CHEMISTRY LETTERS, pp. 489-492, 1974. Published by the Chemical Society of Japan

TEMPERATURE-DEPENDENT ENDOR SPECTRA OF α,α,γ,γ-BISDIPHENYLENE-β-PHENYL ALLYL RADICAL AND ITS DERIVATIVES

Kohji WATANABE, Jun YAMAUCHI, Hiroaki OHYA-NISHIGUCHI*,
Yasuo DEGUCHI**, and Kazuhiko ISHIZU***
Institute for Chemical Research, Kyoto University, Uji 611
* Faculty of Science, Kyoto University, Kyoto 606
** College of Liberal Arts & Science, Kyoto University, Kyoto 606
*** Faculty of Science, Ehime University, Matsuyama 790

ENDOR spectra of α,α,γ,γ-bisdiphenylene-β-phenyl allyl radical and its derivatives have been observed and the hyperfine splitting constants and spin density distribution have been determined.

At low temperature below -85 °C the allyl skeleton twists unsymmetrically on either sides and the wagging activation energy is estimated to be about 2.5 kcal/mole.

α,α,γ,γ-Bisdiphenylene-β-phenyl allyl radical(BDPA) and its derivatives are very stable organic free radicals. Many studies about these radicals in the solid state, e.g., magnetic susceptibility,[1] specific heat measurements,[2] have been published. There are, however, few reports about the ESR hyperfine splittings of these radicals. The ESR spectra observed so far consist of very broad lines, compared with the spectrum of α,α,γ,γ-bisdiphenylene allyl radical(BDA).[3] Therefore, it is not clear whether an unpaired electron spreads all over the molecular frame, since detailed hyperfine splitting constants have never been obtained.

We have observed the ENDOR spectra of these radicals for the first time and the hyperfine splitting constants and spin density distribution have been determined. Temperature-dependent ENDOR spectra of the radicals(BDPA and p-Me-BDPA) are shown in Fig. 1. Similar temperature dependences of ENDOR spectra as is shown in Fig. 1 are also obtained in all other radicals investigated. The results of

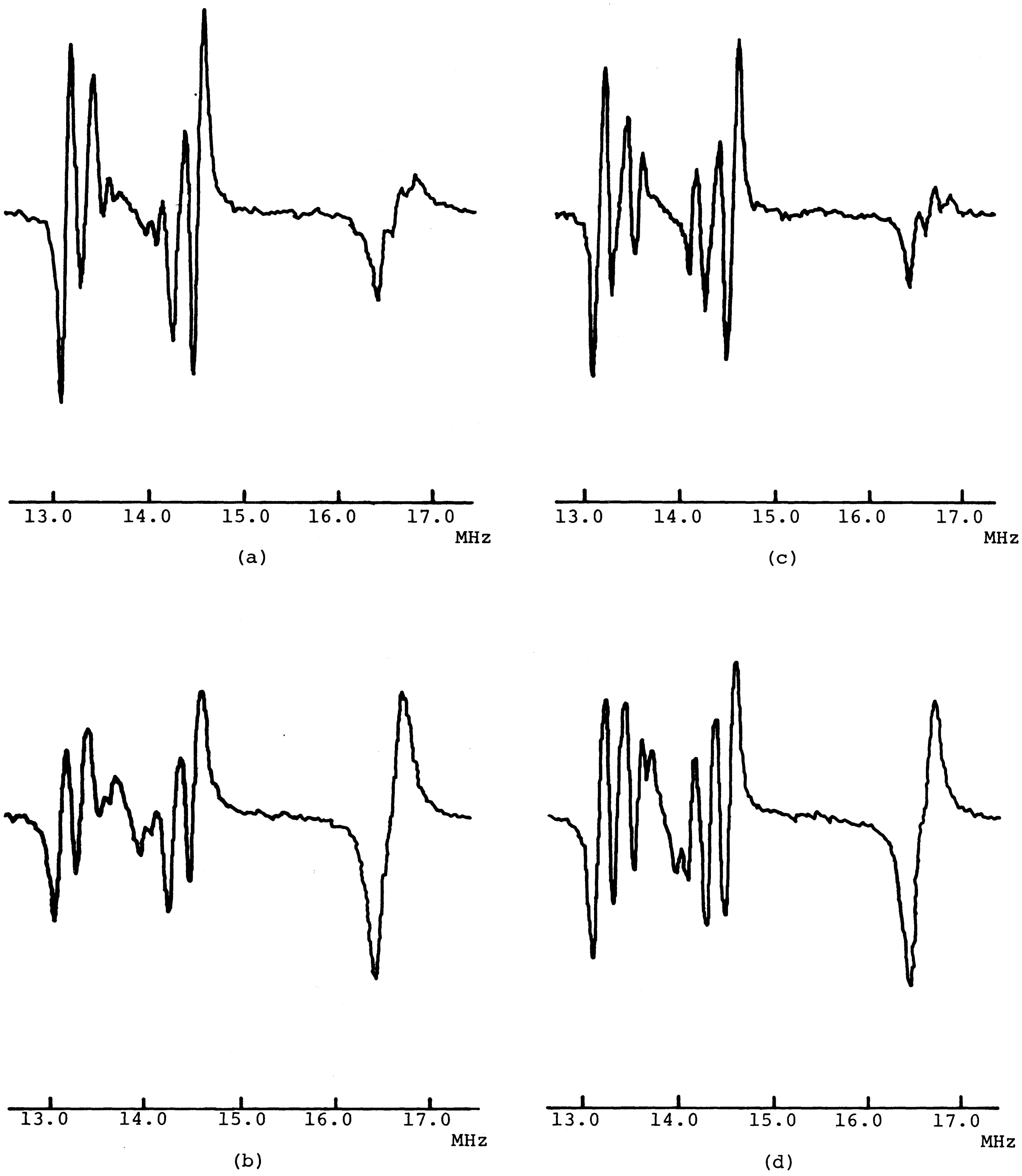


Fig. 1 Temperature-Dependent ENDOR Spectra in Toluene Solution.

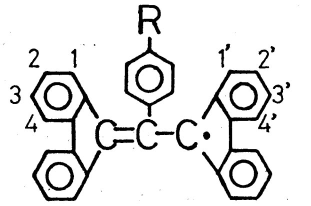
(a) BDPA at -85 °C (b) BDPA -65 °C

(c) p-Me-BDPA at -85 °C (d) p-Me-BDPA at -65 °C

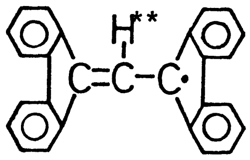
Table 1. Hyperfine Splitting Constants of BDPA Derivatives in Toluene solution from the ENDOR (in MHz)

R-	T.(°C)	A_1	$A_{1'}$	A_3	$A_{3'}$	$A_{2,2'}$	$A_{4,4'}$	A_{aryl}	
H-	-85	5.914	$$$	5.586	5.278	1.397	1.005	0.554	0.350
	-65	5.617		5.412		1.389	0.960	0.532	0.328
	+40*	5.670		5.384		1.408	1.016	0.493	0.267
CH_3-	-85	5.877	$$$	5.530	5.205	1.403	0.977	0.560	$$$
	-65	5.600		5.368		1.400	0.960	0.532	0.347
CH_3O-	-85	5.922	$$$	5.583	5.286	1.383	0.983	0.370	
	-65	5.813		5.552		1.355	0.969	0.386	
Cl-	-85	5.916	$$$	5.550	5.345	1.397	0.969	0.336	
	-65	5.810		5.485		1.375	0.924	0.328	
Br-	-85	5.911	$$$	5.541	5.337	1.417	0.944	0.370	
	-65	5.726		5.480		1.406	0.944	0.350	
B D A	+40*	5.620		5.474		1.456	1.086	$$$**	

$$$ not confirmed
* in liquid paraffin
** 37.52 MHz from the ESR



BDPA (R;H)



B D A

analyses of these spectra are tabulated in Table 1 with those of BDA. Comparing the number of the absorption lines of BDPA etc. with those of BDA, the smallest hyperfine splitting group of BDPA etc., which have never been observed in the ESR spectra, can clearly be identified to be the proton hyperfine splittings in the aryl group attached to the β-position of the allyl skeleton. This fact indicates that the unpaired electron spreads over the aryl group, although the magnitude of the electron density is very small.

The magnitudes of the proton hyperfine splitting constants and the assignments have been determined comparing with the results of McLachlan's Molecular Orbital calculations,4) where we take into account the fact that redistribution of an unpaired electron caused by twisting of the allyl skeleton changes much in the fluorenyl ortho- and para-positions and little in the meta-positions. The results of the MO calculation show the good agreement with the experimental results.

In the temperature dependences of these spectra below -65 °C, the twisting of the allyl skeleton considered in the MO calculations may be ascertained from the following facts that several lines near 16.5 MHz collapse into overlapped lines , while two lines near 14.5 MHz remain unchanged even in temperature region above -65 °C. The wagging activation energy of the allyl skeleton for the present radicals, using the equation used by Hyde et al.[5] is estimated to be about 2.5 kcal/mole for each  $(>C{=}\overset{|}{C}{-}\dot{C}<\ \underset{\Delta E}{\rightleftharpoons}\ >\dot{C}{-}\overset{|}{C}{=}C<)$. For the activation energies are very small, the wagging of the allyl skeleton is very sensitive for the temperature. This effect have been observed for another tetraaryl allyl-type radicals.[6]

As the conclusion of the present communication, it may be grasped from the temperature-dependent ENDOR spectra that an unpaired electron spreads even to the aryl group attached to the β-position of the allyl skeleton of BDPA and its derivatives, and that the allyl skeleton twists unsymmetrically on either sides.

The authors wish to thank Mr. Kazuhiro Uchino for the assistance of preparation of the samples. They are also indebted to Professors Toshio Takada and Hideo Takaki for their encouragement during this work.

REFERENCES

1) J.Yamauchi, Bull. Chem. Soc. Japan, 44 2301 (1971).

2) J.Yamauchi, K.Adachi, and Y.Deguchi, Chem. Lett., 1972 733 (1972).
J.Yamauchi, K.Adachi, and Y.Deguchi, J. Phys. Soc. Japan, 35 443 (1973).

3) R.Kuhn and F.A.Neugebauer, Monatsh., 95 3 (1964)
K.H.Hausser, Z. Naturforsch., 14a 425 (1959).
K.H.Hausser, ibid., 17a 158 (1962).

4) A.D.McLachlan, Mol. Phys., 3 233 (1960).

5) J.H.Hyde, R.Breslow, and C.DeBoer, J. Amer. Chem. Soc., 88 4763 (1966).

6) K.Watanabe, J.Yamauchi, H.O.-Nishiguchi, Y.Deguchi, and H.Takaki, Bull. Chem. Soc. Japan, 45 371 (1972).

(Received February 28, 1974)