcyclohexane solution; the positions of $\lambda_{\max}$ of the ($S_0 \rightarrow S_1$) and ($S_0 \rightarrow S_2$) bands were 540 and 438 nm, respectively, and that of the $\lambda_{\max}^{f}$ was 496 nm (Tables I and II). Moreover, the fluorescences excitation spectra in the solvents used resembled the ($S_0 \rightarrow S_2$) band (not shown), and when the solutions were excited at the ($S_0 \rightarrow S_1$) band, no fluorescence could be observed. On the basis of these experimental results, it seems reasonable to conclude that anethole trithione emits fluorescence, not from the lowest excited singlet state (S_1 $^1(n, \pi^*)$), but from the next higher excited singlet state (S_2 $^1(\pi, \pi^*)$), *i.e.*, so-called ($S_2 \rightarrow S_0$) fluorescence. In thiocarbonyl compounds, such fluorescence has been reported in xanthione,8) thioxanthione,8,9) and aryl alkyl thioketones.10) It may be

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8) J.R. Huber and M. Mahaney, *Chem. Phys. Lett.*, **30**, 410 (1975).
9) M. Mahaney and J.R. Huber, *Chem. Phys.*, **9**, 371 (1975).
10) M.H. Hui, P. de Mayo, R. Suau, and W.R. Ware, *Chem. Phys. Lett.*, **31**, 257 (1975).

explained in terms of the large energy gap between S_1 and S_2 states, which makes vibrational coupling between these states ineffective so that the rate of $S_2 \rightarrow S_1$ internal conversion becomes slow.[8,9] For anethole trithione, the value of the energy gap was 0.6 eV, and it appears to be small compared with those of other thiocarbonyl compounds which exhibit ($S_2 \rightarrow S_0$) fluorescence (~1.0 eV).

As may be seen in Fig. 2, anethole trithione shows broad phosphorescence spectra around 600 nm in solutions. The position of the phosphorescence maximum ($\lambda_{\max}^{p}$) in MeOH solution was at shorter wavelength than that in methylcyclohexane solution, and the lifetimes in iso-BuOH and MeOH were short (~msec.). Thus, the obtained phosphorescence may be assigned to ($\pi^* \rightarrow$n) phosphorescence.[11] In methylcyclohexane, the lifetime could not be measured because the phosphorescence was very weak.

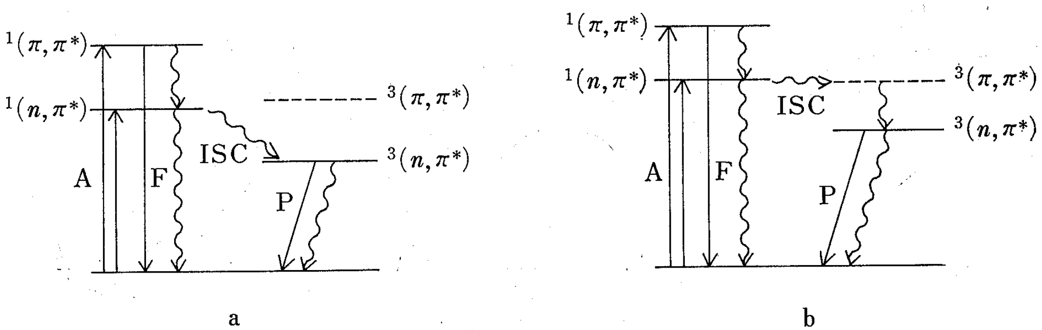

Fig. 3. Energy Level Diagrams of Anethole Trithione in Non-polar (a) and Polar (b) Solvents

A: absorption. F: fluorescence. P: phosphorescence. ISC: intersystem crossing.
⟶: radioactive process. ⇝: radiationless process.

Energy Levels

On the basis of the absorption and emission spectral data described above, it appears that the lowest excited singlet and triplet states of anethole trithione are both (n, π^*) states. On the other hand, as may be seen in the total emission spectra which were measured under the same conditions (insert in Fig. 2), the fluorescence intensity was stronger than the phosphorescence intensity in methylcyclohexane solution, but this was reversed in MeOH solution. According to Lower and El-Sayed,[12] intersystem crossing is most efficient when it is between states of different electronic configuration, so that it is faster for (n, π^*)$\leftrightarrow$(π, π^*) than for (π, π^*)$\leftrightarrow$(π, π^*) or (n, π^*)$\leftrightarrow$(n, π^*). Therefore, the above results may be interpreted as indicating that the ^{1}(n, π^*) level is lower than the ^{3}(π, π^*) level in a nonpolar solvent such as methylcyclohexane (Fig. 3a), while in a polar solvent such as MeOH, the ^{1}(n, π^*) level becomes higher the ^{3}(π, π^*) level as a result of hydrogen bond formation between anethole trithione and the solvent (Fig. 3b). This interpretation is supported by the following result: although phosphorescence could not be observed when the methylcyclohexane solution was excited at 540 nm (($S_0 \rightarrow S_1$) band), in the case of the MeOH solution it appeared near 600 nm in spite of the smaller absorptivity at this wavelength compared with the methylcyclohexane solution (Fig. 1).

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11) A. Kuboyama and S. Yabe, *Bull. Chem. Soc. Jpn.*, **40**, 2475 (1967).
12) S.K. Lower and M.A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).