ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 115 (1998) 243–247

Journal of Photochemistry and Photobiology A:Chemistry

Excited state dynamics of p-chlorotoluene in rigid glass matrices

Tetsuo Okutsu [a,*], Naomi Kounose [a], Hiroaki Nakatsuka [a], Tadashi Suzuki [b], Teijiro Ichimura [b], Hiroshi Hiratsuka [a]

[a] *Department of Chemistry, Gunma University, Kiryu, Gunma 376-8515, Japan*
[b] *Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguroku, Tokyo 152, Japan*

Received 25 November 1997; received in revised form 20 March 1998; accepted 7 April 1998

Abstract

Excited state dynamics of dual phosphorescent p-chlorotoluene (PCT) was investigated in 3-methylpentane (3MP), methylcyclohexane (MCH), ethanol/methanol (EtOH/MeOH) and EPA rigid matrices in the temperature range of 77–110 K. Dual phosphorescence was ascribed to two low-lying triplet states, $^3\pi\pi^*$ and $^3\pi\sigma^*$. The rate of intersystem crossing (ISC) from S_1 to $^3\pi\pi^*$ and $^3\pi\sigma^*$ states depends both on the temperature and solvent. Mutual conversion process between $^3\pi\pi^*$ and $^3\pi\sigma^*$ states was observed above 87 K in 3MP, 92 K in MCH and 105 K in EtOH/MeOH matrices. Non-radiative decay rate constants strongly depend on the viscosity of the solvent; in the more viscous solvent, non-radiative decay rates become smaller. The activation energies depend on the solvent viscosity and it was ascertained that the mutual conversion process between $^3\pi\pi^*$ and $^3\pi\sigma^*$ requires conformational change.

Keywords: p-Chlorotoluene; Rigid glass matrix; Excited state dynamics; Dual phosphorescence; Intersystem crossing

1. Introduction

The phosphorescence spectra of halogenated benzenes in rigid glass solution were reported to exhibit dual phosphorescence originating from two low-lying triplet states, $^3\pi\pi^*$ and $^3\pi\sigma^*$ [1–6]. Takemura et al. [1] investigated kinetic behavior of the phosphorescent triplet states of chlorobenzene (CB), p-dichlorobenzene and p-dibromobenzene. Dual phosphorescence was composed of a slow-decaying component due to the transition $^3\pi\pi^* \rightarrow S_0$ and the fast decaying component due to the transition $^3\pi\sigma^* \rightarrow S_0$ [7,8]. The phosphorescence spectra shift to shorter wavelength with course of time. The intensity ratio of the dual emissions changes when temperature varied. The reason is that two triplet states are converted to each other at high temperature. They determined apparent activation energies for mutual conversion process between the two triplet states. Nagaoka et al. [9] reported potential energy surfaces of low-lying triplet states of CB using the ab initio unrestricted Hartree–Fock (UHF) method. They reported the C–Cl equilibrium bond length of the $^3\pi\pi^*$ state was near that of the ground state, while $^3\pi\sigma^*$ states were bonding at much longer C–Cl bond distances, the lengthening amounting to about 0.6 Å.

p-Chlorotoluene (PCT) also emits its phosphorescence though the phosphorescence was largely shifted to shorter wavelength compared to CB: these peaks were 420 and 510 nm for PCT and CB, respectively. At 110 K, the peak of the phosphorescence shifted largely to longer wavelength, with its peak at 520 nm. Such a large dual phosphorescent behavior has not been reported among chloroaromatics previously.

Photoreaction of CB has been extensively studied and it was revealed that the excited triplet states predominantly photodissociate to the phenyl radical and chlorine atom [10–15]. The photodecomposition quantum yield has been reported in gas phase [10] and in various solvents [11–15]. In hydroxylic solvents like methanol (MeOH), photosubstitution by the solvent simultaneously took place as a minor process via an excited singlet state [16–18]. Nagaoka et al. [19] reported photosubstitution of CB by MeOH took place in the $^3\pi\sigma^*$ state, while Previtali and Ebbesen [20] suggested that radical cation formation via a singlet state seemed to be important in the reaction. On the other hand, few studies of photoreaction of chlorotoluenes have been reported until now. Choudhry et al. [21] reported PCT mainly yielded toluene by photodecomposition and p-methoxytoluene by photosubstitution as a minor product in MeOH when it was sensitized by triplet acetone. Ichimura et al. [22,23] reported photodecomposition took place mostly via triplet levels even

---

* Corresponding author.

1010-6030/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S1010-6030(98)00270-6

in the S_3 state excitation and it took place only in its triplet state in the S_1 excitation but photosubstitution reaction took place both in its singlet and in triplet states in MeOH with a small yield. In gas phase, they also observed benzyl radical by the photolysis of *o*-chlorotoluene [24,25]. *o*-Tolyl radical was to be an intermediate species and it converted into benzyl radical by an intramolecular hydrogen transfer reaction. Our group observed benzyl radical when PCT was photolyzed in non-polar solvent at 77 K, implying that C–Cl bond cleavage took place to yield *p*-tolyl radical.[1] While Tokumura and Itoh [26] reported that excited triplet PCT gave *p*-chlorobenzyl radical in hexane at room temperature, photodissociation occurred in C–H bond in a methyl group. Thus the dual faced triplet states of PCT seem to be responsible for yielding various photoproducts via its triplet states depending on the experimental conditions.

In the present study, the kinetic behavior of the phosphorescent $^3\pi\pi^*$ and $^3\pi\sigma^*$ states of PCT has been investigated. The phosphorescence decays were measured in 3-methylpentane (3MP), methylcyclohexane (MCH), ethanol (EtOH)/MeOH (1:1 vol.%) and EPA solvents at different temperatures between 77 and 110 K. Rate constants and activation energies were determined for the dissociative and mutual conversion processes in or between the two triplet states concerned.

The resulting kinetic data strongly depend on the solvent used. In the high viscous solvent, such as EtOH/MeOH and MCH, mutual conversion process occurs in the temperature range above 90 K. On the other hand, in the low viscous solvent like 3MP and EPA, the conversion process occurs at above 77 K. The relationship between activation energies and solvent viscosity at low temperature are discussed.

2. Experimental

PCT (Wako Chemical G.R.) was purified by a vacuum distillation. 3MP (Tokyo Kasei, spectral grade) was purified by distillation. EtOH (Kanto Chemical UVasol), MeOH (Kanto Chemical UVasol), MCH (Wako Pure Chemical spectral grade), diethylether (Kanto Chemical UVasol) and isopentane (Kanto Chemical UVasol) were used as received.

Absorption spectra were measured by using a Hitachi U3300 spectrophotometer. Emission spectra were measured by a Hitachi M-850 spectrofluorometer. Time-resolved phosphorescence spectra and phosphorescence lifetimes were simultaneously obtained using a UNISOKU TSP 601H nanosecond laser photolysis system with a Nd^{3+}:YAG laser (266 nm output of fourth harmonic, pulse width 3 ns, GCR-130, Spectra Physics) and an oscilloscope (GOULD 4090).

3. Results and discussion

Fig. 1 shows the emission spectra observed by 270 nm excitation of CB at 77 K and PCT at 77, 85, 87, 89 and 90 K in 3MP. Observed emission exhibits phosphorescence spectra in the wavelength range from 350 to 700 nm. All emission bands are broad and no prominent vibrational structure was observed. Emission bands of PCT were observed in shorter wavelength region compared to CB. It is seen that at high temperature phosphorescence of PCT shifts to longer wavelength. Since all excitation spectra determined by monitoring the emission coincided with each other, and emissions were observed after excitation light was cut off, all emissions are assigned to the phosphorescence of PCT. It has been reported [1,2] that the phosphorescence of CB is composed of two emissions; the shorter wavelength emission in the range between 400 and 500 nm is due to the phosphorescence from $^3\pi\pi^*$ and the emission between 450 and 600 nm is originated from $^3\pi\sigma^*$. Emission of CB at 77 K turned out to be mainly due to $^3\pi\sigma^*$ phosphorescence. Assuming that the low-lying triplet states are similar to those of CB, main emission of PCT is ascribed to $^3\pi\pi^*$ phosphorescence [1]. At higher temperature, shorter wavelength emission from $^3\pi\pi^*$ was quenched and $^3\pi\sigma^*$ phosphorescence became dominant. Therefore, it is concluded that PCT reveals dual phosphorescence in analogy to CB and each contribution from low-lying two triplet state depended on the temperature.

The time-resolved phosphorescence spectra of PCT in 3MP observed at 77 and 90 K are shown in Fig. 2. The phosphorescence intensity at 77 K decreased with time and the peak wavelength shifted from 450 to 420 nm. Phosphorescence spectra at 90 K is shown in Fig. 2b. Spectral peak shift was not observed at this temperature. The phosphorescence behavior at different temperature is explained by mutual conversion process between two low-lying triplet states, namely, $^3\pi\pi^*$ and $^3\pi\sigma^*$, similar to the case of CB. The phosphorescence time profiles at 450 and 670 nm at 90 K are shown in Fig. 2c. Phosphorescence at 450 nm decayed rapidly between 10 and 25 ms, whereas slight rise of phosphorescence at 670 nm was observed in the same time range. This is attributed to the population change from $^3\pi\pi^*$ to $^3\pi\sigma^*$ state. In Fig. 3 energy diagram is schematically shown for halogenated benzenes [1].

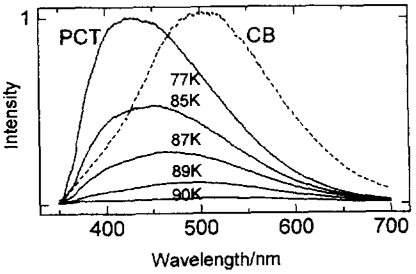

Fig. 1. Phosphorescence spectra of CB (dashed line) at 77 K and PCT (solid line) in 3MP at 77, 85, 87, 89 and 90 K.

---

[1] H. Nakatsuka, Master Thesis, Gunma University, unpublished result, 1995.

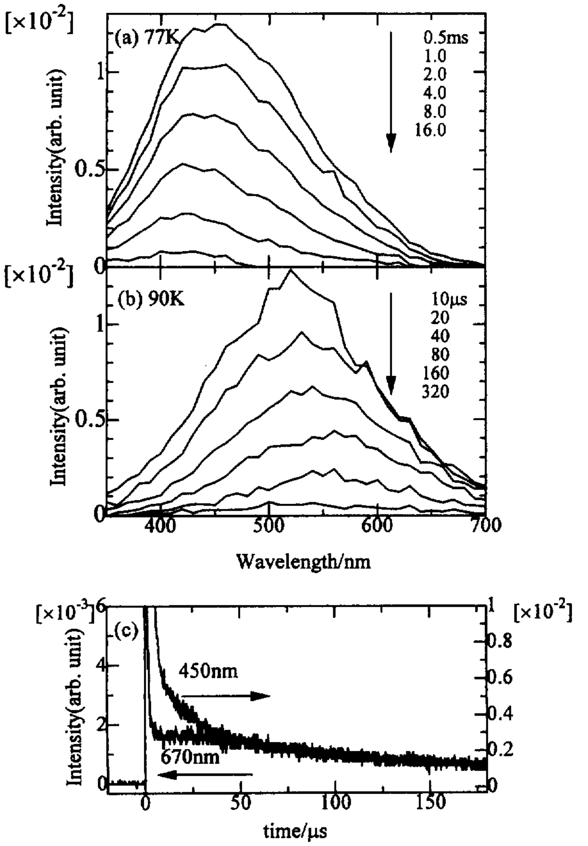

Fig. 2. Time-resolved phosphorescence spectra of PCT in 3MP at 77 K (a) and 90 K (b). Spectra at 77 K are observed at 2, 4, 8, 16 and 32 ms after the laser excitation and spectra at 90 K are observed at 10, 40, 80, 160 and 320 μs after the laser excitation. Phosphorescence decay time profile at 90 K observed at 450 and 670 nm (c)

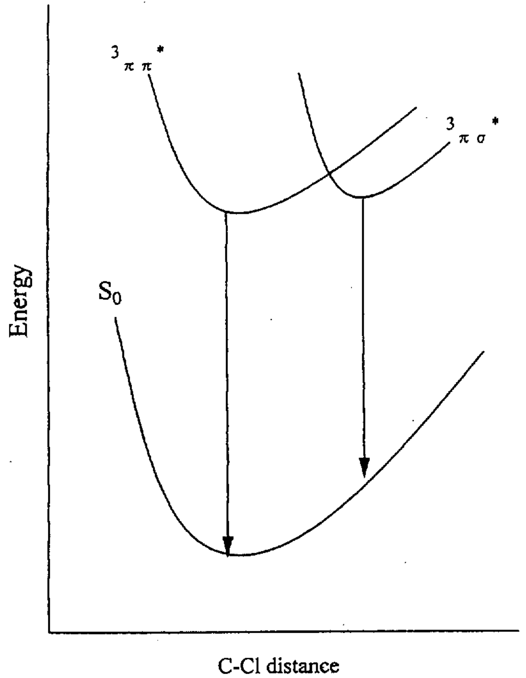

Fig. 3. Schematic potential energy curves of S_0, S_1, $^3\pi\pi^*$ and $^3\pi\sigma^*$ states of halogenated benzenes.

Takemura et al. [27] and Birks [28] analyzed mathematically the excited states kinetics and demonstrated that phosphorescence time profiles could be expressed as biexponential decay. At the temperatures concerned in this study, the phosphorescence decays monitored in the range 350–700 nm were found to be biexponential. At a particular temperature, the decay profile of the phosphorescence intensity ($I_{p\lambda}$) monitored at a wavelength λ can be expressed in the form,

$$I_{p\lambda}(t)=C_s(\lambda)e^{-\theta_s t}+C_f(\lambda)e^{-\theta_f t}, \qquad (1)$$

where θ_s and θ_f are decay rate constants with $\theta_s<\theta_f$; i.e., s and f refer to the slow and fast decay components of phosphorescence, respectively. C_s and C_f are pre-exponential factors of the slow and fast components of phosphorescence. It was confirmed experimentally that the decay constants θ_s and θ_f are independent of the monitoring wavelength λ. The decay constants θ_i (i = s or f) may be expressed in the form,

$$\theta_i=\theta_i^0+A_i e^{-\Delta E_i/RT}, \qquad (2)$$

where θ_i^0 is temperature independent radiative and non-radiative rate constant. A_i is a frequency factor, and ΔE_i is an activation energy. The second term in Eq. (2) is supposed to be mainly due to temperature dependent non-radiative decay process [1]. The values of θ_i^0, A_i and ΔE_i were determined from the results in Fig. 4 and θ_i–θ_i^0 (i = s or f) are plotted against the inverse of T. The results are summarized in Table 1.

We then found that phosphorescence decay rate constants largely depend on the solvent used. Furthermore, it was found the temperature range in which spectral red shift was observed depended on the solvent. Fig. 5 shows the time-resolved phosphorescence spectra of PCT in EtOH/MeOH and MCH at temperature range 80–110 K. Fig. 5a–c shows the phosphorescence spectra in EtOH/MeOH at 80, 100 and 110 K. Phosphorescence spectra even at 100 K showed almost the same contour at any delay time and no red shift was observed. Above 105 K shift to longer wavelength began to be observed. In Fig. 5c time-resolved emission was shown at 110 K. At 110 K in 3MP and EPA, no phosphorescence could be observed. Similar tendency was also observed when MCH was used as a solvent and the results are shown in Fig. 5d–f. In this case the phosphorescence shift was observed between 90 and 92 K.

The constants, θ_i–θ_i^0 in EPA, EtOH/MeOH and MCH are also plotted against $1/T$ in Fig. 4. The results are also given in Table 1. The values obtained in MCH are essentially the same with those of CB in 2-methylpentane [1]. The decay constants in 3MP are compared with those of EtOH/MeOH and MCH. Phosphorescence decay rate constant θ_s at 90 K are widely dispersed from 1.5×10^2 to 1.0×10^4 s^{-1}, whereas θ_s^0, which denotes radiative rate for the most part, and temperature independent non-radiative rate have constant values of 22 s^{-1} for non-polar solvent and about 100–140 s^{-1} for polar solvent, respectively. These data indicates that the phosphorescence lifetimes of the $^3\pi\pi^*$ are governed by the non-radiative decay process, especially mutual conversion

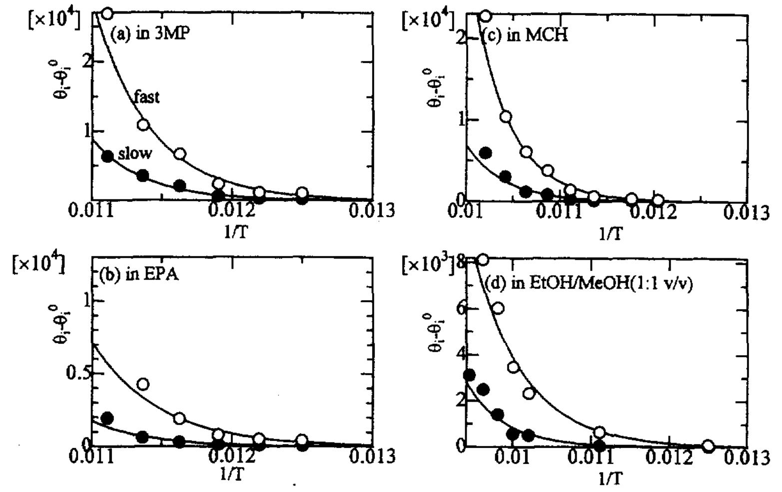

Fig. 4. Plots of θ_i–θ_i^0 vs. $1/T$ (i = s or f) in (a) 3MP, (b) EPA, (c) MCH and (d) EtOH/MeOH, ○ and ● denote fast and slow component, respectively.

process from $^3\pi\pi^*$ to $^3\pi\sigma^*$ state. The values of ΔE_s were also found to depend on the solvent. ΔE_i values obtained in 3MP are 22 kJ mol^{-1} for both ΔE_s and ΔE_f, and are smaller than those in EtOH, 35, 42 kJ mol^{-1}, and in MCH, 26, 34 kJ mol^{-1}, respectively.

Here, we discuss the solvent properties which influence the rate of the non-radiative decay process. First, an idea that the solvent polarity influences the decay process is excluded, because 3MP and MCH are both non-polar solvents. Next, we consider about viscosity of the organic glasses. The values of the viscosity of organic glasses were reported by Ling and Willard [30] and Hutzler et al. [31] and the values are listed in Table 1.

The relative viscosity η/η_{3MP} values are 1.7×10^{11} and 4×10^4 for EtOH and MCH, respectively. It is found that in a more viscous matrix, the θ_i–θ_i^0 value which mainly denotes non-radiative decay rate becomes smaller. This is explained that some particular vibrational motions which is expected to promote non-radiative process are prevented by the rigidity of environment around the PCT. The ΔE_i also depends on the solvent viscosity which means the mutual conversion process between the triplet states is governed by the vibrational motions such as the C–Cl stretching. When the temperature of a matrix is raised, the glasses changes to 'soft', and then the non-radiative process of the mutual conversion should take place.

The spectral red shifts observed just after the laser excitation at higher temperatures in Figs. 2 and 5 could be explained by the change of the branching ratio in intersystem crossing (ISC) from S_1 to $^3\pi\pi^*$ and $^3\pi\sigma^*$. The red shift means the ISC to the $^3\pi\sigma^*$ state increases at high temperature. The C–Cl equilibrium bond length in the $^3\pi\sigma^*$ state of CB [9] was reported to be longer by 0.6 Å than that of the $^3\pi\pi^*$ state, which is identical to the ground state. In the more viscous matrices like EtOH/MeOH, the ISC to the $^3\pi\sigma^*$ state accompanied with lengthening of the C–Cl bond distance is expected to be suppressed. Above a particular temperature at which viscosity of the matrices becomes less enough to allow for lengthening the C–Cl bond distance and the ISC to the $^3\pi\sigma^*$ state becomes feasible.

The concluding remarks are that the dynamics of the excited state of PCT characterized by the dual phosphorescence can be explained by mutual conversion process between the $^3\pi\pi^*$ and $^3\pi\sigma^*$ states, and the branching ratio

Table 1
Kinetic data and viscosities for various solvents

Solvent	θ_s (s^{-1} at 90 K)	θ_s^0 (s^{-1})	θ_s–θ_s^0 (s^{-1})	A_s	ΔE_s (kJ mol^{-1})	η/η_{3MP} [a]
EPA	2.1×10^3	1.3×10^2	2.0×10^3	1.1×10^{15}	21	5.5×10^{-2}
3MP	6.4×10^3	6.0×10	6.3×10^3	8.6×10^{16}	22	1
MCH	3.3×10^2	4.0×10	2.9×10^2	5.2×10^{15}	22	$\sim4\times10^4$
EtOH/MeOH (1:1 v/v)	2.1×10^2	1.5×10^2	6.0×10	7.1×10^{16}	27	1.7×10^{11}
Solvent	θ_f (s^{-1} at 90 K)	θ_f^0 (s^{-1})	θ_f–θ_f^0 (s^{-1})	A_f	ΔE_f (kJ mol^{-1})	η/η_{3MP} [a]
EPA	1.3×10^4	6.3×10^2	1.2×10^4	8.2×10^{15}	21	5.5×10^{-2}
3MP	2.7×10^4	1.8×10^2	2.7×10^4	1.9×10^{16}	22	1
MCH	1.7×10^3	2.8×10^2	1.4×10^3	6.4×10^{15}	23	$\sim4\times10^4$
EtOH/MeOH (1:1 v/v)	1.3×10^3	6.5×10^2	6.5×10^2	3.5×10^{16}	23	1.7×10^{11}

[a] From Ref. [29].

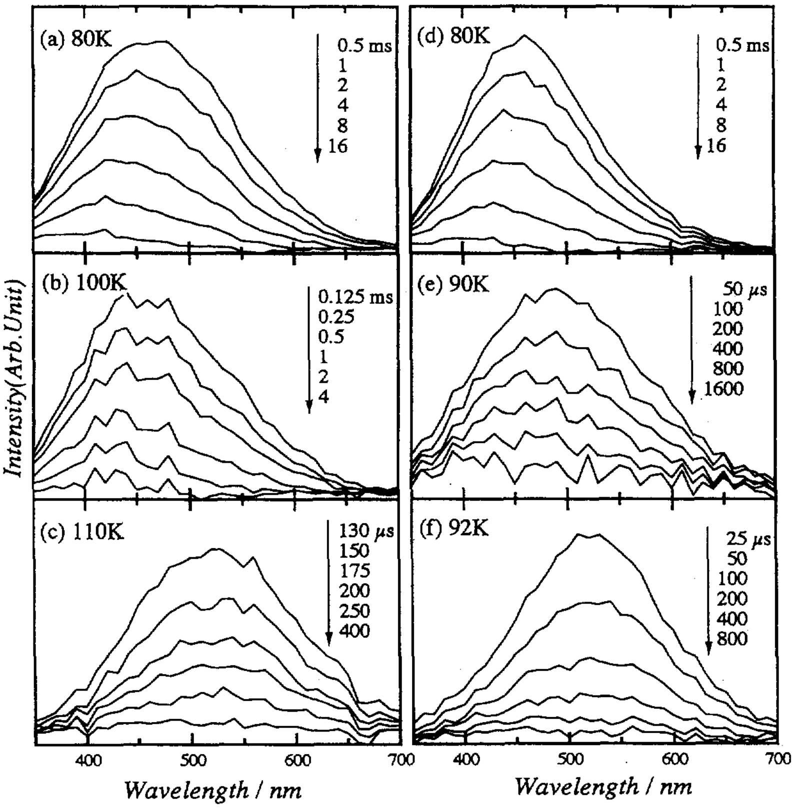

Fig. 5. Time-resolved phosphorescence spectra of PCT in EtOH/MeOH at 80 (a), 100 (b) and 110 K (c), and in MCH at 80 (d), 90 (e) and 92 K (f).

of the ISC from S_1 to the two states. Both processes should be influenced by the viscosity of the solvent.

Acknowledgements

This work was supported in part by a Grant-in-Aid from the SANEYOSHI SCHOLARSHIP FOUNDATION.

References

[1] T. Takemura, Y. Yamada, M. Sugawara, H. Baba, J. Phys. Chem. 90 (1986) 2324.
[2] T. Ichimura, T. Hikida, Y. Mori, J. Phys. Chem. 79 (1975) 291.
[3] T. Takemura, Y. Yamada, H. Baba, Chem. Phys. 69 (1982) 171.
[4] E.C. Lim, S.K. Chakrabarti, Mol. Phys. 13 (1967) 293.
[5] G. Castro, R.M. Hochstrasser, J. Chem. Phys. 45 (1966) 4352.
[6] D.S. McClure, J. Chem. Phys. 17 (1948) 905.
[7] S. Niizuma, L. Kwan, N. Hirota, Mol. Phys. 35 (1978) 1029.
[8] H. Shinohara, N. Hirota, J. Chem. Phys. 72 (1980) 4445.
[9] S. Nagaoka, T. Takemura, H. Baba, N. Koga, K. Morokuma, J. Phys. Chem. 90 (1986) 759.
[10] T. Ichimura, Y. Mori, J. Chem. Phys. 58 (1973) 288.
[11] M.A. Fox, W.C. Nicholas, D.M. Lemal, J. Am. Chem. Soc. 95 (1973) 8164.
[12] D.R. Arnold, D.C. Wong, J. Am. Chem. Soc. 99 (1977) 3361.
[13] N.J. Bunce, P.J. Bergsma, M.D. Bergsma, W. DeGraaf, Y. Kumar, L. Ravanal, Org. Chem. 45 (1980) 3708.
[14] N.J. Bunce, P.J. Hayes, M.E. Lemke, Can. J. Chem. 61 (1983) 1103.
[15] A. Brasinski, E. Latowska, Rocz. Chem. 40 (1966) 1747.
[16] J.T. Pinkey, R.D.G. Rigby, Tetrahedron Lett. (1969) 1267.
[17] J.Ph. Soumillon, B. Dewolf, J. Chem. Soc., Chem. Commun. (1981) 436.
[18] V. Avila, H.E. Gsponer, C.M. Previtali, J. Photochem. 27 (1984) 163.
[19] S. Nagaoka, T. Takemura, H. Baba, Bull. Chem. Soc. Jpn. 58 (1985) 2082.
[20] C.M. Previtali, T.W. Ebbesen, J. Photochem. 30 (1985) 259.
[21] G.G. Choudhry, A.A.M. Roof, O. Hutzinger, J. Chem. Soc., Perkin Trans. I (1982) 2957.
[22] T. Ichimura, M. Iwai, Y. Mori, J. Phys. Chem. 92 (1988) 4047.
[23] T. Ichimura, Y. Mori, H. Shinohara, N. Nishi, J. Chem. Phys. 107 (1997) 835.
[24] T. Ichimura, M. Iwai, Y. Mori, J. Photochem. 39 (1987) 129.
[25] T. Ichimura, Y. Mori, M. Sumitani, K. Yoshihara, J. Chem. Phys. 84 (1986) 1943.
[26] K. Tokumura, M. Itoh, Nippon Kagaku Kaishi (1989) 1311.
[27] M. Takemura, H. Aikawa, H. Baba, Y. Shindo, J. Am. Chem. Soc. 98 (1976) 2205.
[28] J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, New York, 1970, p. 304.
[29] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd edn., Section 12, Marcel Dekker, New York, 1993, pp. 294–296.
[30] A.C. Ling, J.E. Willard, J. Phys. Chem. 72 (1968) 1918.
[31] J.S. Hutzler, R.J. Colton, A.C. Ling, J. Chem. Eng. Data 17 (1972) 324.