Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Identification of the Phenylcyclohexadienyl Radical in the Irradiated Benzene Crystal

T. Nakayama [a] & S. J. Sheng [a]
[a] Radiation Laboratory, University of Notre Dame Notre Dame, Indiana, 46556, U.S.A.
Version of record first published: 20 Apr 2011.

To cite this article: T. Nakayama & S. J. Sheng (1980): Identification of the Phenylcyclohexadienyl Radical in the Irradiated Benzene Crystal, Molecular Crystals and Liquid Crystals, 59:3-4, 175-180

To link to this article: http://dx.doi.org/10.1080/00268948008071421

Mol. Cryst. Liq. Cryst., 1980, Vol. 59, pp. 175–180
0026-8941/80/5903-0175$04.50/0

Printed in the U.S.A.

Identification of the Phenylcyclohexadienyl Radical in the Irradiated Benzene Crystal

T. NAKAYAMA and S. J. SHENG

Radiation Laboratory,† University of Notre Dame, Notre Dame, Indiana 46556, U.S.A.

(*Received August 7, 1979*)

In an irradiated benzene crystal, new absorption lines were observed on the low energy side in addition to the usual lines due to the cyclohexadienyl radical. These lines were attributed to the phenylcyclohexadienyl radical arising from the addition of the phenyl radical to a benzene molecule in the solid lattice. The isolated radical is quite stable for laser fluorescence and excitation studies. The deuterium shifts of the lowest electronic transition for a number of the cyclohexadienyl radicals are presented. A method of using the magnitude of the deuterium shift to estimate the size of the radical is proposed.

I INTRODUCTION

It is known that hydrogen atoms can react with benzene molecules forming cyclohexadienyl radicals.[1–7] One convenient method to prepare cyclohexadienyl radicals is through the bombardment of the benzene crystal with high energy electron beams. The source of the hydrogen atoms, in this case, comes from the breakage of C—H bonds in the benzenes. The phenyl radical, on the other hand, is expected to react with benzene molecules to form phenylcyclohexadienyl radicals. The phenylcyclohexadienyl radical is assumed to be the chemical intermediate of the aromatic phenylation reaction.[8] The intermediate was inferred indirectly from the selective chemical reactions and the CIDNP study of the product after the reaction between the phenyl radical and substituted benzenes.[9] The purpose of this work is to report the direct spectroscopic studies of phenylcyclohexadienyl

† The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1981 from the Notre Dame Radiation Laboratory.

radicals isolated in the benzene crystal. Similar "dimer" radicals in the irradiated naphthalene crystal were identified before.[10–13]

II EXPERIMENTAL SECTION

Spectral grade benzene, perdeuterated benzene with 99.5 per cent isotopic purity, and mixtures of them were sealed in supersil quartz tubes with capillary tips. Transparent crystals were grown in a Bridgman air bath, with the top and bottom parts of the bath kept at room and dry ice temperature, respectively. The crystals were mounted inside a metal can filled with liquid nitrogen. A window made of aluminum foil enables the electrons to penetrate without too much attenuation. The sample was irradiated by the 9 MeV electron beam of a linear accelerator. The dosage used is about 3×10^7 rad. The irradiated sample was transferred to a liquid helium dewar and cooled down to 4.2°K for spectroscopic examination. The setup for absorption, laser induced fluorescence, fluorescence excitation, and lifetime measurement were described elsewhere[7,13] and will not be repeated here.

III RESULTS AND DISCUSSIONS

A Absorption studies

The absorption spectrum of a benzene crystal irradiated at 77 K was examined in the region from 4500 to 8000 Å at 4.2 K. The intense absorption in the high energy side of the spectrum shown in Figure 1, was unequivocally assigned as the lowest doublet doublet absorption of cyclohexadienyl radicals.[3,7] Attention of this work is focussed on the weak absorption lines in the low energy side of the spectrum. The origin of the weak transition is located at 6571 Å through the absorption and the laser induced emission studies. Since the lowest doublet doublet transition of cyclohexadienyl radicals is located at 5586 Å,[7] the 6571 Å absorption can be either derived from the cyclohexadienyl radical involving a transition of different multiplicities or from other chemical species. The emission lifetime of the 6571 Å transition is determined to be 1.5 nsec, too short for the spin forbidden transition. In addition, laser excitation of the origin of the lowest doublet doublet transition of cyclohexadienyl radical gives insignificant amount of the 6571 Å emmission. In contrast laser excitation of the vibrational levels of 6571 Å transition gives very intense fluorescence. These facts clearly indicate that a new species is responsible for the 6571 Å transition. Since the phenylcyclohexadienyl radical is expected to be present, it is reasonable to assume that

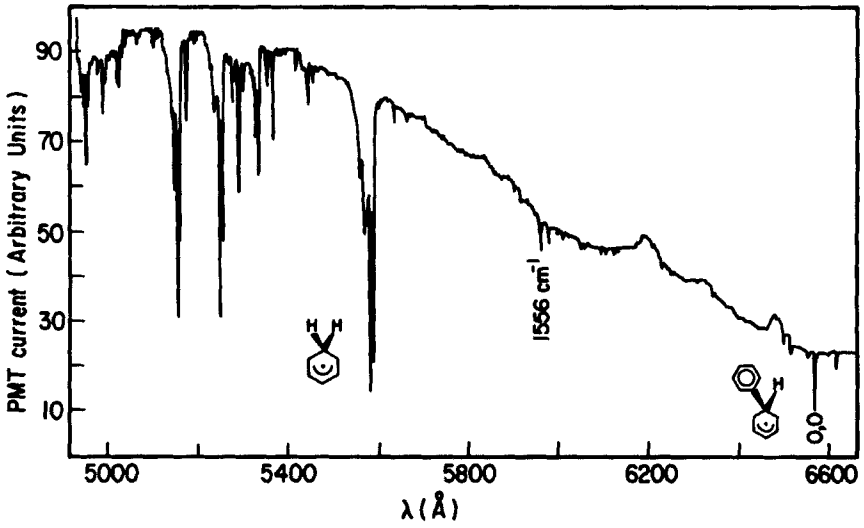

FIGURE 1 The absorption spectrum of an irradiated benzene crystal. The crystal was irradiated at 77 K with a dose of 3×10^7 rad and then cooled to liquid helium temperature for absorption studies. The concentration of cyclohexadienyl radical is about 5×10^{-3}M, whereas the concentration of phenylcyclohexadienyl radical is estimated to be 5×10^{-4}M.

the 6571 Å transition is related to this radical. In the following, we will present the spectroscopic evidence that the new species is indeed the phenylcyclohexadienyl radical. These evidences include the deuterium shift of the electronic origin and the vibrational structure associated with the 6571 Å transition.

B Deuterium shift

It is well known that upon deuteration the lowest electronic transition of aromatic molecule is shifted to the blue.[23] To our knowledge this is the first time it will be shown experimentally that the deuterium shift of the electronic origin is a function of the molecular weight for a class of similar compounds. From a number of deuterium shifts for the known compounds, the size of the unknown compound can be estimated. The deuterium shift of the absorption line at 6571 Å is measured to be 83 cm^{-1}. This is compared with the deuterium shifts of cyclohexadienyl (139 cm^{-1}),[7] α- or β-hydronapthyl (96 cm^{-1}),[14,15] 9-dibenzocyclohexadienyl (71 cm^{-1}),[16] 1-hydrobinaphthyl (58 cm^{-1}),[13] and hydrobianthracenyl (51 cm^{-1})[16] radicals. The relation between the deuterium shift and the number of carbon atoms of the radical is shown in Figure 2. As is evident from the figure, the shift drops in the order of increasing number of carbon atoms. A smooth curve can be drawn from the

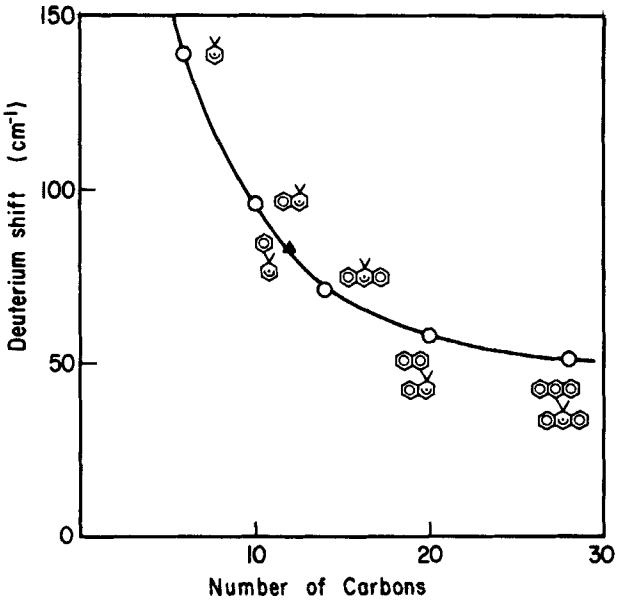

FIGURE 2 Plot of the deuterium shifts of the electron origin vs. number of carbons for a series of cyclohexadienyl radicals. Solid triangle indicates the deuterium shift of the 6571 Å transition.

plot. The 6571 Å line, whose deuterium shift is shown by a solid triangle in Figure 2, is thus expected to originate from a radical species having about twelve carbon atoms. Gordon *et al.*[17] have shown from their mass spectrometic analysis that the most important products in irradiated liquid benzene are biphenyl and phenylcyclohexadiene containing twelve carbons. It should be pointed out that the phenylcyclohexadienyl radical is the precursor of these products. We, therefore, attribute the 6571 Å transition to the phenylcyclohexadienyl radical. This assignment is consistent with the fact that the 6571 Å absorption was not observed in irradiated methanol glass containing even as high as 1 M benzene. The addition of the phenyl radical to benzene is expected to be restricted to the nearest neighbors in the solid lattice.

The lowest doublet doublet transition of the phenylcyclohexadienyl radical is expected to be analogous to that of the cyclohexadienyl radical. The transition involved is a weak but allowed $B_2 \rightarrow A_2$ transition in the C_{2v} symmetry group.[3] The additional phenyl group certainly imposes a sizable perturbation on the cyclohexadienyl radical. The down shift in transition energy of the $B_2 \rightarrow A_2$ transition was measured to be 2684 cm^{-1}. A preliminary MO calculation of phenylcyclohexadienyl radical also indicates that the red shift is comparable to the experimental value.

TABLE I

Vibrational analysis of Phenylcyclohexadienyl Radical

Fluorescence			Absorption and excitation		
λ (Å)	$\Delta\tilde{\nu}$ (cm^{-1})	Biphenyl[a,b] analogue (cm^{-1})	λ (Å)	$\Delta\tilde{\nu}$ (cm^{-1})	Biphenyl[a,b] analogue (cm^{-1})
6569.9	0		6570.9	0	
6642.3	166 (1.11)[d]	174 IR[c](1.09)	6516.1	128	120 IR
6698.0	291	330 R	6499.5	168	174 IR[c]
6766.3	442(1.11)	455 IR(1.11)	6286.4	689	698 IR
6801.6	519		6278.5	709	740 R
6811.2	539	547 R	6208.7	888	904 IR
6825.6	570(1.04)	608 IR(1.04)	6183.9	953	990 IR
7110.1	1156(1.33)	1156 IR(1.37)	6180.4	962	1001 R
7324.9	1569(1.03)	1599 IR(1.02)	6126.0	1105	1100 R
			6106.3	1158	1156 IR
			6094.8	1189	1183 IR
			6058.5	1287	1277 R
			6048.3	1315	1335 R
			6022.0	1387	1431 IR
			6009.9	1421	1467 R
			5979.8	1504	1512 R
			5961.4	1556	1599 IR

a. ref. 19; b. ref. 20; c. ref. 21; d. The values in the parentheses are the vibrational frequency ratios of ordinary compounds vs. deuterium compounds.

C Vibrational analysis

Accurate vibrational frequencies in the ground and excited states of the 6571 Å transition were obtained from fluorescence and fluorescence excitation spectra at 4.2 K. The fluorescence was laser-induced by exciting one of the vibronic levels at 5962 Å. The excitation spectrum was taken by monitoring the fluorescence origin of the prominent site. The vibrational analysis is shown in Table I. The vibrational structure in the ground state has an excellent correlation with the IR and Raman data of the biphenyl molecules.[18–22] The 442, 570, 1156, and 1569 cm^{-1} vibrations in the radical fluorescence are easily correlated with 455, 608, 1166, and 1599 cm^{-1} vibrations in biphenyl. The vibrational frequency ratios of the ordinary vs. perdeuterated radical are nearly the same as those of the biphenyl vs. perdeuterated biphenyl molecule (see Table I). The 166 cm^{-1} vibration, appearing also in absorption, was assigned as a low frequency vibration. This is likely to correspond to the 174 cm^{-1} out of plane b_{3u} vibration in biphenyl.[21] There are more vibrational fundamentals appearing in the fluorescence excitation spectrum as listed in Table I. The correlation between these fundamentals and the IR and Raman modes of biphenyl is satisfactory but is less reliable than the fluorescence assignment.

IV CONCLUSION

The 6571 Å transition was assigned to the phenylcyclohexadienyl radical, formed in a solid state reaction between the phenyl radical and benzene at 77 K. The concentration ratio of the phenylcyclohexadienyl radical to cyclohexadienyl radical can be estimated to be about 0.1 provided the oscillator strength is the same for these radicals. It should be pointed out that the phenylcyclohexadienyl radical isolated in the benzene crystal is only one of the four possible isomers. Work is underway to study other isomeric phenylcyclohexadienyl radicals produced by irradiating the biphenyl crystal.

Acknowledgment

The authors would like to thank Dr. G. Hug for his encouragement during this work and Mr. Michael Kurtis for his assistance in irradiating the crystals.

References

1. R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).
2. S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).
3. T. Shida and I. Hanazaki, *Bull. Chem. Soc. Jpn.*, **43**, 646 (1970).
4. S. DiGregorio, M. B. Yim, and D. E. Wood, *J. Am. Chem. Soc.*, **95**, 8455 (1973).
5. J. E. Jordan, D. W. Pratt, and D. E. Wood, *J. Am. Chem. Soc.*, **96**, 5588 (1974).
6. J. Bardsley, P. J. Baugh, J. I. Goodall, and G. O. Phillips, *J. C. S. Chem. Comm.*, 890 (1974).
7. S. J. Sheng, *J. Phys. Chem.*, **82**, 442 (1978).
8. W. A. Pryor, *Free Radicals*, McGraw-Hill, New York, N.Y., 1966, pp. 251–263.
9. S. R. Fahrenholtz and A. M. Trozzolo, *J. Am. Chem. Soc.*, **94**, 282, (1972).
10. A. Piccini and W. B. Whitten, *Mol. Cryst. Liq. Cryst.*, **18**, 333 (1972).
11. T. Chong and N. Itoh, *Mol. Cryst. Liq. Cryst.*, **11**, 315 (1970); *J. Phys. Soc. Jpn.*, **35**, 518 (1973).
12. K. Nakagawa and N. Itoh, *Chem. Phys.* **40**, 69 (1979).
13. K. Nakayama and S. J. Sheng. *J. Phys. Chem.*, **83**, 2869 (1979).
14. C. W. Jacobson, H. K. Hong, and S. J. Sheng, *J. Phys. Chem.*, **82**, 1537 (1978).
15. S. J. Sheng, K. Nakagawa, T. Nakayama, Y. Kumazawa and N. Itoh, *Radiat. Phys. Chem.*, in press.
16. T. Nakayama and S. J. Sheng, unpublished results.
17. S. Gordon, A. R. Van Dyken, and T. F. Doumani, *J. Phys. Chem.*, **62**, 20 (1958).
18. J. E. Katon and E. R. Lippincott, *Spectrochim. Acta*, **15**, 627 (1959).
19. A. Bree, C. Y. Pang, and L. Rabeneck, *Spectrochim. Acta.*, **27A**, 1293 (1971).
20. A. Bree, M. Edelson, and R. A. Kydd, *Spectrochim. Acta.*, **31A**, 1569 (1975).
21. G. Zerbi and S. Sandroni, *Spectrochim. Acta.*, **24A**, 483; 551 (1968); **26A**, 1951 (1970).
22. R. M. Barrett and D. Steele, *J. Mol. Structure*, **11**, 105 (1972).
23. C. S. Paramenter and M. W. Schuyler, *J. Chem. Phys.*, **52**, 5366 (1970); D. S. McClure, *J. Chem. Phys.*, **24**, 1 (1956); G. J. Small, *J. Chem. Phys.*, **52**, 656 (1970).