Luminescence and Electron Paramagnetic Resonance Studies of the Excited States of a UV Absorber, 2-Methylphenyl 2-Naphthoate

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Fluorescence, phosphorescence, and electron paramagnetic resonance spectra have been observed for the excited states of a new UV absorber, 2-methylphenyl 2-naphthoate (2-MPN), in ethanol at 77 K. The observed phosphorescence spectrum, phosphorescence lifetime, and zero-field splitting parameters of the lowest excited triplet (T_1) state of 2-MPN revealed that the T_1 state of 2-MPN can be regarded as a locally excited triplet state within naphthalene.

The decrease of the ozone layer results in an increase of UV radiation reaching the surface of the earth.[1] The past decade has seen a considerable increase in studies of the photophysics and photochemistry of organic UV absorbers resulting from an increased awareness of the damaging effects of UV radiation on human skin.[2]

Although the effectiveness of UV absorbers is primarily based on absorption and absorption coefficient in the UV-B (280–320 nm) and UV-A (320–400 nm) regions, after-absorption processes are equally important. To be effective as harmless UV-blocking compounds in skin-care sunscreens, the UV absorbers have to ensure that the absorbed UV energy is rapidly transformed into vibrational energy without harmful reactions in the skin. Therefore, it is important to investigate the nature of the photoexcited states of the UV absorbers and their deactivation processes.

In practice, UV absorbers are used in combination with other UV absorbers and many additives. It is especially important to determine the energy levels of the lowest excited triplet (T_1) states of individual UV absorber because triplet–triplet energy transfer from a donor to an acceptor will occur between the UV absorbers.

In the present work, we determined the energy levels of the lowest excited singlet (S_1) and T_1 states of a new UV absorber, 2-methylphenyl 2-naphthoate (2-MPN), by measuring the UV absorption, fluorescence, and phosphorescence spectra in ethanol (EtOH) at 77 K. 2-MPN provides highly safe and effective protection against UV-A and UV-B and is useful for skin cosmetics.[3] We obtained the zero-field splitting (ZFS) parameters of the T_1 state by measuring the electron paramagnetic resonance (EPR) spectra in EtOH at 77 K. The nature of the T_1 state of 2-MPN is discussed. The phosphorescence and EPR spectra of the T_1 state of naphthalene have also been observed for comparison.

2-MPN obtained from Lead Chemical Co. (Toyama, Japan) and EtOH (Wako Super Special Grade) were used without further purification. The sample solutions were prepared at a concentration of 3×10^{-5} or 3×10^{-3} mol dm^{-3} for the luminescence measurements or 3×10^{-3} mol dm^{-3} for the low-temperature UV absorption and EPR measurements.

The UV absorption spectra were measured with a JASCO V-550 spectrometer and a Hitachi U-3210 spectrometer. To prevent the sample from cracking, the samples were prepared as follows: the sample solution was added dropwise on a quartz plate, and it was covered with another quartz plate. The sandwiched samples were rapidly immersed in liquid nitrogen. The optical path length was about 0.05 mm.

The fluorescence spectra were measured with a JASCO FP-6500 spectrofluorometer. For the phosphorescence and EPR measurements, samples were excited with an Ushio 500-W Hg lamp with an Asahi Technoglass UV-D33S glass filter, 5 cm of distilled water, and a Copal DC-494 electromechanical shutter. The details of the phosphorescence and EPR measurements have been described previously.[4]

The UV absorption spectra of 2-MPN were measured at 298 and at 77 K. Although 2-MPN has a very strong absorption band at 240 nm ($\varepsilon = 63200$ mol^{-1} dm^3 cm^{-1}), it also has strong absorption bands in the UV-B region ($\varepsilon \approx 9000$ mol^{-1} dm^3 cm^{-1}) and absorption bands in the UV-A region ($\varepsilon \approx 1600$ mol^{-1} dm^3 cm^{-1}), as shown in Figure 1a. The S_1 energy of 2-MPN was estimated to be 29400 cm^{-1} from the intersection point of the fluorescence and fluorescence-excitation spectra.[5] As shown in Figure 1b, the vibronic bands of the fluorescence spectrum are the same as those of the fluorescence-excitation spectrum, although the latter spectrum shows somewhat blurred vibronic bands.

Figure 2 shows the phosphorescence spectra of 2-MPN and naphthalene. As is clearly seen in Figure 2, the phosphorescence spectrum of 2-MPN is very similar to that of naphthalene. The T_1 energies of 2-MPN and naphthalene were estimated from the first peaks of phosphorescence. The results are shown in Table 1. The T_1 lifetimes were obtained from the decay curves of phosphorescence, as listed in Table 1.

The EPR spectra of the T_1 states of 2-MPN and naphthalene were measured at 77 K, as shown in Figure 3. The assignment of each resonance field of naphthalene has already been performed with the aid of a single-crystal method.[7] The ZFS parameters obtained are listed in Table 1. The lifetimes of the T_1 states obtained from the decay of the EPR signals are also listed in Table 1. We find that the T_1 lifetimes obtained from the decay curves of the EPR signals, τ_{EPR}, are in good agreement with those obtained from the decay curves of phosphorescence, τ_{phos}. This agreement shows that the EPR and phosphorescence signals originate from the same photoexcited state.

We can see from Table 1 that the D value of 2-MPN obtained is about 0.1 cm^{-1} and the T_1 state has the lifetime of the order of 1 s. Therefore the T_1 state of 2-MPN possesses mainly a $^3\pi\pi^*$ character. We can also see from Table 1 that the T_1 energy, T_1 lifetime, and ZFS parameters of 2-MPN are similar to those of naphthalene, although the $|E|$ value of 2-MPN is larg-

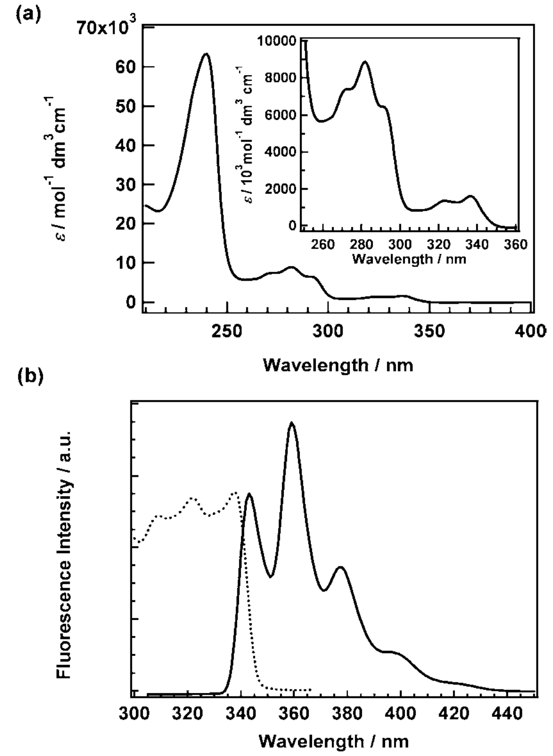

Figure 1. (a) UV absorption spectra at 298 K (b) fluorescence (full line, $\lambda_{\mathrm{exc}} = 294$ nm) and fluorescence-excitation (dotted line, $\lambda_{\mathrm{obs}} = 377$ nm) spectra at 77 K of 2-MPN in EtOH.

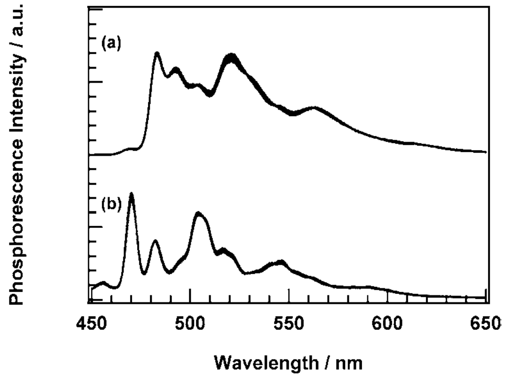

Figure 2. Phosphorescence spectra of (a) 2-MPN and (b) naphthalene in EtOH at 77 K.

er than that of naphthalene. The ester substituent affects the *E* value of naphthalene because the *E* value is very sensitive to the change in the anisotropy of the electron spin dipole–dipole interaction in the molecular plane. As a result, the T_1 state of 2-MPN can reasonably be assigned to a locally excited triplet state within naphthalene, and the two unpaired electrons of 2-MPN in the T_1 state localize on the naphthalene fragment. On the other hand, it should be noted here that the delocalized character of the unpaired electrons in the T_1 state has been observed for the UV absorber analogues, cinnamic acid and 4-methylcinnamic acid, where the fragments are connected by the ethylenic C=C bond.[8]

Further detailed studies including fluorescence lifetime and luminescence quantum yields are currently in progress to elucidate the relaxation processes of the photoexcited states of 2-MPN.

Table 1. T_1 energies, E_{T_1}, T_1 lifetimes, τ, and ZFS parameters, *D* and *E*, of 2-MPN and naphthalene observed in EtOH at 77 K

Molecule	E_{T_1} /cm^{-1}	τ_{phos} /s	τ_{EPR} /s	D /cm^{-1}	E /cm^{-1}
2-MPN	20700	2.24	2.26	0.0957	−0.0218
Naphthalene	21300	2.45	2.46[a]	0.1008[a]	−0.0154[a]

[a] Ref. 6.

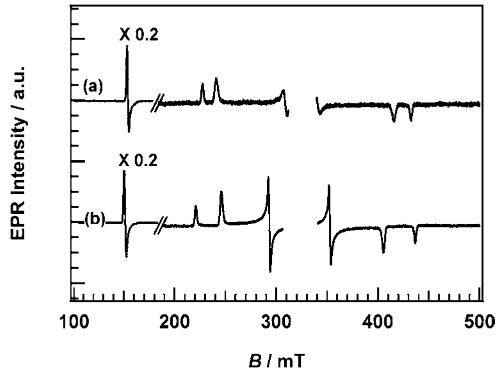

Figure 3. EPR spectra of (a) 2-MPN and (b) naphthalene in EtOH at 77 K.

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