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Electronic Structures and Electronic Absorption Spectra of Cyclohexadienyl and Related Radicals Produced by γ-Irradiation

Tadamasa SHIDA and Ichiro HANAZAKI

The Institute of Physical and Chemical Research, Yamatomachi, Kitaadachi-gun, Saitama

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The electronic absorption spectrum for the cyclohexadienyl radical produced upon γ-irradiation of pure benzene and benzene-alcohol solutions both at 77°K was investigated. In addition to the absorption band at 3.9 eV, a weak band with a prominent vibrational structure was observed at 2.2 eV. An SCF-CI molecular orbital calculation was carried out for the radical taking into account explicitly the hyperconjugation effect of methylene group. The theory predicts the two observed bands with satisfactory accuracy. The calculated spin densities are also in good agreement with the existing ESR data of the radical. Vibrational analysis was carried out for the band system at about 2 eV as well as for the corresponding bands of isotopically mixed radicals, C_6H_6D, C_6D_6H, and C_6D_7. Parallel calculations for hydronaphthyl radicals are also in harmony with the available experimental data of optical and ESR measurements.

Cyclohexadienyl-type radicals are assumed as the reaction intermediates in radical substitution reactions at the benzene ring.[1] They are also known to be important intermediates in the radiolysis of benzene and its derivatives. Both the liquid benzene at room temperature[2] and the solid at 77°K,[3] produce the radical upon γ-irradiation which has been identified by its characteristic absorption band in the near UV and the triplet ESR spectrum. In the irradiated solid benzene the radical is assumed to be formed by the reactions,[3]

$$C_6H_6 \xrightarrow{\gamma} \cdot C_6H_5 + H \qquad (1)$$

$$C_6H_6 + H \longrightarrow \cdot C_6H_7 \qquad (2)$$

The same radical can also be produced in dilute benzene solutions in alcoholic solvents γ-irradiated at 77°K,[4,5]

$$CH_3OH \xrightarrow{\gamma} CH_3OH^+ + e^- \qquad (3)$$

$$C_6H_6 + e^- \longrightarrow C_6H_6^- \qquad (4)$$

$$C_6H_6^- + CH_3OH \longrightarrow \cdot C_6H_7 + CH_3O^- \qquad (5)$$

Similarly γ-irradiation of naphthalene single crystal or naphthalene in methanol glass at 77°K produces α-hydronaphthyl radical which has been confirmed by ESR and optical absorption measurements.[6,7]

The characteristic feature common to these radicals is the participation of ring methylene group in the π electron system through hyperconjugation. In the present work we have undertaken an open-shell SCF-CI calculation for electronic states of these radicals taking into account explicitly the effect of hyperconjugation. A method previously developed for the benzenium ion and related cations[8] was applied to the neutral radicals.

The results for cyclohexadienyl radical predicts a new electronic absorption band in the visible region in addition to the band in the near UV region.[5] Hence the absorption spectrum of the radical was carefully reexamined for irradiated solid benzene and benzene in alcoholic solvents. We have found the corresponding weak absorption band in the visible region with a marked vibrational structure which can be analyzed directly on the basis of fundamental vibrational frequencies close to those of the benzene molecule.

Experimental

Pure benzene and benzene in alcohols both degassed thoroughly were frozen at 77°K to a polycrystalline and a glassy solid. The samples were kept at the same temperature throughout the measurements of absorption

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[1] M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); *J. Amer. Chem. Soc.*, **77**, 1949 (1955); M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957).

[2] R. Cooper and J. K. Thomas, *J. Chem. Phys.*, **48**, 5097 (1968).

[3] S. Ohnishi, T. Tanei and I. Nitta, *ibid.*, **37**, 2402 (1962).

[4] J. A. Leone and W. S. Koski, *J. Amer. Chem. Soc.*, **88**, 224 (1966).

[5] T. Shida and W. H. Hamill, *ibid.*, **88**, 3689 (1966).

[6] J. A. Leone and W. S. Koski, *ibid.*, **88**, 656 (1966).

[7] T. Okubo, N. Itoh and T. Suita, *Molecular Crystals*, to be published.

[8] I. Hanazaki and S. Nagakura, This Bulletin, **38**, 1298 (1965).

spectrum before and after irradiation with γ-rays from a 12 kCi (kilocurie) ^{60}Co source. Optical cells of the thicknesses of 2.0 and 1.5 mm were made of Suprasil quartz. A quartz Dewar with flat quartz windows was placed in the sample compartment of a Cary spectrophotometer Model 14RI which was equipped with a high-intensity source attachment 1417200 operated at 110 V. The accessory was indispensable for the optical measurements because pure benzene solidifies at 77°K to an opaque polycrystalline and transmits light only to a small extent. Since the absorption induced by irradiation appears at wavelengths longer than 280 mμ where neither benzene nor methanol absorbs, the difference in the optical density before and after irradiation was taken to be due to the absorption of products formed upon irradiation.

Thiophene-free benzene was purified by distillation with a theoretical plate number of about 40 followed by repeated crystallization. Perdeuterobenzene of a stated atomic purity (>99%) from E. Merck AG was used. Methanol was purified by the standard method.[9] CH_3OD and C_2H_5OD were supplied from CIBA AG. Methanol and methanol-d_1 were added with 4% of water and D_2O respectively which formed clear glass with cracks at 77°K, while the ethanols vitrified without water. The cracks did not interfere with the optical measurement in the thin absorption cells. The aqueous methanols used as a solvent for benzene will be designated simply "methanol" hereafter.

Theoretical

In a previous paper[8] the electronic structures of benzenium ion and some related compounds were studied in the framework of the Pariser-Parr-Pople SCF-CI theory.[10] The hyperconjugation effect of the methylene group was treated explicitly in the following manner. The H_2 unit of CH_2 in the ion is regarded as a pseudo atom which provides a σ- and a π-type valence electrons to the ring system. The ionization potential and electron affinity of the pseudo π atomic orbital (AO) of the H_2 "atom" is calculated non-empirically to be 9.4219 and −0.7007 eV, respectively, by reducing the integrals over the pseudo AO into those over the hydrogen $1s$ AO's. The two-center Coulomb repulsion and core resonance integrals are also evaluated by the standard method by reducing them into the intergrals over the hydrogen $1s$ AO's. Satisfactory agreement with the experimental results for the benzenium ion and its derivatives encouraged us to use the same method of calculation for the corresponding neutral radicals. The method developed by Longuet-Higgins and Pople[11] for the open-shell electron system was applied to the radical in combination with the above method of evaluating the molecular integrals.

Results and Discussion

The Cyclohexadienyl Radical. One mol/l of benzene in methanol irradiated at 77°K to the dose of 1.1×10^{19} eV/g produced absorption spectra shown in Fig. 1. In accordance with the previous conclusion[5] they are associated with cyclohexadienyl radicals, C_6H_7 and C_6D_7 produced by reactions (3)—(5). The band at 3.9 eV was observed for a sample treated similarly, while the band system in the visible region was not detected apparently because of a high level of noise in the previous experiment.[5] By irradiating for a longer period the band system at about 2 eV became intense enough to reveal the structure as shown in Fig. 2 for the two isomeric radicals. The molar extinction coefficient of the most intense peak in the visible band system can be estimated knowing that of the band at 3.9 eV as 1.21×10^4 $l$mol^{-1} cm^{-1}.[12]

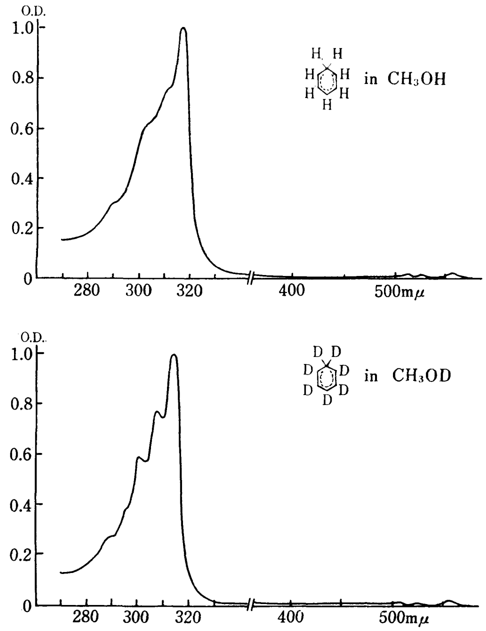

Fig. 1. Absorption spectra of cyclohexadienyl radicals in benzene-methanol solutions γ-irradiated at 77°K.

Upper: C_6H_7 produced from C_6H_6 (1 mol/l) in CH_3OH.

Lower: C_6D_7 produced from C_6D_6 (1 mol/l) in CH_3OD.

Dose$=1.1\times10^{19}$ eV/g for both samples.

A cell 1.5 mm thick was used for both.

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[9] H. Seki and M. Imamura, *J. Phys. Chem.*, **71**, 870 (1967).

[10] R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953). J. A. Pople, *Proc. Phys. Soc.*, *A*, **68**, 81 (1955).

[11] H. C. Longuet-Higgins and J. A. Pople, *ibid.*, *A*, **68**, 591 (1955).

[12] T. Shida, to be published.

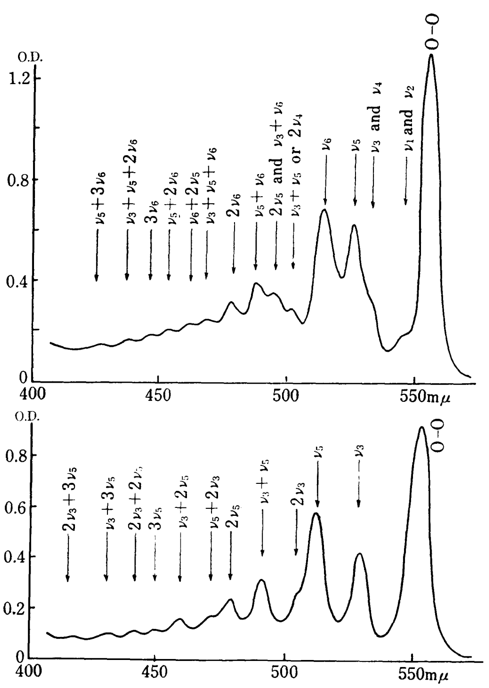

Fig. 2. Weak bands in the visible region of Fig. 1 magnified.

Upper: C_6H_7 in C_6H_6-CH_3OH solution.
Lower: C_6D_7 in C_6D_6-CH_3OD solution.
Dose$=2.1\times10^{21}$ eV/g. The cell, 1.5 mm thick.

Table 1. Electronic transitions of cyclohexadienyl radical, C_6H_7.

Symmetry[a)]	Theroretical		Experimental	
	Energy (eV)	Oscillator strength	Energy (eV)	Oscillator strength
A_2	2.030	4.07×10^{-4}	2.22	4.3×10^{-4}
B_1	3.626	3.20×10^{-4}		
A_2	3.950	1.35×10^{-1}	3.92	1.27×10^{-1}
B_1	5.649	4.20×10^{-2}		

a) The molecule has the C_{2v} symmetry.

Table 1 summarizes the theoretical results for the cyclohexadienyl radical together with the experimental results obtained. The prediction that a weak absorption should be observed at 2.03 eV is well substantiated. The first A_2 transition can be correlated to the benzene B_{2u} transition strongly mixed with the charge transfer transitions between the methylene pseudo AO and the π electron system of the aromatic ring. Similarly, the second A_2 transition comes from the benzene E_{1u} transition strongly affected by the charge transfer interactions.

The first B_1 transition predicted at 3.6 eV was not observed. We consider that either the intensity of the band is too small or the band is over-shadowed by the strong absorption at 3.9 eV.[*1]

The ESR spectrum of the radical has been studied by previous workers[3,4] who attributed the observed splittings of 47.5, 10.4, and 2.5 gauss to the methylene protons, three ring protons at ortho and para positions and two protons at meta position, respectively. The calculated spin densities are given in Fig. 3. The splitting due to the ring protons

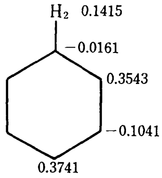

Fig. 3. Calculated spin densities of cyclohexadienyl radical.

are calculated by means of McConnell's relation with the proportionality constant of 30 gauss. The values of 10.6, 11.2, and 3.1 gauss for the ortho, para, and meta protons, respectively, are in fairly good agreement with the observed values. The splitting due to the methylene protons is derived to be 49.9 gauss by the following procedure. The pseudo AO χ is written as

$$\chi=[2(1-S)]^{-1/2}(\chi_1-\chi_2) \tag{6}$$

where χ_1 and χ_2 are the hydrogen 1*s* AO's and S is the overlap integral between them. Assuming the geometrical conformation of methane S is estimated as 0.282 from the table given by Mulliken *et al.*[13] The net atomic spin density ρ^{net} on each 1*s* AO is

$$\rho^{\text{net}}=[2(1-S)]^{-1}\rho \tag{7}$$

where ρ stands for the spin density on χ. With this relation and the calculated value of $\rho=0.1415$, we obtain $\rho^{\text{net}}=0.09854$. Using the hyperfine splitting of 506.8 gauss for the hydrogen atom the splitting due to the methylene protons is obtained as 49.9 gauss.[*2]

The general agreement between the theoretical and experimental results on the optical and ESR

[*1] We have not succeeded in observing this weak band for radicals of lower symmetry (*e.g.*, the radical derived from ortho xylene),[5] where the intensity of the band might be enhanced a little by the removal of symmetry of the radical.

13) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[*2] The contribution from the "overlap" spin density has been neglected. This gives an error of about 7% for the splitting. The odd electron on the $2p\pi$ AO of methylene carbon may induce an additional spin density on the methylene protons by the mechanism of spin polarization. This effect, however, can also be neglected since the $2p\pi$ spin density on the methylene carbon is minute.

properties of the radical indicates the adequacy of the present theoretical treatment. It must be emphasized that the effect of hyperconjugation is crucial in the electronic behavior of the radical. The striking resemblance of the electronic absorption spectrum of the cyclohexadienyl radical to that of the benzyl[14] may be an indication that the pseudo π electron in the former radical is as important as the $2p\pi$ electron of the methylene group in the latter radical.

The α-Hydronaphthyl Radical. Theoretical results for the electronic transition energies and intensities of α-hydronaphthyl radical are summarized in Table 2. Upon γ-irradiation an H atom may be added to naphthalene at α- and/or β position. The calculation for the total π electron energy predicts a lower value for the α radical by the amount of 4.2 eV. Thus the experimentally observed absorption bands are regarded as predominantly due to the α radical*[3]

TABLE 2. ELECTRONIC TRANSITIONS OF α-HYDRONAPHTHYL RADICAL

Theoretical			Experimental[a)]
Energy (eV)	Oscillator strength	Polarization[b)] (deg.)	Energy (eV)
2.402	1.20×10^{-3}	-86	2.34
2.986	3.39×10^{-4}	-18	3.14
3.681	1.82×10^{-3}	-14	3.68
3.752	5.38×10^{-2}	-72	
4.029	2.41×10^{-1}	$+65$	
4.615	1.77×10^{-3}	$+18$	

a) T. Okubo, N. Itoh and T. Suita; to be published in Molecular Crystals.

b) The direction of transition moment defined as measured from the $x+$axis toward the $y+$ axis shown in Fig. 4.

In Table 2 the experimental transition energies obtained for the γ-irradiated naphthalene single crystal are also included.[7] Agreement between the theoretical and observed values is satisfactory. Because of the overlapping of absorption bands due to several species produced in the irradiated crystal, it is difficult to determine the intensity of each band accurately. However, the intensity ratio of the observed three bands seems to be consistent with the calculated oscillator strengths.[7]

The spin densities calculated for the α-hydronaphthyl radical are shown in Fig. 4. By a similar procedure to that for the cyclohexadienyl radical the triplet splitting due to the methylene protons was found to be 29.3 gauss in comparison with the observed 37 gauss.[6] We assign, in conformity with the previous workers,[6] the observed minor triplet of splitting of 12.8 gauss to the ring protons at the 2 and 4 positions whose theoretical splittings are 12.6 and 11.3 gauss, respectively. The calculated spin densities for the β-radical cannot explain the ESR spectrum even qualitatively.

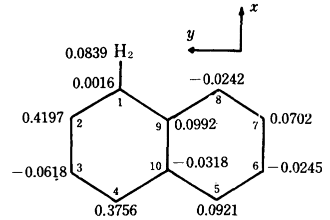

Fig. 4. Calculated spin densities of α-hydronaphthyl radical.

The Vibrational Analysis of the Visible Band System of Cyclohexadienyl Radical. γ-Irradiation of pure solid benzene produced sharp peaks in the region of 400—560 mμ as shown in Fig. 5. Owing to the stability of benzene towards radiation the total dose of the magnitude of 10^{21} to 10^{22} eV/g

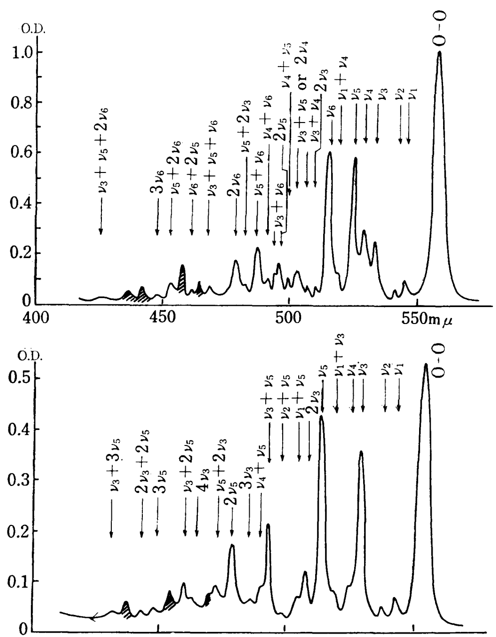

Fig. 5. Absorption spectra of the visible band of cyclohexadienyl radicals produced in pure benzene solids γ-irradiated at 77°K.

Upper: C_6H_7 in C_6H_6
Lower: C_6D_7 in C_6D_6
Dose$=2.1\times10^{21}$ eV/g. The cell, 2.0 mm thick.

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[14] E. J. Land, "Progress in Reaction Kinetics," Vol. III, ed. by G. Porter, Pergamon Press, London (1965), p. 378

*[3] This is consistent with the result of localization energy method which shows a larger methyl affinity for the α-position than the β-position.[15]

[15] T. Fueno, T. Tsuruta and J. Furukawa, *Nippon Kagaku Zasshi*, **78**, 1075 (1957).

was required to obtain the optical density of 0.5 to 1.0. In irradiated benzene concomitant reactions could yield species other than the cyclohexadienyl radical,[16] while in the methanol solution reactions (3)—(5) are predominant processes and no other species is expected which absorbs in the visible region.[5] Since Fig. 5 for the irradiated benzene is strikingly corresponding to Fig. 2 for the methanol solution, it can be concluded that in irradiated benzene also cyclohexadienyl radical is the main species responsible for the absorption in the visible region. It is fortunate that only a few minor bands are foreign. The other product of reactions (1) and (2), that is, the phenyl radical, is known to absorb in the region of 432—530 mμ.[17] However, the radical is so reactive that it may not exist as such in the irradiated solid but transform itself to other species transparent in the visible region. Even if the radical survives, it may have eluded our observation because the extinction coefficients of the radical may be extremely small as Porter and Ward implied.[17]

The appearance of the spectrum in Figs. 2 and 5 indicates clearly that the strongest peak is the 0–0 band. This is in accord with the theoretical prediction that the visible band is symmetry-allowed. All other peaks in Figs. 2 and 5 can be readily analyzed in terms of six and five fundamentals for

TABLE 3. VIBRATIONAI ANALYSIS FOR C_6H_7 IN C_6H_6

Wave number (cm^{-1})	Difference (cm^{-1})	Assignment
17904	—	0–0
18350	446	ν_1
18442	538	ν_2
18750	846	ν_3
18890	986	ν_4
19033	1129	ν_5
19331	1427	$\nu_1+\nu_4$
19386	1482	ν_6
19582	1678	$2\nu_3$
19753	1849	$\nu_3+\nu_4$
19886	1982	$\nu_3+\nu_5$ or $2\nu_4$
20018	2114	$\nu_4+\nu_5$
20170	2266	$2\nu_5$
20218	2314	$\nu_3+\nu_6$
20374	2470	$\nu_4+\nu_6$
20522	2618	$\nu_5+\nu_6$
20721	2817	$\nu_5+2\nu_3$
20858	2954	$2\nu_6$
21361	3457	$\nu_3+\nu_5+\nu_6$
21528	3624	foreign
21652	3748	$\nu_6+2\nu_5$
21868	3964	foreign
22003	4099	$\nu_5+2\nu_6$
22346	4442	$3\nu_6$
22636	4732	foreign
22823	4919	$\nu_3+\nu_5+2\nu_6$

The fundamentals above correspond to those of benzene as follows.

ν_1 C–C–C out-of-plane bending;
(e_{2u}) 404(cm^{-1}) Raman(forbidden)
ν_2 C–C–C in-plane bending
(e_{2g}) 605.6 Raman
ν_3 C–H out-of-plane bending;
(e_{1g}) 848.9 Raman
ν_4 C–C stretching;
(a_{1g}) 991.6 Raman
ν_5 C–H in-plane bending;
(e_{1u}) 1037 IR
ν_6 C–C stretching;
(e_{1u}) 1485 IR

TABLE 4. VIBRATIONAL ANALYSIS FOR C_6D_7 IN C_6D_6

Wave number (cm^{-1})	Difference (cm^{-1})	Assignment
18042	—	0–0
18433	391	ν_1
18605	563	ν_2
18891	849	ν_3
18979	937	ν_4
19284	1242	$\nu_1+\nu_3$
19467	1425	ν_5
19736	1694	$2\nu_3$
19855	1813	$\nu_1+\nu_5$
20032	1990	$\nu_2+\nu_5$
20310	2268	$\nu_3+\nu_5$
20396	2354	$\nu_4+\nu_5$
20593	2551	$3\nu_3$
20896	2854	$2\nu_5$
21164	3122	$\nu_5+2\nu_3$
21277	3235	foreign
21646	3604	$4\nu_3$
21739	3697	$\nu_3+2\nu_5$
21978	3936	foreign
22303	4261	$3\nu_5$
22576	4534	$2\nu_3+2\nu_5$
22857	4815	foreign
23164	5122	$\nu_3+3\nu_5$

The fundamentals above correspond to those of benzene as follows.

ν_1 C–C–C out-of plane bending;
(e_{2u}) 337(cm^{-1}) Raman(forbidden)
ν_2 C–C–C in-plane bending;
(e_{2g}) 576.7 Raman
ν_3 C–H in-plane bending;
(e_{1u}) 813 IR
ν_4 C–C stretching;
(a_{1g}) 944.7 Raman
ν_5 C–C stretching;
(e_{1u}) 1333 IR

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16) F. S. Dainton and G. A. Salmon, *Proc. Roy. Soc., Ser. A*, **285**, 319 (1965).

17) G. Porter and B. Ward, *ibid.*, **287**, 457 (1965).

the light and the heavy radicals, respectively. Tables 3 and 4 list the assignment for the two radicals. The deduced fundamentals bear close resemblance to those of ${}^1A_{1g}$ benzene.[18] Because of the wavelength accuracy of the monochromator the reproducibility of the measured wave number is roughly $\pm 10\ \mathrm{cm}^{-1}$ for the sharp peaks in solid benzene and $\pm 20\ \mathrm{cm}^{-1}$ for the blunt peaks in alcohol solutions.

The 0–0 band of C_6H_7 in CH_3OH is blue-shifted by about 45 cm^{-1} compared with that of the same radical in C_6H_6 (Tables 3 and 5). Similarly C_6D_7 in CH_3OD and C_6D_6 has a difference of about 40 cm^{-1} (Tables 4 and 8). Since the inherent error of the wave number is about 10 cm^{-1}, this amount of difference is quite significant. The wave number difference $\Delta\tilde{\nu}$, however, is more or less similar in the methanol and the benzene matrices. This implies that both C_6H_7 and C_6D_7 are stabilized in their ground electronic state by the dielectric alcohol matrix but that the vibrational levels of the electronically excited radicals are little affected by the environment. Parallel experiments using ethanol instead of methanol show that the stabilization effect is roughly equal for both alcohols (Tables 5 through 8).

Table 5. Vibrational analysis for C_6H_7 in alcohols

Methanol		Ethanol		
Wave number (cm^{-1})	Difference (cm^{-1})	Wave number (cm^{-1})	Difference (cm^{-1})	Assignment
17950	—	17947	—	0–0
19073	1123	19065	1118	ν_5
19425	1475	19420	1473	ν_6
20530	2580	20528	2581	$\nu_5+\nu_6$
20914	2964	20916	2969	$2\nu_6$

Table 6. Vibrational analysis for C_6H_6D in alcohols

Methanol-d$_1$		Ethanol-d$_1$		
Wave number (cm^{-1})	Difference (cm^{-1})	Wave number (cm^{-1})	Difference (cm^{-1})	Assignment
17973	—	17968	—	0–0
19087	1124	19080	1112	ν_5
19444	1471	19439	1471	ν_6
20546	2573	20541	2573	$\nu_5+\nu_6$
20928	2955	20922	2954	$2\nu_6$

Table 7. Vibrational analysis for C_6D_6H in alcohols

Methanol		Ethanol		
Wave number (cm^{-1})	Difference (cm^{-1})	Wave number (cm^{-1})	Difference (cm^{-1})	Assignment
18055	—	18054	—	0–0
18918	863	18916	862	ν_3
19475	1420	19477	1423	ν_5
20333	2278	20332	2278	$\nu_3+\nu_5$
20906	2851	20901	2847	$2\nu_5$

Table 8. Vibrational analysis for C_6D_7 in alcohols

Methanol-d$_1$		Ethanol-d$_1$		
Wave number (cm^{-1})	Difference (cm^{-1})	Wave number (cm^{-1})	Difference (cm^{-1})	Assignment
18080	—	18071	—	0–0
18941	861	18929	858	ν_3
19512	1432	19493	1422	ν_5
20361	2281	20343	2272	$\nu_3+\nu_5$
20924	2844	20919	2848	$2\nu_5$

The difference in 0–0 band of C_6H_7 in C_6H_6 and C_6D_7 in C_6D_6 amounts to 138 cm^{-1}. Likewise C_6H_7 in CH_3OH and C_6D_7 in CH_3OD has a difference of 130 cm^{-1} (Tables 5 and 8). Similar isotopic shift of about 190 cm^{-1} is observed for another 0–0 band at 3.9 eV as shown in Fig. 1. The shifts between the light and the heavy radicals are attributed to the smaller zero point energies of the heavy radical in the two electronic states concerned.

According to the mechanism of reactions (3)—(5) it is possible to produce two other isotopically different cyclohexadienyl radicals; light benzene in methanol-d$_1$ and heavy benzene in the normal methanol will yield C_6H_6D and C_6D_6H respectively. Leone and Koski[4] have shown by ESR that both are actually produced, although they did not clarify the reaction mechanism of radical formation.[4,5] We found that both C_6H_6D and C_6D_6H give rise to very similar spectra to those of C_6H_7 and C_6D_7, respectively. Barely significant differences (in the 0–0 band between C_6H_7 and C_6H_6D (Tables 5 and 6), and between C_6D_6H and C_6D_7 (Tables 7 and 8) are again atrributed to the slight difference in the mass of the radicals.

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[18] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., N. Y. (1949).