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Synthesis and Adiabatic Photochemistry of a 1,4-Difluorobenzene – Naphthalene Biplanemer

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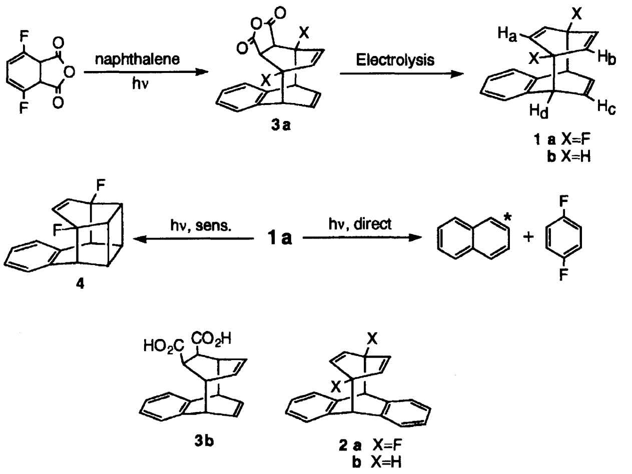
Synopsis. A naphtalene-1,4-difluorobenzene biplanemer **1a** has been prepared through the electrolytic oxidative didecarboxylation. The direct irradiation of **1a** gave 1,4-difluorobenzene and excited naphthalene in both a singlet state ($\Phi_f=0.098$) and a triplet state ($\Phi_p=0.029$) at 77 K in EPA. In the triplet-sensitized reaction, the biplanemer **1a** underwent intramolecular $[2\pi+2\pi]$ cycloaddition to give a cage compound instead of the formation of the triplet naphthalene.

Synthesis and photochemistry of energy-rich compounds have been carried out for development of a new synthetic method and clarifying an adiabatic process providing excited products.[1—4] Among adiabatic photoreactions of biplanemers,[2—4] the most efficient one is photocycloreversion of a series of anthracene–benzene biplanemers **2** to the singly excited anthracenes characterized by the $^1L_a \rightarrow {}^1A$ emission band (an allowed mode).[5] We were interested in weather there is a relation between the efficiencies and the kind of emission bands of excited products and intended to investigate the photocycloreversion of benzene–naphthalene biplanemers **1** probably providing singly excited naphthalene characterized by the $^1L_b \rightarrow {}^1A$ emission band (a forbidden mode).[5] Although Yang et al. reported the synthesis and the thermal Cope rearrangement of unsubstituted **1b**,[2] its photochemical behavior has not been investigated yet due to lack of thermal stability. We have prepared a thermally more stable biplanemer **1a** possessing two bridge bonds enforced by introduction of fluorine atoms on the bridgeheads, and wish to report the first observation of excited naphthalene in both a singlet state and a triplet state on direct irradiation of **1a** at 77 K. Intramolecular $[2\pi+2\pi]$ cycloaddition occurred on sensitized irradiation providing the cage compound **4** via energy transfer from the sensitizer to the triplet state of **1a**, as discussed in the case of 1,4,9,10,11,12-hexahydro-1,4-*p*-benzenonaphthalene, instead of the triplet naphthalene expected.[3f] The structure of **4** was assigned by comparing its ^{1}H NMR spectrum with that of previously synthesized 12,15-difluorohexacyclo[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7,13-tetraene.[3e] We will discuss the adiabatic reaction on the basis of energy surfaces and emission bands by comparing the results of the biplanemers **1a** and **2a** with those of dewarnaphthalene[3a] and dewaranthracene[3b] which undergo the adiabatic photo-ring opening reaction providing the same excited products as in the case of the biplanemers **1a** and **2a**.

Our synthetic route to the biplanemer **1a** is shown in Scheme 1. The photoreaction of naphthalene with 3,6-difluoro-1,2-dihydrophthalic anhydride gave a $[4\pi+4\pi]$ cycloadduct **3a** as a sole product. The acid anhydride **3a** was decarboxylated successfully to **1a** by electrolytic oxidation using a pair of platinum plate electrodes. It has been noted that the biplanemer **1b** could not be derived through direct oxidative decarboxylation of dicarboxylic acid **3b**.[2a] Introduction of fluorine atoms helped to make it possible to form **1a** in one step from **3a**. It is notable that when electrolysis was performed in the presence of a small amount of silica gel, a better yield of **1a** (17%) was attained than in the absence of silica gel (7—10%). Biplanemer **2a** was prepared by our method.[2b—e] In the ^{1}H NMR spectrum of **1a**, three characteristic olefin signals at 6.37, 6.65, and 5.85 ppm were assigned to resonance peaks for H_b, H_c, and H_a respectively as follows. The resonance peak of H_a appears at higher field than those of H_b and H_c because of the anisotropic effect of the benzene moiety located just over H_a. Irradiation at 6.65 ppm (H_c) causes the multiplet peak of H_d to simplify to a doublet coupling with the adjacent fluorine atom (27 Hz). Electronic absorption spectra of **1a**, **3a**, and **4** are shown in Fig. 1. It is notable that the absorption band at the long wavelength side for **1a** is shifted to longer wavelength than those of **3a** and **4**. This shift is attributable to bathochromic effect of the longicyclic [2,2,2,2]conjugation in **1a**.[3b]

Thermal stability of **1a** is sufficient to allow the study of the photocycloreversion even at room temperature. In the UV spectrum, **1a** shows a small absorption band



Scheme 1.

Table 1. Fluorescence and Phosphorescence Quantum Yields of **1a**, **2a**, Dewararenes and Reference Arenes

Compd	Solvent(Temp)	Φ_f	$\Phi_p(\tau_p/S)$	$\Phi_{ad}$$^{a)}$	Φ_f/Φ_p
1a	hexane (r.t.)	$0.10^{c)}$	—	0.55	—
	EPA (77 K)	$0.098^{c)}$	$0.029^{c)}(2.4)$	$0.24\ (0.72)^{b)}$	0.3
2a	hexane(r.t.)	$0.30^{d)}$	—	1.0	—
	EPA (77 K)	$0.27^{d)}$	—	1.0	—
Dewarnaphthalene$^{e)}$	hexane (r.t.)	0.095	—	—	—
	EPA (77 K)	0.14	0.04	—	0.3
Dewaranthracene$^{f)}$	hexane (r.t.)	0.024	—	—	—
Naphthalene	benzene (r.t.)	$0.19^{g)}$	—	—	—
	EPA (77 K)	$0.41^{h)}$	$0.04\ (2.25)^{g,i)}$	—	0.1
Anthracene	hexane (r.t.)	$0.30^{d)}$	—	—	—
	EPA (77 K)	$0.27^{j)}$	—	—	—

a) Quantum yield of adiabatic reaction. b) Quantum yield of the reaction providing excited products. c) Determined using naphthalene as reference. d) Determined by the method of Berlman using 9,10-diphenylanthracene as reference. e) Ref. 4a. f) Ref. 4b. g) Ref. 7a. h) Ref. 8. i) Ref. 9. j) Ref. 10.

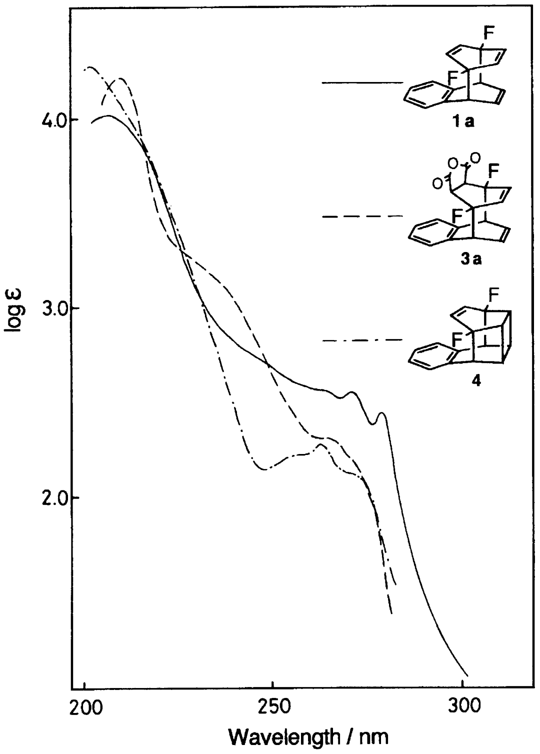


Fig. 1. Electronic absorption spectra of **1a** and related compounds (**3a**, **4**). **1a** in hexane, **3a** in ether, **4** in hexane.

at 280 nm tailing until about 300 nm corresponding to an *o*-xylene chromophore. When **1a** in hexane was irradiated at 280 nm at room temperature, an efficient naphthalenic fluorescence was selectively observed as an evidence for the adiabatic cycloreversion to excited naphthalene [Fig. 2(a)]. Naphthalene and 1,4-difluorobenzene were the products of the irradiation and the fluorescence band is identical to that of **1a**. The emission from naphthalene as impurity is negligible because its excitation spectrum (corrected) shows no contamination of naphtalene [Fig. 2(a)]. The quantum yields of the fluorescence of **1a** and **2a** (Φ_f), and of the adiabatic photocycloreversion (Φ_{ad}) are listed in Table 1. When irradiation was carried out in an EPA (diethylether–isopentane–ethanol) matrix (77 K), both a naphthalenic fluorescence and a naphthalenic phosphorescence were observed [Fig. 2(b)]. These emission spectra are also identical to those of naphthalene. The lifetime of the phosphorescence was 2.4 s which is the same as that of naphthalene phosphorescence (Table 1). These emissions are reasonably assigned to the fluorescence of the $^1L_b \rightarrow {}^1A$ emission band and the phosphorescence from $^3N_p^*$ ($^3L_a \rightarrow {}^1A$). Three notable results are shown for the efficiencies of these emissions and the cycloreversions. (i) The ratio ($\Phi_p/\Phi_f=0.3$) is three times larger than that ($\Phi_p/\Phi_f=0.1$) of naphthalene. The same ratio was recorded in the electrocyclic ring opening of dewarnaphthalene.[4a] (ii) The efficiency of adiabatic photocycloreversion ($\Phi_{ad}=0.25$) at 77 K is lower than that at room temperature ($\Phi_{ad}=0.55$). (iii) The total efficiency of the formation of excited naphthalene is 0.72. There must be a pathway(s) for the formation of $^3N_p^*$ other than the intersystem crossing of the excited naphthalene itself ($^1L_b \rightarrow {}^3L_a$). Influence of 1,4-difluorobenzene as a coproduct on the variation of the ratio is negligible, because the ratio of naphthalene did not change even in the presence or in the absence of 1,4-difluorobenzene. In the case of **2a**, however, the efficiency of the adiabatic photocycloreversion is substantially the same at room temperature as at 77 K because there is no such variation on the efficiency. For the efficient formation of singly excited anthracene from **2b**, Yang et al. proposed a possible explanation on the basis of the energy surface topology; the exothermic nature of this reaction tilts the reaction coordinate enough to effectively remove any barrier to escape from the pericyclic mini-

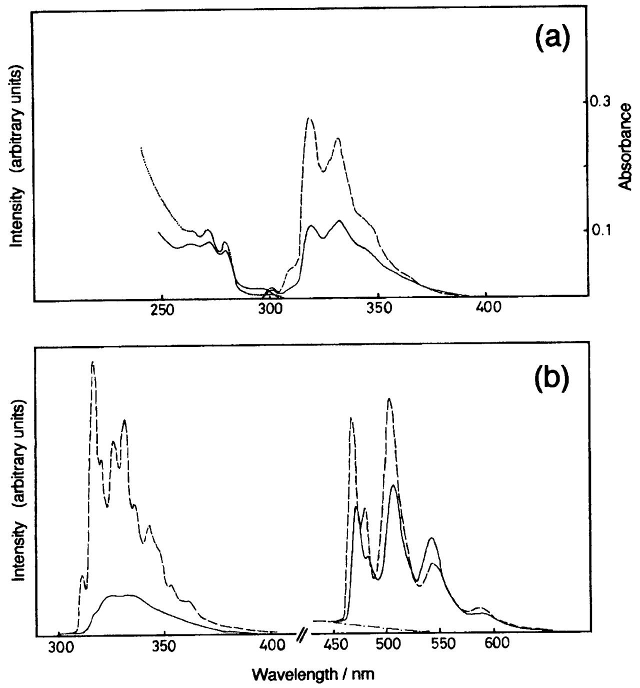


Fig. 2. The emission spectra of **1a** and reference naphthalene. (a) The fluorescence emission, excitation (corrected) (——) and absorption (····) bands of **1a** (2.4×10^{-4} M) in hexane at r.t., the fluorescence emission band of naphthalene (2.7×10^{-5} M) (---). Excitation at 279 nm, excitation and emission slit width 3.5 nm. (b) The fluorescence and phosphorescence emission bands of **1a** (——) and naphthalene (---) in EPA at 77 K. Blank of solvent (-··-). Fluorescence part; **1a** (2.6×10^{-4} M), naphthalene (3.0×10^{-5} M) excitation at 279 nm, excitation and emission slit width 3 nm. Phosphorescence part; **1a** (4.3×10^{-4} M), naphthalene (5.4×10^{-5} M), excitation at 279 nm, excitation and emission slit width 8 nm.

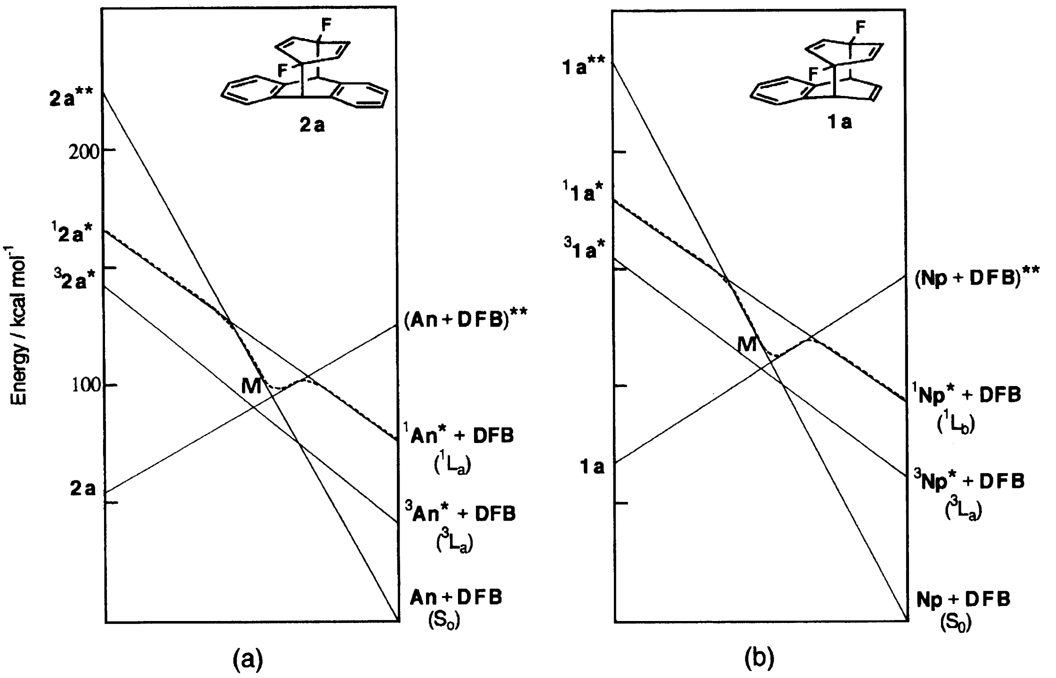
mum (M) corresponding to a biradical structure [Fig. 3-(a)].[3a)] The marked variations shown in the case of **1a** imply the presence of a higher energy barrier between the minimum (M) and the excited naphthalene (^1L_b) than between the corresponding M and the ^1L_a state of anthracene as shown in Fig. 3(b). Because the steeper slope of the correlation line from **1** to N_p^{**} than from **2** to An** makes the potential barrier higher. Further, the $^1L_a\rightarrow{}^1A$ emission band is an allowed mode, wheras the $^1L_b\rightarrow{}^1A$ one is a forbidden mode. Therefore, in the case of **1a**, the relative probability of intersystem crossing to the triplet surface at M may be higher due to the decrease in the rate of the formation of $^1N_p^*$ via the higher potential barrier. As the results, more efficient intersystem crossing to the triplet surface takes place in the case of **1a** than in the case of **2a**. The diabatic jump to ground state surface from the M should be a minor process because the total quantum yield of the formation of the excited naphthalene is 0.72. Therefore the ratios ($\Phi_p/\Phi_f=0.3$) probably reflect partitioning from M. The photocycloreversion of **1a** at 77 K results in the increase in the ratio (Φ_p/Φ_f) and the decrease in the efficiency (Φ_{ad}) of the adiabatic reaction. We would like to point out that these clear contrasts in the cases of **1a** and **2a** are also shown even in the adiabatic photocyclic ring-opening reaction of the pair of dewarnaphthalene and dewaranthracene. These parallel results obtained in these adiabatic photoreactions of the pair of **1a** and **2a** and the pair of the dewararenes are ascribable to the common thermally forbidden mode involving 4n electrons and providing common excited products of naphthalene and anthracene whose transition modes and their energy surface topologies are responsible for determination of both the Φ_{ad} and the Φ_p/Φ_f ratio.

Experimental

Apparatus and General Procedures. Melting points were measured with a Yanagimoto micro melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a JEOL JNM PMX-60 spectrometer or a Varian XL-500 in $CDCl_3$. IR spectra were recorded on a JASCO FT-IR 5000 spectrometer. UV spectra were recorded on a Hitachi 228 spectrophotometer. Fluorescence spectra were recorded on a Hitachi PF-4 spectrophotometer. After three freeze-pump-thaw cycles ($<2\times10^{-4}$ mmHg, 1mmHg=133.322 Pa), phosphorescence spectra were recorded in EPA on a Hitachi PF-4 spectrophotometer with phosphorescence attachment. Elemental analyses were performed on a Yanaco MT-2 CHN-corder. All solvents used for measurements of absorption and emission were purified by conventional procedures. Anthracene-1,4-difluorobenzene biplanemer **2a**, photoadduct **3a**, and **4** were prepared by our method.[3d,3e)]

Biplanemer 1a. An ice-cooled mixture of **3a** (250 mg, 0.795 mmol), 4-t-butylcatechol[12)] (25 mg) and silica gel (ca. 20 mg) in 25 ml of a mixed solvent (MeCN : pyridine : water : triethylamine=18 : 5 : 2 : 1) was electrolyzed using a pair of platinum plate electrodes with a current of 150 mA for 3.5 h. After filtration of silica gel, the filtrate was concentrated under reduced pressure to ca. 5 ml. The residual brown tar was extracted with ether (50 ml). The extract was washed with 2 M HCl (1M=1 mol dm^{-3}) and then with ice-water twice. The ethereal solution was dried over anhyd. $MgSO_4$ and ether was evaporated under reduced pressure. The residue was chromatographed using TLC (silica gel, CH_2Cl_2 : pentane=3 : 8) and a fraction containing **1a** (R_f=0.50—0.67) was collected. Recrystallization from $CHCl_3$-EtOH gave colorless prisms (32 mg, 0.132 mmol, 17%), mp 79—82 °C. ^{1}H NMR (60 MHz) δ=7.18 (m, 4H, ArH), 6.65 (m, 2H, H_c), 6.37 (m, 2H, H_b), 5.85 (m, 2H, H_a), and 3.92 (m, 2H, $J_{\text{H-F}}$=27 Hz, H_d); IR (KBr) 3040, 3010, 2950, 1465, 1445, 1060, 965, and 960 cm^{-1}; UV (hexane) 263 (log ε 2.59), 271 (2.58), and 279 nm (2.47). Found: C, 78.98; H, 5.07%. Calcd for $C_{16}H_{12}F_2$: C, 79.32; H, 4.99%.

Photoreaction of 1a. **1) (a) Direct Irradiation.** A degassed solution of **1a** (25 mg, 0.10 mmol) in 2 ml of hexane was irradiated with a 100-W high-pressure Hg lamp through a Pyrex filter for 1 h. After evaporation of the solvent and 1,4-difluorobenzene formed under reduced pressure, the residue (16 mg) was confirmed as a 1 : 4 mixture of the starting **1a** and naphtahalene by ^{1}H NMR analysis. (b) A



(a) (b)

Fig. 3. State correlation diagrams for the cycloreversion of biplanemers **1a** and **2a**. The ground state energy of **2a** is set to 57.5 kcal mol^{-1} by adopting Yang's model,[3a)] and that of **1a** is calculated by consideration of the absence of resonance energy of a benzene moiety (13 kcal mol^{-1}). Doubly excited states of products are estimated as the sum of the triplet energies of **DFB** and **An** or **Np**.[11)]**Np**=naphthalene, **An**=anthracene, **DFB**=1,4-difluorobenzene.

nitrogen purged $CDCl_3$ (0.3 ml) solution of **1a** (24 mg, 0.1 mmol) in an NMR tube was irradiated for 40 min with a 100-W high-pressure Hg lamp through a Pyrex filter. ^{1}H NMR analysis confirmed the complete conversion to a 1 : 1 mixture of naphthalene (δ=7.2—8.0) and 1,4-difluorobenzene (δ=6.93, t, J=6.0 Hz).

2) Sensitized Irradiation. An ice-cooled solution of **1a** (10 mg, 0.041 mmol) and xanthone (4 mg, 0.021 mmol) or benzophenone (3.7 mg, 0.021 mmol) in 0.3 ml of $CDCl_3$ was purged with nitrogen and irradiated with a 100-W high-pressure Hg lamp through a combined filter system (Pyrex and UV-DIC, 300—400 nm). After 30 min. of irradiation, quantitative intramolecular [2π+2π] cycloaddition to form **4** was observed by ^{1}H NMR analysis; ^{1}H NMR (500 MHz) δ=7.26 (m, 2H, ArH), 7.20 (m, 2H, ArH), 5.80 (d, J=17 Hz, 2H), 54.15 (br d, J=29 Hz), 3.20 (br d, J=17 Hz, 2H), and 3.09 (m, 2H). This ^{1}H NMR spectrum is identical with that reported for **4** in Ref. 3e.

References

1) N. J. Turro, J. McVey, V. Ramamurthy, and P. Lechtken, *Angew. Chem., Int. Ed. Engl.*, **18**, 572 (1979).

2) a) K. T. Mac, K. Srinivasachar, and N. C. Yang, *J. Chem. Soc., Chem. Commun.*, **1979**, 1038; b) H. Gen, J. L. King, and N. C. Yang, *Tetrahedron Lett.*, **30**, 1205 (1989).

3) a) N. C. Yang, M.-J. Chen, and P. Chen, *J. Am. Chem. Soc.*, **106**, 7310 (1984); b) M. Kimura, K. Shirasu, H. Okamoto, K. Satake, and S. Morosawa, *Tetrahedron Lett.*, **32**, 6975 (1992); c) M. Kimura, H. Okamoto, S. Morosawa, and S. Kashino, *Acta. Crystallogr, Sect. C*, **C47**, 779 (1991); d) M. Kimura, H. Okamoto, H. Kura, A. Okazaki, E. Nagayasu, K. Satake, S. Morosawa, M. Fukazawa, H. Abdel-Halim, and D. O. Cowan, *J. Org. Chem.*, **53**, 3908 (1988); e) M. Kimura, H. Kura, K. Nukada, H. Okamoto, K. Satake, and S. Morosawa, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 3307; f) M. Kimura, K. Nukada, K. Satake, and S. Morosawa, *J. Chem. Soc., Perkin Trans. 1*, **1986**, 885.

4) a) R. V. Carr, B. Kim, J. McVey, N. C. Yang, W. Gerhartz, and J. Michl, *Chem. Phys. Lett.*, **39**, 57 (1976); b) N. C. Yang, R. V. Carr, E. Li, J. K. McVey, and A. Rice, *J. Am. Chem. Soc.*, **96**, 2297 (1974).

5) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, New York (1964), p. 301.

6) A. Albini and E. Fasani, *J. Am. Chem. Soc.*, **110**, 7760 (1988).

7) a) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker Inc., New York (1973), pp. 4 and 10; b) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York and London (1965), p. 14.

8) G. Heinlich, D. Donnert, and H. Guston, *J. Photochem.*, **37**, 1304 (1972).

9) R. Li and E. C. Lim, *J. Chem. Phys.*, **57**, 605 (1972).

10) C. Parker and C. Hatchard, *Analyst*, **87**, 664 (1962).

11) a) W. Gerhartz, R. D. Poshusta, and J. Michl, *J. Am. Chem. Soc.*, **98**, 6427 (1976); b) R. A. Caldwell, *J. Am. Chem. Soc.*, **102**, 4004 (1980).

12) C. B. Warren and J. J. Broomfield, *J. Org. Chem.*, **38**, 4011 (1973).