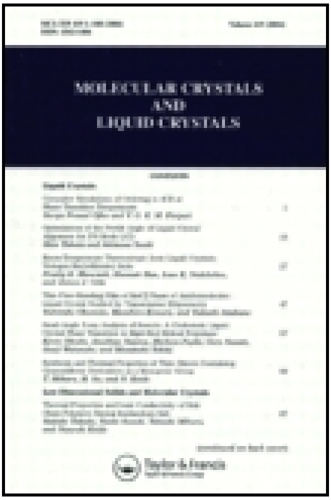

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Optical Studies of Hydronaphthyl Radicals Embedded in Dihydronaphthalene Crystal

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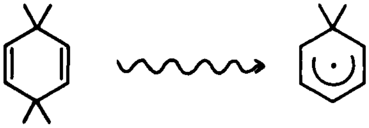
Radiation-induced radicals in dihydronaphthalene have been investigated at 4.2 K by absorption, fluorescence and fluorescence excitation studies. It was shown that the radicals in dihydronaphthalene are hydronaphtyl radicals. The advantages of using the dihydro compounds in the identification of cyclohexadienyl type radicals is discussed.

1. INTRODUCTION

It is well known that cyclohexadienyl type radicals are produced in aromatic hydrocarbon crystals by ionizing radiation.[1-7] The structure of these radicals was identified by ESR or ENDOR.[8,9] According to the ESR work by Fessenden and Schuler,[10] the cyclohexadienyl radical was observed in irradiated 1,4-cyclohexadiene,



This result indicates that the C—H bonds with allylic hydrogens are relatively weaker than C—H bonds with vinyl hydrogens and that one of the C—H bonds with allylic hydrogens is easily broken by ionizing radiation. Similar results are expected in irradiated dihydronaphthalene and other dihydro aromatic compounds.

Optical studies of these radicals also have been carried out extensively by many authors. Optical work, however, was mainly done with absorption measurements. Recently tunable dye lasers were used as powerful tools for

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fluorescence and fluorescence excitation studies of radicals[11-13]. The narrow band tunable dye lasers enabled us to do vibrational analysis of ground and excited states of radicals.

In this paper laser spectroscopic studies of radicals in irradiated naphthalene and dihydronaphthalene are reported. It is shown that radicals in irradiated 1,4- and 1,2-dihydronaphthalene are 1-hydronaphtyl radical (1-HNR) and 1- and 2-hydronaphthyl radical (2-HNR), respectively. The absorption spectrum of an irradiated 9,10-dihydroanthracene crystal is also measured. Advantage of using the dihydro compounds in the identification of cyclohexadienyl type radicals in aromatic hydrocarbon crystals through optical spectroscopy is discussed.

2. EXPERIMENTAL

Single crystals of naphthalene and 9,10-dihydroanthracene were grown by Bridgman method from extensively zone-refined materials which were recrystalized from ethanol. 1,2- and 1,4-dihydronaphthalene purchased from ICN Pharmaceuticals, Inc. were used without purification. Dihydronaphthalene polycrystals were grown by lowering the sample tube slowly into a liquid nitrogen dewer. All of the crystals used in the present work were irradiated at liquid nitrogen temperature by 9 MeV electron beams generated from an ARCO-7 LINAC. The total dose was about 5×10^7 rad. The irradiated samples were transfered to a liquid helium dewer and cooled to 4.2 K for spectroscopic studies. The experimental setup for absorption, laser induced fluorescence and fluorescence excitation was described elsewhere.[11-13]

3. RESULTS AND DISCUSSIONS

3-1 Absorption

Absorption spectra of irradiated naphthalene and 1,2- and 1,4-dihydronaphthalene crystals are shown in Figure 1. In 1,4-dihydronaphthalene (A), one prominent peak was observed at about 539 nm. In irradiated 1,2-dihydronaphthalene (B), on the other hand, a small peak was observed at about 635 nm in addition to a peak at 539 nm. The vibronic structures were not clearly resolved in either case. These absorption peaks corresponded to the peaks[14] of 1-HNR (C) and 2-HNR (D) in irradiated naphthalene crystal as shown in Figure 1. Since the absorption spectrum of an irradiated naphthalene crystal has been studied in detail by Nakagawa and Itoh,[14] only the origins of 1- and 2- HNR were reproduced. The wavelength scale is expanded for 1- and 2- HNR so that two site splittings (5387 and 5396 Å lines for 1-

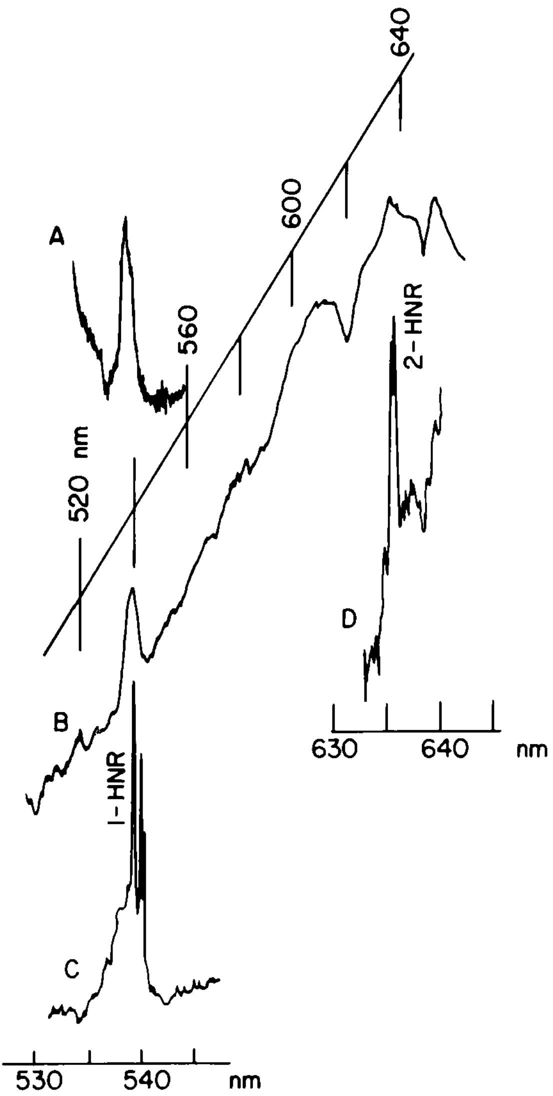


FIGURE 1 Absorption spectra of hydronaphtyl radicals measured at 4.2 K. A: in 1,4-dihydronaphthalene, B: in 1,2-dihydronaphthalene, C and D: in naphthalene. Strong absorptions about 539 nm are due to 1-hydronaphthyl radical and peaks about 635 nm are due to 2-hydronaphthyl radical.

HNR, 6355 and 6353 Å lines for 2-HNR) can be seen clearly. The longest wavelength peak (5402Å) in the absorption spectrum of 1-HNR is not a site effect. This peak disappears on warming the irradiated naphthalene crystal to room temperature although the other two peaks are stable at that temperature. From a comparison of these absorption spectra, it can be seen that one of the radicals produced in dihydronaphthalene is probably 1-HNR. This will be demonstrated more clearly by fluorescence study in the next section.

3-2 Fluorescence

In the case of irradiated naphthalene, absorptions corresponding to 0-0 transition of 1- and 2-HNR showed the sharp lines. On the other hand, the line width of the absorption peak at about 539 nm in irradiated 1,4- and 1,2-dihydronaphthalene was very broad. This is probably due to inhomogeneous site broadening. The inhomogeneous line width of phenylcyclohexadienyl radicals due to different site in biphenyl crystal is more than 30 Å.[15] Site selective excitation using a narrow band laser is a powerful method for studying the vibronic structure in such a case.

The laser induced fluorescence spectra of 1-HNR in naphthalene and radiation-induced radical corresponding to the peak about 539 nm in 1,2-dihydronaphthalene are shown in Figure 2 (right). Fluorescence spectrum in 1,2-dihydronaphthalene (upper) is not as well-resolved as in naphthalene (lower). This is due to the wide slit that was used in order to detect the weak fluorescence. The correspondence of the main peaks in the two spectra was very good. Analysis of the fluorescence spectrum of 1-HNR has been done in detail by Jacobsen et al[12] and will not be repeated here.

Fluorescence excitation spectra are shown in Figure 2 (left). The spectrum in naphthalene (lower) was observed by monitoring the 601 cm^{-1} vibrational line of 1-HNR. In 1,2-dihydronaphthalene (upper), the 0–0 line was monitored instead of this vibrational line since the fluorescence intensity was weak except for the 0-0 line. Peaks labelled by R in the lower spectrum which were not observed in 1,2-dihydronaphthalene are the Raman lines derived from the host naphthalene molecule. Prominent vibrational frequencies of the excited state of 1-HNR are listed in Table I. These agree completely with those measured in 1,2-dihydronaphthalene except four peaks observed at 5244, 5203, 5184 and 4994 Å. The fluorescence and excitation spectra of 539 nm band in irradiated 1,4-dihydronapthalene were also measured and coincided with the results for irradiated naphthalene. These results indicate that one of the radicals produced in 1,4- and 1,2-dihydronaphthalene is 1-HNR and that the C—H bonds with allylic hydrogens are more easily broken than the C—H bonds with vinyl hydrogens.

2-HNR decays rapidly during the spectroscopic measurement so that no fluorescence can be observed. We can not compare the vibrational frequencies

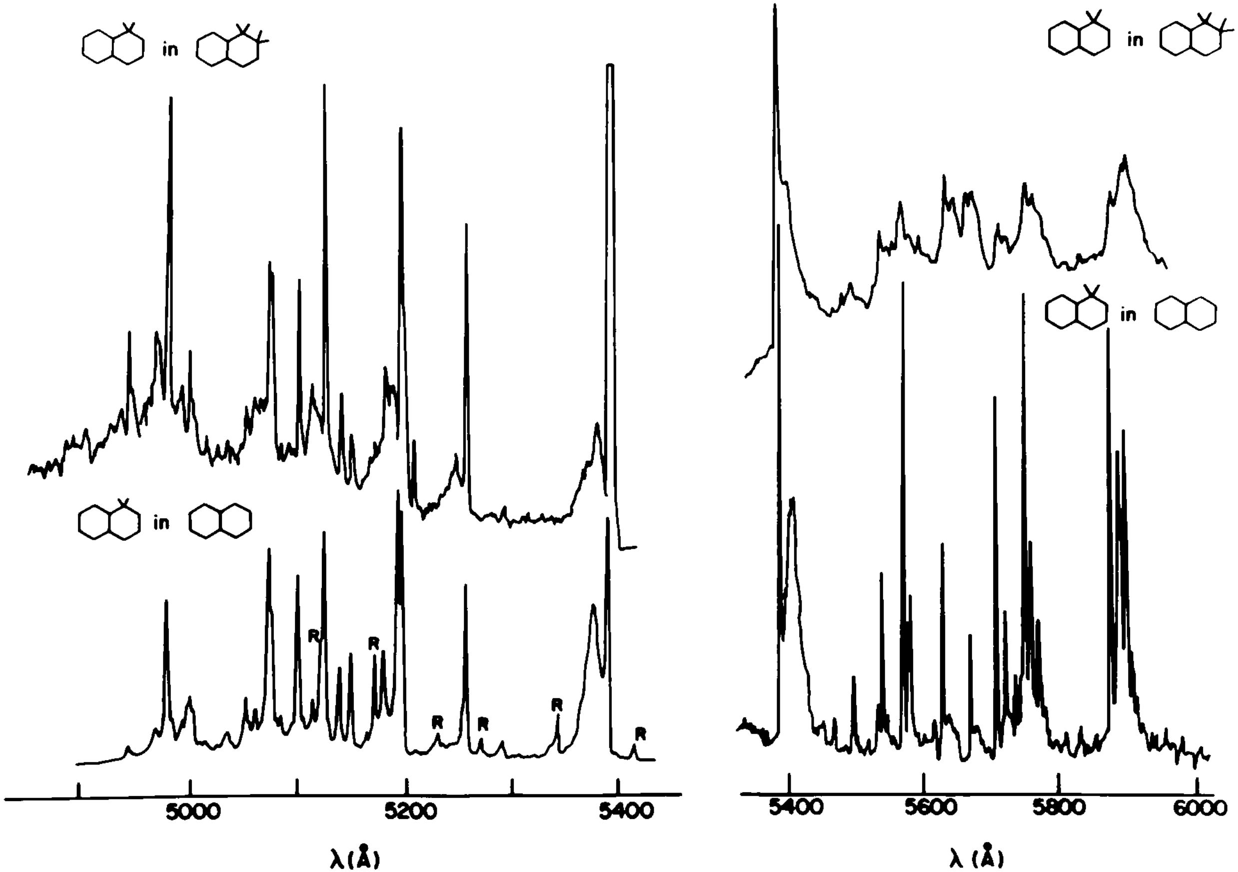


FIGURE 2 Laser induced fluorescence (right) and fluorescence excitation (left) spectra of 1-hydronaphthyl radical measured at 4.2 K. Excitation spectra were obtained by monitoring the 601 cm^{-1} vibrational line in naphthalene (lower) and 0-0 line in 1,2-dihydronaphthalene (upper). Lines labeled by R are the Raman bands derived from naphthalene. For fluorescence measurements, the laser wavelength was tuned to 5178 Å, which is a vibronic level of 5387 Å absorption line.

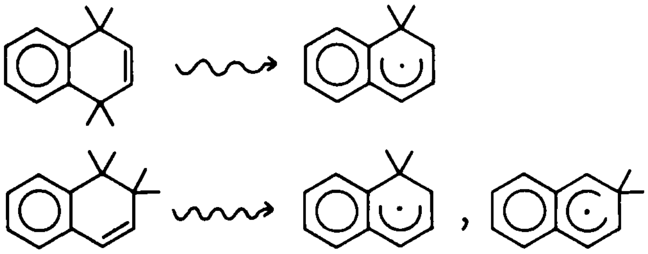
TABLE I
The fluorescence excitation spectrum of 1-HNR.[a]

in naphthalene			in 1,2-dihydronaphthalene		
λ(Å)	$\tilde{\nu}$(cm^{-1})[b]	$\Delta\tilde{\nu}$(cm^{-1})	λ(Å)	$\tilde{\nu}$(cm^{-1})[b]	$\Delta\tilde{\nu}$(cm^{-1})
5387.3	18557	0	5387.3	18557	0
5287.4	18908	351	5288.6	18903	346
5253.7	19029	472	5252.5	19033	476
			5244.0	19064	507
			5202.7	19215	658
5194.1	19247	690	5193.5	19249	692
5190.7	19260	703	5190.7	19260	703
			5183.7	19286	729
5177.6	19309	752	5176.3	19313	756
5161.9	19367	810	5166.9[c]	19349	837
5146.7	19425	868	5146.3	19426	869
5136.4	19463	906	5136.3	19464	907
5122.0	19518	961	5122.0	19518	961
5110.2	19563	1006	5110.9	19561	1004
5097.9	19610	1053	5098.9	19607	1050
5082.3	19671	1114	5082.6[c]	19669	1112
5073.7	19704	1147	5075.1	19699	1142
5071.7	19712	1155	5072.5	19709	1152
5058.8	19762	1205	5058.9	19762	1205
5049.6	19798	1241	5051.9	19789	1232
4998.4	20001	1444	5001.0	19990	1433
			4994.0	20018	1461
4978.3	20082	1525	4981.3	20069	1512
4967.2	20127	1570	4970.2	20114	1557
4941.8	20230	1673	4950.3	20195	1638

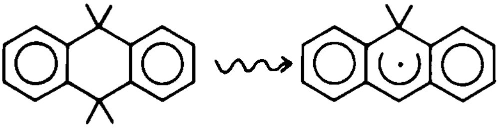
[a] Excludes phonon and Raman line.
[b] Corrected to wavenumber in vacuo.
[c] Not clear due to noise.

of 2-HNR in 1,2-dihydronaphtalene and in naphthalene. Considering the result obtained above, however, the radical in 1,2-dihydronaphthalene which absorbs a light about 635 nm is expected to be 2-HNR.

These results mean that the following reactions take place in dihydronaphthalene crystal by ionizing radiation,



One can expect such a reaction to be useful in identifying the cyclohexadienyl type radicals in aromatic hydrocarbon crystals by the use of optical spectroscopy. It has been established by optical, ESR[6b,7] and ENDOR[8] experiments that 9-dibenzocyclohexadienyl radical (9-DBCR) is the most dominant and stable radical in irradiated anthracene crystal. The absorption peak position of the 0-0 transition for this radical is 535 nm[6b]. We measured the absorption spectrum of 9,10-dihydroanthracene irradiated at liquid nitrogen temperature. The absorption peak corresponding to 9-DBCR was observed at 534 nm. Here again, the following reaction also takes place in 9,10-dihydroanthracene by ionizing radiation,



Since specific radicals can be produced in specific disubstituted compounds, the use of these compounds enables us to identify the structure of cyclohexadienyl type radicals whose identification by ESR experiments is sometimes difficult because of low concentrations and/or because of overlapping signals from other radicals. From thermal annealing of an irradiated anthracene crystal, 2-DBCR was also proposed by Chong and Itoh.[6b] To ascertain this, absorption and fluorescence studies of 2,3-dihydoranthracene crystal is suggested.

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