© 1981 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 54, 2517—2518 (1981)

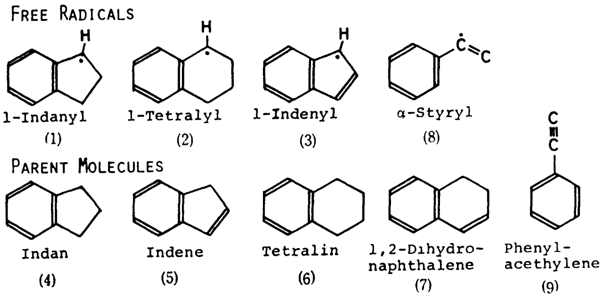
Electronic Spectra of Some Aromatic Free Radicals

Tatsuo Izumida, Kunihiko Inoue, Shoji Noda,* and Hiroshi Yoshida
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060

(Received December 22, 1980)

Synopsis. Electronic spectra are reported for 1-indanyl, 1-tetralyl, and 1-indenyl radicals generated photolytically or radiolytically in rigid matrices; the former two radicals show spectral features similar to those of benzyl radical, whereas the latter radical has a different spectrum because of its non-alternant π electron system.

Aromatic hydrocarbon radicals have been attracting interest as possible intermediates in such reactions as radiolysis of aromatic hydrocarbons,[1] soot formation from combustion,[2] and coal liquefaction.[3] However, there have been very few reports on the observation of the fluorescence spectra of the aromatic free radicals, except for benzyl radical and its methylsubstituted derivatives.[4] We report here for the first time the electronic spectra of 1-indanyl (**1**), 1-tetralyl (1,2,3,4-tetrahydro-1-naphtyl, **2**), and 1-indenyl (**3**) radicals generated photolytically or radiolytically from indan (**4**), indene (**5**), tetralin (1,2,3,4-tetrahydronaphthalene, **6**), and 1,2-dihydronaphthalene (**7**). The electronic spectra will be discussed for α-styryl radical (**8**) generated from phenylacetylene (**9**) also.



Experimental

4, **5**, **6**, and **9** were vacuum-distilled before use. **7** from Tokyo Kasei Co. (GR grade) and spectrograde ethanol (EtOH) were used as received. 3-Methylhexane (3MHx) was purified as described elsewhere.[5] Solutions of the parent aromatic compounds (about 10 $\mathrm{mmol \cdot dm^{-3}}$) in EtOH or 3MHx were thoroughly degassed by freeze-pump-thaw cycles and sealed in quartz sample tubes (0.4 cm diameter) for optical emission and ESR measurements and in a quartz flat cell (optical path-length of 0.2 cm) for optical absorption measurements. The sample solutions were irradiated at 77 K either with γ-rays from a ^{60}Co source to a dose of 2×10^5 rad or with UV light from a high pressure mercury lamp. Optical emission and excitation spectra of the irradiated samples were recorded with a Hitachi MPF-2A fluorescence spectrophotometer at 77 K. Occasionally, optical absorption and ESR spectra were examined with a Shimadzu MPS-5000 spectrophotometer and a Varian E-109 ESR spectrometer.

Results and Discussion

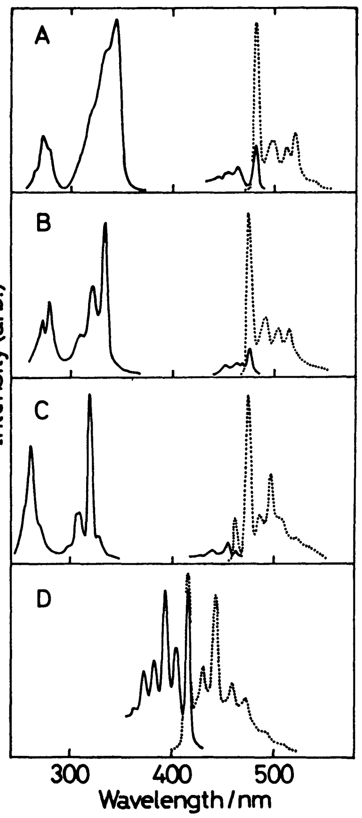


Fig. 1. Emission (……) and excitation (——) spectra of 1-indanyl (A), 1-tetralyl (B), benzyl (C) and 1-indenyl (D) radicals in 3MHx matrix at 77 K.

1-Indanyl and 1-Tetralyl Radicals. The UV-irradiation of **4** and **6** in nonpolar 3MHx matrix gave the emission and excitation spectra shown in Figs. 1A and B. The spectra comprise three excitation bands in visible wavelength region (400—490 nm), near-UV region (300—350 nm), and far-UV region (250—300 nm). The visible excitation band is a mirror image with the emission band. The spectra are attributed to 1-indanyl (**1**) or 1-tetralyl (**2**) radical generated by the photoinduced C–H bond scission in the corresponding parent molecule.

When **5** or **7** was γ-irradiated in a polar protic matrix of EtOH, the spectra were essentially the same as Figs. 1A or B. The previous study on the proton transfer to styrene anion gave similar results.[6] These spectra are attributed to **1** or **2**, which result from the electron capture of **5** or **7** followed by the proton transfer from matrix EtOH. The formation of the molecular anions of **5** and **7** was proven by the observation of their absorption spectra which were obtained by γ-irradiating the polar aprotic matrices of 2-methyltetrahydrofuran (MTHF) with **5** and **7**. The absorption spectra of the molecular anions consist of two broad peaks ($\lambda_{\max}$ of 400 and 710 nm for **5**, and 400 and 600 nm for **7**), which are readily bleached with light from an incandescent lamp.

The emission and excitation spectra of benzyl radical generated by UV-irradiation of toluene in the 3MHx matrix are shown for comparison in Fig. 1C. Three excitation bands in the visible, near-UV, and far-UV regions have been assigned to the transitions to $^2A_2$, $^2A_2$, and $^2B_2$ excited states from the $^2B_2$ ground state in the π electron system with C_{2v} symmetry.7) Both the **1** and **2** radicals, which have the same π electron system, show similar features of the electronic spectra, though a red-shift of the spectra and the removal of the forbidden character of the lowest $^2B_2$—$^2B_2$ transition8) (comparatively intense 0-0 vibration bands in the visible emission and excitation bands) possibly results from a deviation of the symmetry from C_{2v}. The larger shift observed for **1** may be due to a more constrained structure due to its five-membered ring.

1-Indenyl Radical. The UV-irradiation of **5** in the 3MHx matrix gave two set of emission and excitation spectra generally overlapping each other. The one set was apparently due to **1** mentioned above. The other set could be separated, as shown in Fig. 1D, from the spectra due to **1** by choosing proper wavelengths for excitation and observation. The ESR signal of the same irradiated sample showed a three-line spectrum with a hyperfine separation of 1.2 mT superimposed on a broad spectrum due to 3-methylhexyl radicals and probably due to **1**. The three-line spectrum is assigned to 1-indenyl (**3**) radical on the basis of the hyperfine coupling constants reported by Livingston *et al.*9) This ESR spectrum and the spectra shown in Fig. 1D slowly disappeared at 77 K, while the emission and excitation spectra of **1** remained unchanged.

The above observations lead to the assignment that the spectra of Fig. 1D is due to **3**. The band origin lies at 415 nm, appreciably shorter than that for benzyl, **1**, and **2** radicals. **3** has a non-alternant π electron system, and it has been suggested that the transition energy to the first excited state is larger.10) The excited **5** undergoes both the scission of C–H bond giving **3** and the abstraction of H giving **1**; it is not known whether the precursor states for these reactions are the same or not.

α-Styryl Radical. The γ-irradiation of **9** in the MTHF matrix gave the absorption spectrum with maxima at 370 and 533 nm due to the molecular anion of **9**. The irradiation in the EtOH matrix gave the absorption spectrum comprising a visible band with the band origin at 480 nm and a near-UV band with the maximum at 320 nm (no far-UV band could be observed, because of the intense overlapping absorption of the parent molecule). The same near-UV band has been reported previously by Shida and Hamill.11) This absorption spectrum is very probably due to α-styryl (**8**) radical, because it indicates a π electron system similar to that of benzyl radical.12) **8** can be generated by the proton transfer to the molecular anion of **9** in the EtOH matrix.

The emission and excitation spectra of **8** were difficult to detect: a weak emission from the irradiated EtOH matrix with **9** was mostly due to α-methylbenzyl radical,13) probably from impurity styrene contained in **9**. It is unknown why the fluorescence efficiency of **8** is very low compared to that of benzyl radicals, in spite of the fact that both radicals have a similar π electron system. In contrast to the present result, Brocklehurst *et al.* have observed an intense green thermoluminescence spectrum with the band origin at 474 nm upon melting the methylcyclohexane–isopentane mixed solvent containing **9** after γ-irradiating it at 77 K; they have tentatively assigned this luminescence spectrum to **8**.14)

References

1) S. Noda, M. Ohi, and H. Yoshida, *J. Phys. Chem.*, **84**, 2210 (1980).

2) I. Glassman, "Combusiton," Academic Press (1977), Chap. 8.

3) Y. Sanada, S. Yokoyama, and T. Chiba, *Shokubai*, **22**, 60 (1980).

4) T. Izumida, T. Ichikawa, and H. Yoshida, *J. Phys. Chem.*, **84**, 60 (1980) and references cited in the paper.

5) M. Irie, M. Shimizu, and H. Yoshida, *J. Phys. Chem.*, **80**, 2008 (1976).

6) S. Noda, Y. Fujii, and H. Yoshida, *Bull. Chem. Soc. Jpn.*, **50**, 2226 (1977).

7) J. Baudet and M. Suard, *J. Chim. Phys.*, **67**, 1088 (1972).

8) A. Bromberg, D. M. Friedlich, and A. C. Albrecht, *Chem. Phys.*, **6**, 353 (1974).

9) R. Livingston, H. Zeldes, and M. S. Conradi, *J. Am. Chem. Soc.*, **101**, 4312 (1979).

10) B. Brocklehurst, J. S. Robinson, and D. N. Tawn, *J. Phys. Chem.*, **76**, 3710 (1972).

11) T. Shida and W. H. Hamill, *J. Am. Chem. Soc.*, **88**, 3689 (1966).

12) J. E. Bennett and J. A. Howard, *Chem. Phys. Lett.*, **9**, 460 (1971).

13) T. Saito and H. Yoshida, *Bull. Chem. Soc. Jpn.*, **47**, 3167 (1974).

14) B. Brocklehurst, J. S. Robinson, and D. N. Tawn, *Chem. Phys. Lett.*, **12**, 610 (1972).