JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 355–360 (1992)

# PHOTOCHEMICAL REACTIONS OF 2,2′-FURIL. SOLVENT DEPENDENT PHOTOREDUCTION VIA THE LOWEST EXCITED SINGLET AND TRIPLET STATES

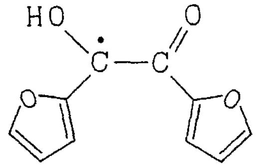
HIROYASU INOUE* AND TADAMITSU SAKURAI
*Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Kanagawa-Ku, Yokohama 221, Japan*
TOSHIHIKO HOSHI AND ISAO ONO
*Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Setagaya-ku, Tokyo 157, Japan*
AND
JUN OKUBO
*Department of Natural Science for General Education, Faculty of Engineering, Tokyo Denki University, Inzai-machi, Inba-gun, Chiba 270-13, Japan*

**2,2′-Furil (di-2-furyl diketone) undergoes photoreduction to give furoin on irradiation at 366 nm in triethylamine-containing benzene and ethers. On the other hand, in ethanol the photoirradiation leads to the formation of an enediol type of compound, 1,2-di(2-furan)ethene-1,2-diol. The results of quenching and sensitization both for the photoreactions and the phosphorescence demonstrate that furoin and the enediol are formed via the lowest excited singlet and the triplet states of 2,2′-furil, respectively.**

## INTRODUCTION

Although the photochemical behaviour of various alkyl and aromatic $\alpha$-diketones has been investigated,[1-3] little is known about the photoreaction of 2,2′-furil (di-2-furyl diketone). In view of the reported photoreactions of benzil,[4-8] it can be expected that aromatic $\alpha$-diketones will undergo a variety of photoreactions such as the dissociation of the central carbonyl—carbonyl bond affording an aldehyde (or carboxylic acid), the acryloin or enediol formation depending on the solvents used. Moreover, similarly to benzil,[9-11] furil adopts a skewed conformation in the ground state in which the central carbonyl—carbonyl bond is substantially twisted,[12] and electronic excitation causes photorotamerism, giving nearly planar structures (*s-cis* or *s-trans*).

Recently, we reported that 2,2′-pyridil, a pyridine analogue of benzil, was reduced to afford an enediol type of compound, 1,2-di(2-pyridyl)ethene-1,2-diol, on irradiation in several solvents, and the triplet mechanism was proposed.[13] In this case, it is noteworthy that the enediol produced is stabilized by intramolecular hydrogen bonding, and the corresponding acyloin type of compound is not known, although benzoin and furoin are available.



As for 2,2′-furil, ESR and CIDNP studies have been performed on the furil radical shown, produced in the initial photochemical reduction process.[14-18] However, the final product has not been ascertained. So far the organic photochemistry of 2,2′-furil hardly been reported. Therefore, it seemed of interest to investigate the photochemical reactions of 2,2′-furil from an organic photochemical point of view.

In this paper, we describe the photochemical reactions of 2,2′-furil in ethanol, amine-containing benzene and ethers. These solvents were employed

---

[*] Author for correspondence.

0894–3230/92/060355–06$08.00

*Received 19 December 1991*
*Revised 20 February 1992*

because it has been found that 2,2'-furil affords two different photoproducts, depending on the solvent used. The reaction paths of such distinct photoreactions are discussed on the basis of the results of quenching and sensitization for both photoreaction and the phosphorescence.

## EXPERIMENTAL

*Materials.* 2,2'-Furil, *trans*-stilbene, furoin and fluoren-9-one (Wako Pure Chemical) were recrystallized from ethanol. Cyclohexa-1,3-diene and triethylamine (TEA) were distilled. Tripropylamine (TPA) and tributylamine(TBA) (Kanto Chemical) were used as received. 1,4-Dioxane and tetrahydrofuran (Wako Pure Chemical) were of spectroscopic grade and used without further purification.

*Measurements.* Absorption spectra were measured with a Shimadzu UV-210 A spectrophotometer. Phosphorescence spectra were recorded on a Shimadzu RF-500 spectrofluorimeter equipped with a cylindrical rotating sector at 77 K. IR spectra were taken with a Hitachi 270-30 infrared spectrometer in a KBr disk. Proton NMR spectra were obtained with a JEOL JNMFX-200 FT NMR spectrometer in deuterated chloroform.

*Light sources and irradiation.* Three light sources were employed: (I) for preparative purposes a 400 W high-pressure mercury lamp (Rikagaku Sangyo UVL-400 HA) was used without filters in an immersion-type Pyrex vessel; (II) for quantitative studies 366 nm light was obtained by use of a 450 W high-pressure mercury lamp (Ushio UM-452) and a set of glass filters (Corning CS-7-54 and CS-0-52); (III) in sensitization experiments, a 500 W xenon-lamp (Ushio XS-501A) and a grating monochromator (Shimadzu Grating 2700) were used for irradiation at 460 nm.

All irradiations for the quantitative experiments were carried out in a $5 \times 10^{-2}$ dm$^3$ quartz cylindrical cell at room temperature under nitrogen.

*Actinometry.* The light intensities were determined by use of a potassium trioxalatoferrate(III) solution as an actinometer for determination of quantum yields for the photoreactions.[19] The amounts of 2,2'-furil and the photoproducts were determined spectrophotometrically.

*Analysis of photoproduct in ethanol.* A $5 \times 10^{-3}$ mol dm$^{-3}$ solution (500 ml) of 2,2'-furil in ethanol was irradiated by use of light source I until a secondary photoreaction started. The initial photoproduct formed in ethanol was not stable enough to be isolated and it easily decomposed during the procedures. Therefore, acetylation of the photoproduct was attempted. Acetic anhydride and sodium acetate were added to the irradiated solution and the mixture was allowed to stand in the dark for 24 h. After evaporation of the solution to dryness, the acetylating agents were removed by washing with water. The product was extracted with chloroform and purified by column chromatography with Kieselgel 60 (Merck) as stationary phase and chloroform as eluent and thin-layer chromatography using Kieselgel GF 254 plates (Merck) with chloroform as eluent. The compound thus obtained showed the following properties: UV, $\lambda_{max}$ (ethanol) 326 nm; IR (KBr), 3110, 2960, 2900 (st $CH_3$), 1780(C=O), 1657(C=C), and 1470 cm$^{-1}$ ($\delta$ $CH_3$); $^1$H NMR ($CDCl_3$), $\delta$ 2·32(s, 6H) and 6·14–7·54 (m, 6H, furan ring).

*Analysis of photoproduct in benzene–triethylamine.* A $1 \cdot 1 \times 10^{-2}$ mol dm$^{-3}$ solution (500 ml) of 2,2'-furin in benzene containing TEA (1 mol dm$^{-3}$) was irradiated by use of light source I until the intensities of the 280 nm band of the product reached a maximum. After the irradiation the solution was evaporated to dryness under reduced pressure. The crude material thus obtained was subjected to column chromatography with Kieselgel 60 as stationary phase and benzene–chloroform as eluent and then recrystallized. The photoproduct obtained showed the UV, IR and NMR spectra identical with those of an authentic sample of furoin.

## RESULTS AND DISCUSSION

### Photoreaction in ethanol

The 366 nm irradiation of an ethanol solution of 2,2'-furil ($1 \times 10^{-4}$ mol cm$^{-3}$) led to the absorption spectral changes shown in Figure 1. The photoproduct with a

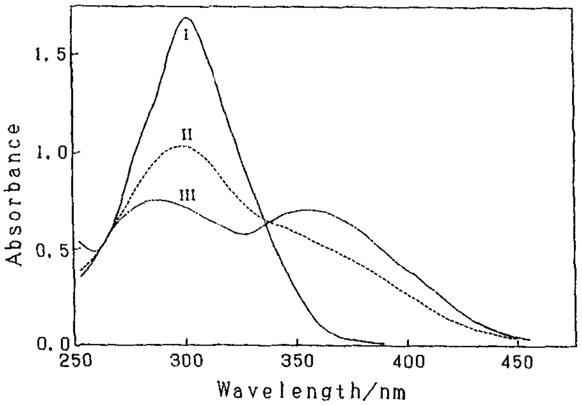
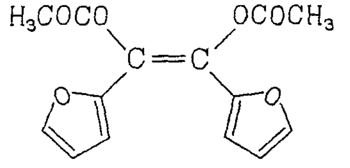
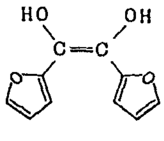


Figure 1. Absorption spectral changes caused by irradiation at 366 nm of an ethanol solution of 2,2'-furil ($1 \times 10^{-4}$ mol dm$^{-3}$) Irradiation time: I, 0; II, 15; III, 35 min

357 nm band is formed in the initial stage of photoreaction within an appropriate irradiation time. Further irradiation, however, causes a secondary photoreaction, leading to a decrease in intensity of the 357 nm band of the primary photoproduct and a deviation of the absorption spectrum from the isosbestic point at 336 nm. The present study in ethanol was confined to the initial photoreaction producing a compound showing the 357 nm band.

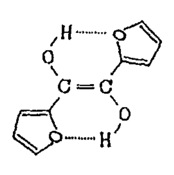
The photoproduct in ethanol cannot be considered as any possible decomposition products or furoin, because the relatively long wavelength absorption band at 357 nm cannot be assigned to these compounds. As mentioned above, the product was subjected to acetylation by treatment with acetic anhydide and sodium acetate. From the IR and NMR spectral data presented in the Experimental section, the compound thus obtained can be identified as the diacetylated compound shown, whose conformation (*cis* or *trans*), however, is not clear at present. Consequently, the primary photoproduct from 2,2′-furil in ethanol is identified as 1,2-di(2-furan)ethene-1,2-diol (hereafter called enediol), with the alternative formulae shown. However, at present it is not clear which isomer is favoured, *cis* or *trans*. In this connection, as reported previously,[13] 2,2′-pyridil is photochemically reduced in alcohols, etc., to the enediol, 1,2-di(2-pyridyl)ethene-1,2-diol, which takes the *trans* conformation and has an absorption band at 377 nm. This *trans*-enediol is known to be stabilized through the formation of six-membered intramolecular hydrogen bonds between the enolic hydroxyl groups and the heterocyclic nitrogen atom.[20–24] By analogy with this *trans*-enediol, it is plausible that the present enediol takes the *trans* form, being stabilized through the formation of six-membered intramolecular hydrogen bonds as illustrated in the formula. The *trans* isomer may be more stable than the *cis* isomer, i.e. the stabilization energy due to coplanarity of the π-electronic system of the *cis* isomer is considered to be smaller than that of the *trans* isomer, even if five-membered hydrogen bonds are formed.





cis-Enediol

or



trans-Enediol

In order to establish the reactive excited state of 2,2′-furil participating in the enediol formation, quenching and sensitization experiments were performed. Cyclohexa-1,3-diene and *trans*-stilbene were found to act as quenchers for the photoreduction of 2,2′-furil in ethanol. The Stern–Volmer quenching plots are presented in Figure 2. From the consideration of the energies of the lowest excited singlet ($E_S$) and the lowest triplet states ($E_T$) [$E_S = 71$ kcal mol$^{-1}$ and

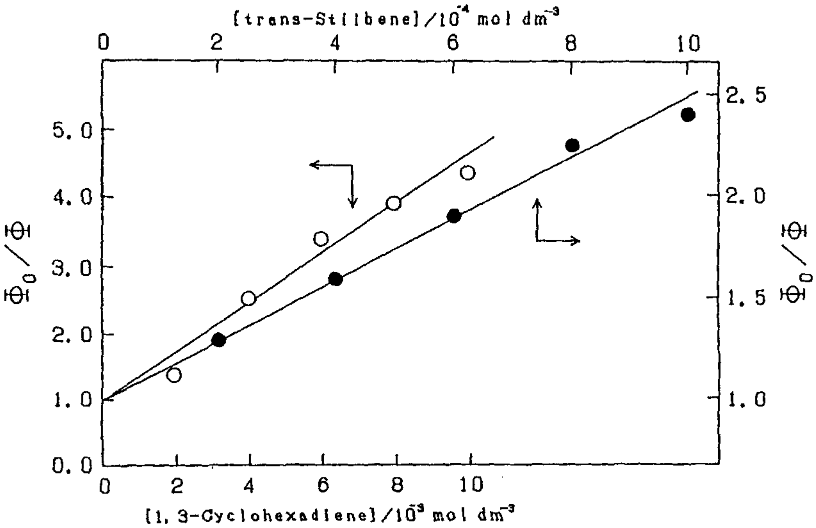


Figure 2. Stern–Volmer plots for the quenching of enediol formation by cyclohexa-1,3-diene and *trans*-stilbene. [2,2′-Furil] = $1{\cdot}0 \times 10^{-4}$ mol dm$^{-3}$. Excitation wavelength = 366 nm

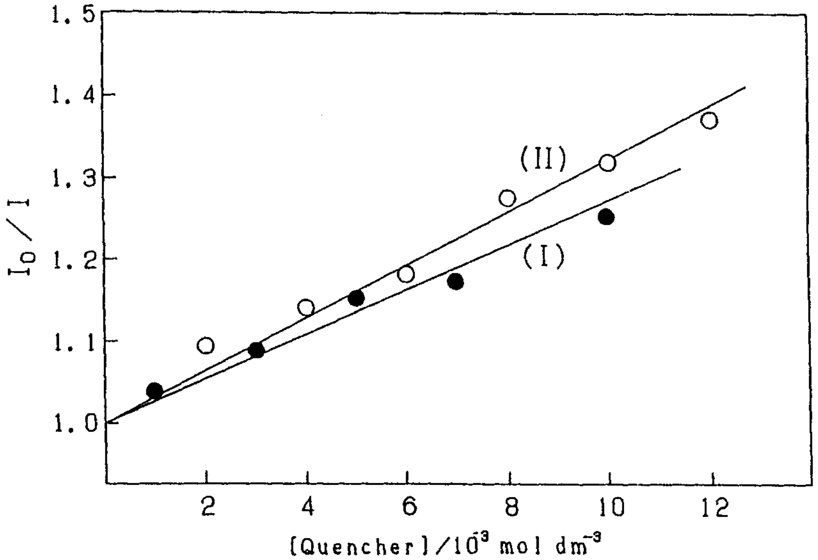


Figure 3. Stern–Volmmer plot for the quenching of phospherescence of 2,2′-furil by (I) cyclohexa-1,3-diene and (II) *trans*-stilbene. $I_0$ and $I$ are the phosphorescene intensities without and with the quencher, respectively

$E_T = 55\cdot0$ kcal mol$^{-1}$ for 2,2′-furil (the $E_s$ value was esti-mated from the absorption band at 400 nm[25]), $E_S = 90$ kcal mol$^{-1}$ and $E_T = 52\cdot0$ kcal mol$^{-1}$ for cyclohexa-1,3-diene and $E_S = 94\cdot2$ kcal mol$^{-1}$ and $E_T = 50$ kcal mol$^{-1}$ for *trans*-stilbene[26] (1 kcal = 4·184 kJ)], the observed quenching for the photoreduction in ethanol may be attributed to the triplet–triplet energy transfer from 2,2′-furil to the quenchers. In addition, the phosphorescence of 2,2′-furil observed at 77 K was also quenched by cyclohexa-1,3-diene and *trans*-stilbene, as seen in Figure 3, in which the values of $I_0/I$ are plotted against the concentration of the quenchers,

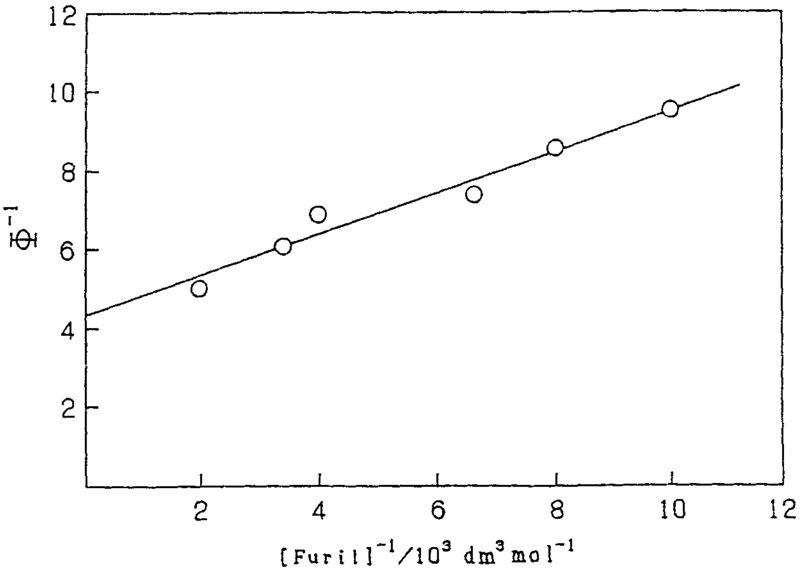


Figure 4. Sensitization plots for the formation of enediol in ethanol. [Fluorenone] = 5 × 10$^{-3}$ mol dm$^{-3}$. Excitation wavelength = 460 nm

where $I_0$ and $I$ are phosphorescence intensities of 2,2′-furil at 518 nm without and with quenchers, respectively. This phosphorescence quenching gives evidence for the occurrence of the triplet–triplet energy transfer in the present quenching systems. Accordingly, it can be said that the enediol formation from 2,2′-furil in ethanol takes place through the lowest excited triplet state of 2,2′-furil.

Further supporting evidence for the triplet mechanism of the enediol formation was obtained from the sensitization of the photoreaction by fluore-9-none. This compound has a smaller $E_S$ value (63·2 kcal mol$^{-1}$)[26] and a comparable $E_T$ value (53·3 kcal mol$^{-1}$)[27] compared with the corresponding values for 2,2′-furil, so it is expected to act as a sensitizer of the photoreduction in ethanol through triplet–triplet energy transfer from fluoren-9-one to the substrate. Light of 460 nm was used for excitation of fluoren-9-one. With this light, 2,2′-furil undergoes no photoreaction without the sensitizer. The results of the photosensitization are shown in Figure 4, in which the reciprocals of the quantum yields are plotted against the reciprocals of the concentrations of 2,2′-furil at a fixed concentration of fluoren-9-one sensitizer. As expected, fluoren-9-one sensitizes the enediol formation, indicating that triplet 2,2′-furil is produced by triplet–triplet energy transfer from excited fluoren-9-one and undergoes hydrogen abstraction from ethanol to afford the enediol. A similar photochemical reduction of 2,2′-furil was observed when other alcohols such as 2-propanol, ethylene glycol and glycerol were used as solvents.

### Photoreaction in benzene–triethylamine and ethers

It has been found that 2,2′-furil undergoes a different photoreaction in benzene containing TEA from that in ethanol described above. The absorption spectral change caused by irradiation at 366 nm of a benzene solution of 2,2′-furil containing TEA (1 mol dm$^{-3}$) is shown in Figure 5. In contrast to the results for the ethanol solution (Figure 1), the photoproduct in benzene–TEA shows an absorption band at 280 nm. This photoproduct was identified as furoin from the physical properties given in the Experimental section. In this photoreaction, TEA acts as a hydrogen donor.

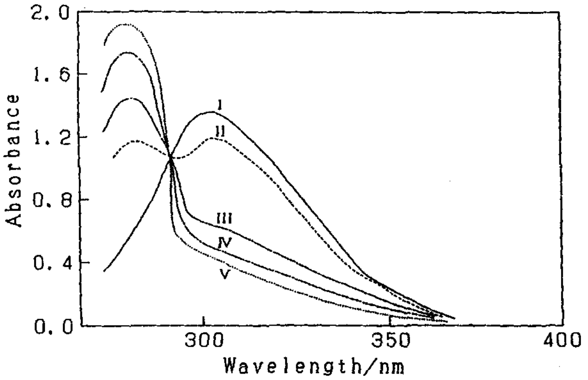


Figure 5. Absorption spectral change caused by irradiation at 366 nm of a benzene–TEA (1 mol dm$^{-3}$) solution of 2,2′-furil ($1{\cdot}0 \times 10^{-4}$ mol dm$^{-3}$). Irradiation time: I, 0; II, 20; III, 40; IV, 60; V, 100 min

Quenching experiments were performed in a similar manner to that for the ethanol solution to elucidate the reactive excited state in the furoin formation. Cyclohexa-1,3-diene and *trans*-stilbene, which act as quenchers in the enediol formation in ethanol, have no quenching effect on furoin formation in the benzene–TEA solution. Similarly to the case with the ethanol solution, these compounds show a quenching effect on the phosphorescence of 2,2′-furil in this solvent system. This clearly indicates that, in contrast to the enediol formation in ethanol, the lowest excited triplet state of 2,2′-furil does not participate in the furoin formation. In addition, the photosensitization by fluoren-9-one was not observed in benzene–TEA, indicating that the triplet mechanism is not operating. It should be noted that 2,2′-furil is known to be nonfluorescent, so one cannot conduct fluorescence quenching experiments. Nevertheless, the present results can be interpreted by furoin formation proceeding through the lowest excited singlet state of 2,2′-furil. Therefore, the differences between the photoreactivities in ethanol and TEA–benzene can be attributed to the differences in the reactive excited states, i.e., triplet or singlet.

In the photoreduction of some ketones by amines, electron transfer processes from amines to excited ketones possibly participates in the initial photochemical step. The ionization potentials of amines and the polarity of the solvent should affect the reactivity of 2,2′-furil if electron transfer is operating in the initial photochemical step in the furoin formation. The effects of alkylamines on the quantum yield of the furoin formation were examined, since the ionization potentials ($I_P$) of alkylamines are dependent on the alkyl group. In TPA (1 mol dm$^{-3}$, $I_P = 7{\cdot}23$ eV)–benzene and TBA (1 mol dm$^{-3}$)–benzene systems, the quantum yields were determined as 0·55 and 0·63, respectively. Although the ionization potential of TBA is not available, it seems to be smaller than that of TEA, because TBA has a longer alkyl group. The quantum yields in TPA ($\Phi = 0{\cdot}55$) and TBA ($\Phi = 0{\cdot}63$) are higher than that in the TEA ($I_P = 7{\cdot}50$ eV)–benzene system ($\Phi = 0{\cdot}22$), reflecting the lower ionization potentials of higher alkylamines.

The polarity of the solvent is also expected to influence the efficiency of an electron transfer-initiated photoreaction. In fact, the quantum yields for the furoin formation in TEA–methanol and TEA–acetonitrile systems were determined as 0·31 and 0·30, respectively, which are higher than that in TEA–benzene system (0·22). These results indicate that the furoin formation in amine-containing solvent systems is initiated by electron transfer from amines to the lowest singlet excited state of 2,2′-furil. This contrasts with the case of the enediol formation in ethanol, in which hydrogen or proton abstraction is operating in the initial step.

In order to examine the dependence of the reaction mechanism on the solvent, the photoreactivity of 2,2′-furil in ethers such as 1,4-dioxane and tetrahydrofuran was studied. In these ethereal solutions, 2,2′-furil undergoes the furoin formation, but no enediol formation. It is noteworthy that the ionization potentials of 1,4-dioxane ($I_P = 9\cdot43$ eV) and tetrahydrofuran ($I_P = 9.74$ eV) are lower than that of ethanol ($I_P = 10\cdot64$ eV).[28] This may be supporting evidence for the proposed reaction mechanism.

## REFERENCES

1. R. G. Zepp and P. J. Wagner, *J. Am. Chem. Soc.* **92**, 7466 (1970).
2. N. J. Turro and T.-J. Lee, *J. Am. Chem. Soc.* **92**, 7467 (1970).
3. P. J. Wagner, R. G. Zepp, K.-C. Lin, M. Thomas, T.-J. Lee and N. J. Turro, *J. Am. Chem. Soc.* **98**, 8175 (1976).
4. D. L. Bunbury and C. T. Wang, *Can. J. Chem.* **46**, 1473 (1968).
5. D. L. Bunbury and T. T. Chuang, *Can. J. Chem.* **47**, 2045 (1969).
6. D. L. Bubury and T. M. Chan, *Can. J. Chem.* **50**, 2499 (1972).
7. K. Maruyama, K. Ono and J. Osugi, *Bull. Chem. Soc. Jpn.* **45**, 847 (1972).
8. H. Inoue, S. Takido, T. Somemiya and Y. Nomura, *Tetrahedron Lett.* 2755 (1973).
9. C. J. Brown and R. Sadanaga, *Acta Crystallogr.* **18**, 158 (1965).
10. P. H. Curetone, C. G. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.* 4447 (1961).
11. C. W. N. Cumper and A. P. Thurston, *J. Chem. Soc., Perkin Trans. 2* 106 (1972).
12. S. C. Biswas, S. Ray and A. Podder, *Chem. Phys. Lett.* **134**, 541 (1987).
13. H. Inoue, T. Sakurai, T. Hoshi, I. Ono and J. Okubo, *J. Photochem. Photobiol. A* **60**, 121 (1991).
14. H. M. Vyas and J. K. S. Wan, *Mol. Phys.* **34**, 887 (1977).
15. A. J. Elliot and J. K. S. Wan, *Can. J. Chem.* **56**, 887 (1977)
16. J. W. N. Deboer, D. A. Hutchinson and J. K. S. Wan, *Chem. Phys. Lett.* **62**, 300 (1979).
17. J. W. M. Deboer, D. A. Hutchinson, R. Hawley and J. K. S. Wan, *Chem. Phys.* **43**, 81 (1979).
18. C. J. Sandroff and I. Y. Chan, *Chem. Phys. Lett.* **97**, 30 (1983).
19. C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A* **235** 518 (1956).
20. W. Luttke and H. Marsen, *Z. Elektrochem.* **57**, 680 (1953).
21. H. R. Hensel, *Angew. Chem.* **65**, 491 (1953).
22. F. Cramer and W. Krum, *Chem. Ber.* **86**, 1586 (1953).
23. C. A. Buehler, J. W. Addleburg and D. M. Glenn, *J. Org. Chem.* **20**, 1350 (1955).
24. T. Ashida and S. Hirokawa, *Acta Crystallogr.* **18**, 122 (1965).
25. T. R. Evans and P. A. Leermakers, *J. Am. Chem. Soc.* **89**, 4380 (1967).
26. S. L. Murov, *Handbook of Photochemistry*, p. 3. Marcel Dekker, New York.
27. J. G. Calvert and J. N. Pitts, Jr, *Photochemistry*, p. 298. Wiley, New York (1967).
28. K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*. Japan Scientific Societies Press, Tokyo (1981).