Time-resolved electron paramagnetic resonance study of the lowest excited triplet state of *trans*-cinnamic acid

Yasushi Shioya *, Mikio Yagi **

Department of Physical Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240, Japan

Abstract

Time-resolved and steady-state electron paramagnetic resonance spectra and luminescence spectra have been observed for the lowest excited states of *trans*-cinnamic acid in rigid solutions at 77 K. The zero-field splitting parameters in the lowest excited triplet (T_1) state are $D = 0.1061$ cm^{-1} and $E = -0.0497$ cm^{-1}. The T_1 state is estimated to be 20 100 cm^{-1} and the T_1 lifetime is 45 ms in ethanol at 77 K. The T_1 lifetime decreases as the solvent polarity becomes less polar. The sublevel preferentially populated by intersystem crossing is T_y (y close to in-plane short axis and to the C=O direction). These results are explained in terms of vibronic and spin–orbit mixings between the $^3n\pi^*$ and $^3\pi\pi^*$ states in the T_1 state.

Keywords: Electron paramagnetic resonance; Triplet state; *trans*-cinnamic acid

1. Introduction

Poly(vinyl cinnamate) is well known as one of the most common photosensitive resins. The photo-cross-linking mechanism of poly(vinyl cinnamate) is similar to the photo-dimerization mechanism of cinnamic acid [1]. Nakamura and Kikuchi studied the photosensitization mechanism of poly(vinyl cinnamate) by measuring the phosphorescence spectra of cinnamic acid and sensitizers [2]. They reported that phosphorescences of sensitizers are exceedingly quenched when cinnamic acid is introduced into their solutions, and it is because of the excitation energy transfer from the triplet state of the sensitizer to the triplet state of cinnamic acid. Tsuda et al. measured the phosphorescence and phosphorescence–excitation spectra of cinnamic acid in diethyl ether + isopentane + ethanol (EPA) at 77 K [3]. They reported that the excitation spectrum is in good agreement with the absorption spectrum.

Cinnamic acid contains an ethylenic C=C double bond. The nature of the lowest excited triplet (T_1) states of organic molecules containing an ethylenic double bond, such as stilbene, is poorly known, although the cis–trans isomerization reaction of the molecules has been extensively investigated [4,5]. This is because

of their very weakly phosphorescent character and short T_1 lifetimes.

The measurements of electron paramagnetic resonance (EPR) spectra by photoexcitation are well suited for a study of the T_1 state. However, no EPR of the T_1 state of cinnamic acid has previously been observed because of its short lifetime. The time-resolved EPR technique first proposed by Kim and Weissman [6] is a powerful tool for the study of short-lived T_1 molecules.

In the present work, we have observed the time-resolved and steady-state EPR spectra of the T_1 state of *trans*-cinnamic acid in rigid solutions at 77 K. The zero-field splitting (ZFS) parameters, triplet lifetime and relative populating rates of individual T_1 sublevels are discussed. We have also observed the luminescence spectra of *trans*-cinnamic acid to discuss the nature of the lowest excited singlet (S_1) and T_1 states.

2. Experimental details

Trans-cinnamic acid (Tokyo Kasei G.R. grade) was purified by recrystallization from ethanol–water mixtures. Ethanol (Katayama Kagaku Luminasol) was purified by distillation by the method reported previously [7]. Methylcyclohexane (MCH) (Dotite Spectrosol), *n*-pentane (Wako Pure Chemicals Special grade) and 2-methyltetrahydrofuran (2-MTHF) (Tokyo Kasei G.R.

* Present address: Tokyo Research Laboratories, Kao Corporation, Bunka, Sumida-ku, Tokyo 131, Japan.
** Corresponding author.

grade) were used without further purification. All solvents were carefully checked for the absence of an extraneous EPR signal before use. The sample solutions of trans-cinnamic acid for the EPR measurements were prepared at the concentration of 1.5×10^{-3} or 3×10^{-3} mol dm^{-3}.

A pure PVA film was obtained by the same method as described previously [8]. After heat treatment for about 1 h at 80 °C and swelling in distilled water at 40 °C, the swollen film was soaked in the methanol solution of a sample until an appropriate amount had penetrated into the film by diffusion. Then the film was stretched at 70 °C using a Shibayama SS-60 film stretcher. The films thus obtained have about 250% of stretch in the stretched direction s.

The transient EPR signals were measured using a JEOL-FE1XG spectrometer without field modulation. A Lumonics HE-420 excimer laser (XeCl, 308 nm) was used as an exciting light source with a repetition rate of 25 Hz. The transient EPR signals were recorded with an Iwatsu DM-901 digital memory. With the aid of an NEC PC-8801 microcomputer system, the transient signals were integrated numerically between 0.30 and 0.94 μs after the laser excitation to obtain the time-resolved EPR spectrum. For the magnetophotoselection experiments, a Glan–Thompson polarizer was placed between the laser and the sample cavity to polarize the laser light.

The apparatus for the conventional steady-state EPR measurements were described previously [9]. The excitations were carried out using a Canrad–Hanovia 1 kW Xe–Hg arc lamp equipped with a Toshiba UV-

D33S glass filter and a Copal DC-494 electromechanical shutter.

For the phosphorescence measurements, samples were excited using an Ushio 500 W Hg lamp equipped with Toshiba UV-D33S and UV-29 glass filters. For the fluorescence measurements, they were excited at 297 nm using the Hg lamp through a Jobin Yvon H-20UV monochromator. The emissions from a sample were detected by a Hamamatsu Photonics R453 photomultiplier tube. The sample solutions ranging in concentration from 1×10^{-5} to 3×10^{-3} mol dm^{-3} were prepared. All measurements were carried out at 77 K.

3. Results and discussion

3.1. Emission spectra

The phosphorescence and total emission spectra of trans-cinnamic acid were measured in ethanol at 77 K, as shown in Fig. 1. The observed phosphorescence spectrum is similar to that observed in EPA at 77 K [2,3]. There exists a monomer–dimer equilibrium for carboxylic acids owing to hydrogen bonds in inert solvents such as n-heptane [10–12]. Conversely, when ether or alcohol is present in solution, hydrogen bonds between neighbouring carboxylic acids are broken [10–12]. In the present work, the phosphorescence spectrum observed in ethanol does not depend on the concentration of the sample solution in the range from 1×10^{-5} to 3×10^{-3} mol dm^{-3}. Consequently, it is considered that trans-cinnamic acid exists as a monomer in ethanol at

trans-cinnamic acid

(a)

(b)
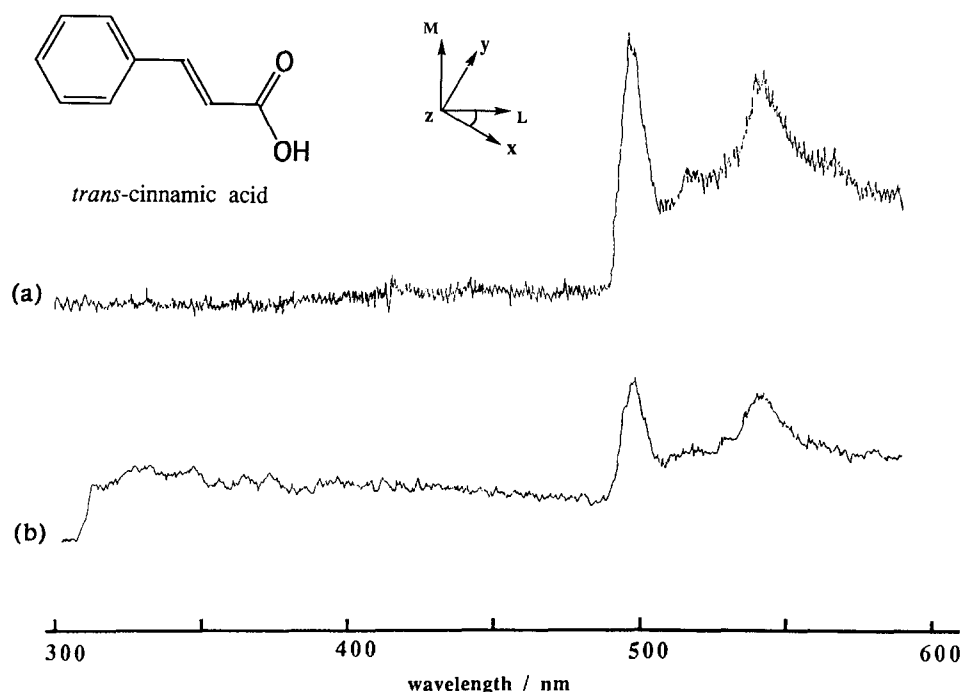
300   400   500   600
wavelength / nm

Fig. 1. (a) Phosphorescence and (b) total emission spectra of trans-cinnamic acid in ethanol at 77 K.

the concentration of 3×10^{-3} mol dm^{-3}. The T_1 state of trans-cinnamic acid in ethanol at 77 K is estimated to be 20 100 cm^{-1} from the first vibronic band. Although the phosphorescence spectrum has been observed by Tsuda et al. [3], the phosphorescence lifetime has not yet been reported. We determined the T_1 lifetime to be 46 ms from the decay of phosphorescence in ethanol at 77 K.

3.2. Electron paramagnetic resonance spectra

The steady-state and time-resolved EPR spectra of the T_1 state of trans-cinnamic acid were measured at 77 K, as shown in Fig. 2. Cis–trans geometrical isomerization of organic molecules containing an ethylenic double bond, such as stilbene, has been investigated by many workers [13]. The fluorescence quantum yield of trans-stilbene is 1.0 and the quantum yield of trans → cis photoisomerization is zero in rigid solutions at 77 K [14,15]. The intensity of EPR and phosphorescence of trans-cinnamic acid in ethanol at 77 K does not change through the continuous ultraviolet irradiation within our observation time of 1 h. Therefore, the

observed EPR and phosphorescence spectra can be assigned to the trans isomer.

The $\Delta M_S = \pm 1$ transition signals of trans-cinnamic acid are too weak to be observed through the steady-state EPR measurements, as shown in Fig. 2(a). Therefore, the assignment of the observed EPR signals was carried out for the time-resolved spectrum with the aid of the stretched-polymer film method [8], as shown in Figs. 3(b), 3(c) and 3(d). Assuming the molecular planarity in the T_1 state, the principal axes (x, y, z) of the ZFS tensor were taken to be as shown in Fig. 1 [16,17]. According to the general relations concerning the orientation of guest molecules [18], the assignment of the resonance field is straightforward. The intensity of the X signals is strong when the external magnetic field B is parallel to the stretched direction of a film s, as can been seen in Fig. 3(d). However, the intensity
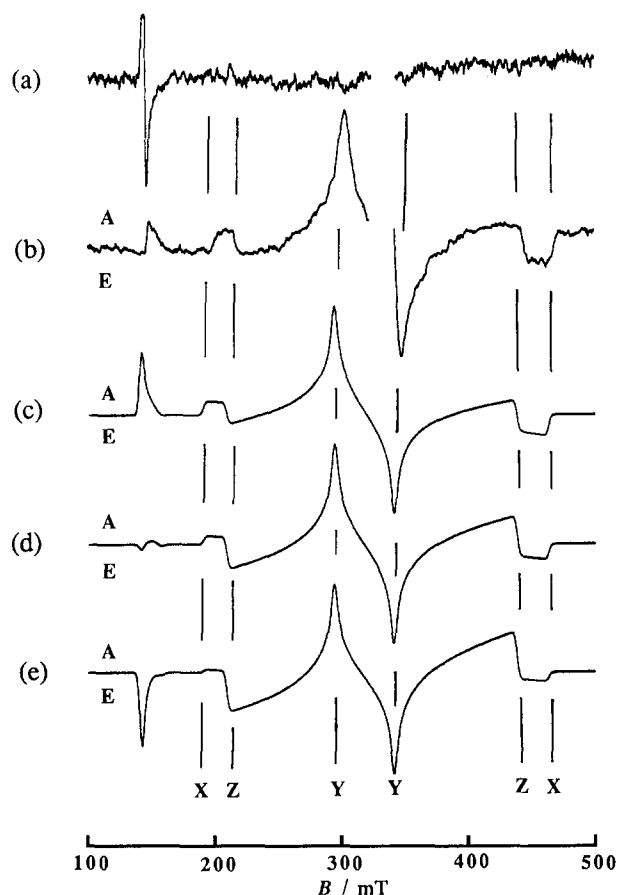

Fig. 2. (a) Steady-state; and (b) time-resolved EPR spectra for the T_1 state of trans-cinnamic acid in ethanol at 77 K; (c) computer-simulated spectrum obtained by using $D = 0.1061$ cm^{-1}, $E = -0.0497$ cm^{-1} and $P_x{:}P_y{:}P_z = 0{:}1.0{:}0$; (d) 0.15:0.85:0; (e) 0.25:0.75:0.

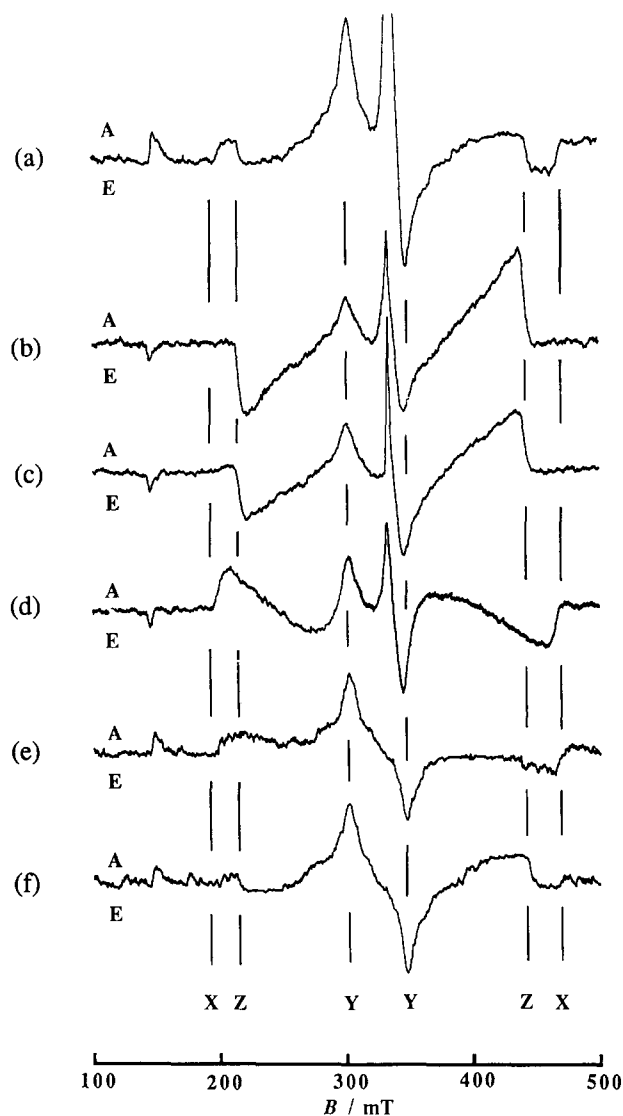Fig. 3. Time-resolved EPR spectra for the T_1 state of trans-cinnamic acid (a) in ethanol; (b) in PVA $(B\|n)$; (c) in PVA $(B\|c)$; (d) in PVA $(B\|s)$; (e) in ethanol with $B\|E$; and (f) in ethanol with $B\perp E$ at 77 K.

of the Z signals is relatively enhanced when B is parallel to the normal of the film plane n, as shown in Fig. 3(b).

We have applied the magnetophotoselection method to confirm the assignment of the $\Delta M_S = \pm 1$ transition signals mentioned above. The time-resolved EPR spectra in ethanol obtained with $B\|E$ and $B \perp E$ are shown in Figs. 3(e) and 3(f). Here, E denotes the electric vector of the laser light. It has been found that trans-cinnamic acid has two types of absorption bands, a K-band (36 600 cm^{-1}) and E-bands (45 000 and 46 300 cm^{-1}) in the 25 000–50 000 cm^{-1} region [19]. Tanaka found, by measuring the polarized ultraviolet absorption spectrum, that the K-band of trans-cinnamic acid is the intramolecular charge transfer absorption band from the highest occupied orbital of the styryl group to the vacant orbital of the carboxyl group [20]. Namely, the in-plane x-polarized absorption takes place dominantly with excitation at 308 nm (K-band) for trans-cinnamic acid. Consequently, the intensity of the X signals is strong with $B\|E$, while the intensity of the Y and Z signals is strong with $B \perp E$, as can be seen in Figs. 3(e) and 3(f). As a result, all the observed signals can reasonably be assigned as shown in Fig. 3.

The T_1 lifetime obtained from the decay of the steady-state EPR B_{min} signal, 45 ms, is in good agreement with that obtained from the decay of phosphorescence, within the limitations of experimental error.

3.3. ZFS parameters, triplet lifetime and relative populating rates

We can see from Table 1 that the D value is 0.1061 cm^{-1} and T_1 lifetime is 45 ms. These values suggest that the T_1 state possesses mainly a $^3\pi\pi^*$ character. As is known comprehensively, T_z sublevels are the lowest in energy for $^3\pi\pi^*$ states [21]. Consequently, it

should be noted that the order of the T_1 sublevels was determined to be T_x, T_y and T_z from the top.

The D values of benzene and formaldehyde were estimated to be 0.1581 cm^{-1} [22] and 0.42 cm^{-1} [23], respectively. The D value of ethylene has been calculated: $|D| = 0.1847$ cm^{-1} [24]. If the two unpaired electrons localize on the benzene fragment, the ethylenic one or the carbonyl one, the $|D|$ value of trans-cinnamic acid should be larger than 0.1061 cm^{-1}. The delocalized character of the unpaired electrons in the T_1 state has also been observed for trans-stilbene [25].

The polarities of the time-resolved EPR signals of trans-cinnamic acid at the stationary fields are A,AEA/ EAE from the low-field to the high-field, as shown in Fig. 2(b). Here, E and A denote emission and absorption respectively of the microwaves. The spectrum of the randomly oriented triplet state with spin polarization was simulated in the same manner as presented by Kottis and Lefebvre with some modifications [26]. In the present simulation a Gaussian line width of 3 mT was used. With the aid of the computer simulation, the relative populating rate was estimated to the $P_x:P_y:P_z = 0.0:1.0:0.0$, as shown in Fig. 2(c). The sublevel preferentially populated by intersystem crossing (ISC) was found to be T_y, the middle sublevel.

The triplet sublevel populating rates are not highly anisotropic for $^3\pi\pi^*$ states of aromatic hydrocarbons, such as naphthalene [21,27], while they are fairly anisotropic for aromatic carbonyls [28]. The sublevel preferentially populated by ISC is known to be T_z for aromatic carbonyls of benzaldehyde type (z is along the C=O direction) [28]. In this paper, the principal axis y is close to the C=O direction as shown in Fig. 1. Therefore, the sublevel preferentially populated is expected to be T_y for trans-cinnamic acid as observed.

The T_1 lifetime of trans-cinnamic acid with the 0–0 energy of the $T_1 \rightarrow G$ (ground state) transition of 20

Table 1

Solvent effects on the lifetime, τ, zero-field splitting parameters and relative populating rates, P_i, in the T_1 state of trans-cinnamic acid (1.5×10^{-3} mol dm^{-3}) observed at 77 K

Solvent	τ [a] (ms)	D [b] (cm^{-1})	E [c] (cm^{-1})	P_x	P_y	P_z
Ethanol [d]	45	0.1061	−0.0497	0	1	0
2-MTHF	45	0.1039	−0.0484	0	1	0
2-MTHF + MCH + n-pentane (50.0:37.5:12.5) [e]	45	0.1039	−0.0490	0	1	0
2-MTHF + MCH + n-pentane (12.0:66.0:22.0) [e]	45	0.1039	−0.0490	0	1	0
2-MTHF + MCH + n-pentane (0.60:74.55:24.85) [e]	39	0.1046	−0.0490	0	1	0
2-MTHF + MCH + n-pentane (0.25:74.81:24.94) [e]	34	0.1053	−0.0493	0	1	0
2-MTHF + MCH + n-pentane (0.10:74.92:24.98) [e]	28	0.1057	−0.0497	0	1	0
MCH + n-pentane (75.0:25.0) [e]	27	0.1065	−0.0499	0	1	0

[a] Obtained from the decay of the B_{min} signal;
[b] $D = (-3/2)Z$;
[c] $E = (1/2)(Y-X)$;
[d] The concentration of trans-cinnamic acid is 3.0×10^{-3} mol dm^{-3};
[e] By weight.

100 cm^{-1} is 45 ms in ethanol at 77 K. The T_1 lifetimes of typical aromatic molecules with similar T_1 energies to trans-cinnamic acid are about 2.5 s, as shown in Table 2. Namely, T_1 lifetime of trans-cinnamic acid is much shorter than those of aromatic molecules with similar T_1 energies to trans-cinnamic acid. The remarkable shortening of the T_1 lifetime of trans-cinnamic acid should not be attributed to the lowering of the T_1 excitation energy.

3.4. Nature of the T_1 state

We tried to discuss the observed shortening of the T_1 lifetime of trans-cinnamic acid in terms of vibronic and spin–orbit mixings between the $^3n\pi^*$ and $^3\pi\pi^*$ states. The host dependence of the T_1 lifetime, ZFS parameters and relative populating rates was examined by changing the solvent polarity in 2-MTHF-MCH-n-pentane mixtures. The results are shown in Table 1. The T_1 lifetime decreases and the $|D|$ value slightly increases as the solvent becomes less polar, while the sublevel preferentially populated by ISC is T_y in all solvents studied.

The value of $Z = (-2/3)D$ is known to be negative for $^3\pi\pi^*$ states, but positive for $^3n\pi^*$ states [21]. According to the works of Hayashi and Nagakura [32,33] and Harrigan and Hirota [28], the Z value (z is along the C=O direction in their works) increases when the $^3\pi\pi^*$ state mixes with the $^3n\pi^*$ state because of the spin–orbit mixing matrix element, $\langle ^3n\pi^*|H_{so}|^3\pi\pi^*\rangle$, in aromatic carbonyls of benzaldehyde type. Therefore, the D value of the $^3\pi\pi^*$ state is expected to increase when the $^3\pi\pi^*$ state mixes with the $^3n\pi^*$ state in the aromatic carbonyls. The observed solvent effects on the T_1 lifetime and the D value can be explained in terms of the mixing between the $^3n\pi^*$ and $^3\pi\pi^*$ states, that is, the purity of the T_1 state should be recovered in

a polar solvent because the $^3n\pi^*$ excitation energy increases in a polar solvent.

Trans-cinnamic acid is non-fluorescent or very weakly fluorescent in all solvents studied, while the observed time-resolved EPR signals are fairly strong. Sakurovs and Ghiggino [34] and Krishnamurthy and Dogra [35] reported that trans-cinnamic acid is non-fluorescent, even at high concentration, in organic solvents. As the T_1 state possesses mainly a $^3\pi\pi^*$ character, one possible explanation of the weakly fluorescent property arises from a consideration of the nature of the S_1 state. The ISC between $^1n\pi^*$ and $^3\pi\pi^*$ states should be much faster than that between $^1\pi\pi^*$ and $^3\pi\pi^*$ states, as suggested by El-Sayed [36]. The very weakly fluorescent character of trans-cinnamic acid may be caused by the fast ISC to the triplet state. In the present work, however, we cannot examine this point more precisely because we have no information about the exact location of the $^1n\pi^*$ state.

Trans-cinnamic acid is weakly phosphorescent and its steady-state EPR signals are very weak. However, the time-resolved EPR signals are fairly strong. These facts show that the decay from the T_1 state is dominantly radiationless, although we do not have quantitative data of the phosphorescence yield. It should be noted that this situation is analogous to the cases of $^3\pi\pi^*$ aromatic carbonyls of benzaldehyde type [28].

4. Conclusions

Our time-resolved EPR experiments indicate that the triplet sublevel populating rates of trans-cinnamic acid are fairly anisotropic. The observed ZFS parameter D shows the delocalized character of the unpaired electrons in the T_1 state. The T_1 lifetime of trans-cinnamic acid is much shorter than that of an aromatic molecule with a similar T_1 energy to trans-cinnamic acid. These results indicate that the T_1 state possesses mainly a $^3\pi\pi^*$ character and there are vibronic and spin–orbit mixings between the $^3n\pi^*$ and $^3\pi\pi^*$ states in the T_1 state.

Acknowledgments

The authors wish to thank Mr. Kazumasa Takemura of our laboratory for his help in measuring the luminescence spectra. We also thank Dr. Kanekazu Seki of our faculty for his kind advice.

Table 2
The 0–0 energies of the $T_1 \rightarrow G$ transitions, E_T, and T_1 lifetimes, τ, of aromatic molecules in rigid solutions at 77 K

Molecule	Solvent	E_T (cm^{-1})	τ (s)
Trans-cinnamic acid [a]	Ethanol	20100	0.045
Dibenz[a,h]acridine [b]	EA [e]	19100	2.31
Chrysene [b]	EA [e]	20000	2.54
Picene [b]	EA [e]	20100	2.7
p-terphenyl [c,d]	EPA [f]	20400 [g]	2.6

[a] Obtained in the present work;
[b] Ref. [29];
[c] Ref. [30];
[d] Ref. [31];
[e] Diethyl ether + ethanol (2:1 by volume);
[f] Diethyl ether + isopentane + ethanol;
[g] Obtained in ethyl iodide + diethyl ether + ethanol + toluene (2:2:1:1 by volume).

References

[1] J.L.R. Williams, Fortschr. Chem. Forsch., 13 (1969) 227.
[2] K. Nakamura and S. Kikuchi, Bull. Chem. Soc. Jpn., 41 (1968) 1977.

[3] M. Tsuda, S. Oikawa and R. Miyake, *Nipp. Shashin Gakkaishi*, *35* (1972) 90; M. Tsuda, S. Oikawa and R. Miyake, *Chem. Abstr.*, *78* (1973) 9744.

[4] T. Ikeyama and T. Azumi, *Chem. Phys. Lett.*, *212* (1993) 551.

[5] F.W. Langkilde, R. Wilbrandt, A.M. Brouwer, F. Negri, F. Zerbetto and G. Orlandi, *J. Phys. Chem.*, *98* (1994) 2254.

[6] S.S. Kim and S.I. Weissman, *J. Magn. Reson.*, *24* (1976) 167.

[7] J.A. Riddick, W.B. Bunger and T.K. Sakano, *Organic Solvents*, Wiley, New York, 1986, p. 871.

[8] J. Higuchi, M. Yagi, T. Iwaki, M. Bunden, K. Tanigaki and T. Ito, *Bull. Chem. Soc. Jpn.*, *53* (1980) 890.

[9] M. Yagi, K. Makiguchi, A. Ohnuki, K. Suzuki, J. Higuchi and S. Nagase, *Bull. Chem. Soc. Jpn.*, *58* (1985) 252.

[10] H. Hosoya, J. Tanaka and S. Nagakura, *J. Mol. Spectrosc.*, *8* (1962) 257.

[11] T. Takemura, K. Chihara, R.S. Becker, P.K. Das and G.L. Hug, *J. Am. Chem. Soc.*, *102* (1980) 2604.

[12] T.J. Curley, K. P. Ghiggino, R. Sakurovs and G.J. Smith, *J. Photochem. Photobiol. A: Chem.*, *45* (1988) 289.

[13] F.W. Langkilde, R. Wilbrandt, F. Negri, F. Zerbetto and G. Orlandi, *Chem. Phys. Lett.*, *165* (1990) 66.

[14] S. Malkin and E. Fischer, *J. Phys. Chem.*, *68* (1964) 1153.

[15] M. Sumitani, N. Nakashima, K. Yoshihara and S. Nagakura, *Chem. Phys. Lett.*, *51* (1977) 183.

[16] J. Ladell, T.R.R. McDonald and G.M.J. Schmidt, *Acta Cryst.*, *9* (1956) 195.

[17] R.F. Bryan and D.P. Freyberg, *J. Chem. Soc. Perkin Trans. 2*, (1975) 1835.

[18] T. Ito, J. Higuchi and T. Hoshi, *Chem. Phys. Lett.*, *35* (1975) 141.

[19] O.H. Wheeler and C.B. Covarrubias, *J. Org. Chem.*, *28* (1963) 2015.

[20] J. Tanaka, *Bull. Chem. Soc. Jpn.*, *36* (1963) 833.

[21] M. Kinoshita, N. Iwasaki and N. Nishi, *Appl. Spectrosc. Rev.*, *17* (1981) 1.

[22] J. Zuclich, *J. Chem. Phys.*, *52* (1970) 3586.

[23] W.T. Raynes, *J. Chem. Phys.*, *41* (1964) 3020.

[24] S.A. Boorstein and M. Gouterman, *J. Chem. Phys.*, *39* (1963) 2443.

[25] M. Yagi, *Chem. Phys. Lett.*, *124* (1986) 459.

[26] Ph. Kottis and R. Lefebvre, *J. Chem. Phys.*, *39* (1963) 393.

[27] M.A. El-Sayed, W.R. Moomaw and J.B. Chodak, *Chem. Phys. Lett.*, *20* (1973) 11.

[28] E.T. Harrigan and N. Hirota, *Mol. Phys.*, *31* (1976) 663.

[29] D.D. Morgan, D. Warshawsky and T. Atkinson, *Photochem. Photobiol.*, *25* (1977) 31.

[30] A.P. Marchetti and D.R. Kearns, *J. Am. Chem. Soc.*, *89* (1967) 768.

[31] R.E. Kellogg and R.P. Schwenker, *J. Chem. Phys.*, *41* (1964) 2860.

[32] H. Hayashi and S. Nagakura, *Mol. Phys.*, *24* (1972) 801.

[33] H. Hayashi and S. Nagakura, *Mol. Phys.*, *27* (1974) 969.

[34] R. Sakurovs and K.P. Ghiggino, *J. Photochem.*, *22* (1983) 373.

[35] M. Krishnamurthy and S. Dogra, *Ind. J. Chem. A*, *26* (1987) 245.

[36] M.A. El-Sayed, *Ann. Rev. Phys. Chem.*, *26* (1975) 235.