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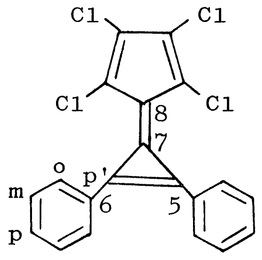
ESR SPECTRA OF RADICAL ANIONS OF CALICENE DERIVATIVES. —— LINE WIDTH ALTERNATION DUE TO ADJACENT n-PROPYL GROUPS

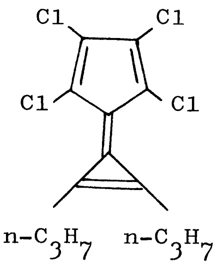
Shigeya NIIZUMA, Shiro KONISHI, Hiroshi KOKUBUN, and Masao KOIZUMI
Department of Chemistry, Faculty of Science
Tohoku University, Katahira, Sendai, Japan

ESR spectra of radical anions from 1,2,3,4-tetrachloro-5,6-diphenylcalicene (PhC) and 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene (PrC) were studied. An unpaired electron spin is localized on 5- and 6-carbon atoms and its substituents for both. PrC shows a typical line width alternation, which was explained by a hindered internal rotation (the three-membered and five-membered rings are not coplanar) of two n-propyl groups with a barrier of ~ 1.5 kcal/mole.

1,2,3,4-Tetrachloro-5,6-diphenylcalicene (PhC) and 1,2,3,4-tetrachloro-5,6-di-n-propylcalicene (PrC), which were synthesised for the first time respectively in 1965 and 1966 by Ueno et al.,$^{1)}$ were found to yield the radical anions by bringing them into contact with alkali metal (sodium and potassium) in tetrahydrofuran (THF).



PhC



PrC

Monoanion produced from PhC is bluish green and stable at room temperature. By a prolonged contact with alkali metal, the THF solution turned reddish brown and ESR signal disappeared. This diamagnetic species is considered to be a dianion. ESR spectrum of monoanion is given in Fig. 1(a). This spectrum can be simulated by using two coupling constants corresponding to two groups each consisting of four magnetically equivalent protons (2.80 and 0.95 gauss) and one coupling constant corresponding to two equivalent protons (3.20 gauss) as shown in Fig. 1(b). ESR signal of the monoanion from PrC can be observed only at temperatures lower than -30°C and the color of the solution is yellow. Although this monoanion is unstable at room temperature, it is quite stable below -30°C and the dianion is not produced even by a prolonged contact with alkali metal.

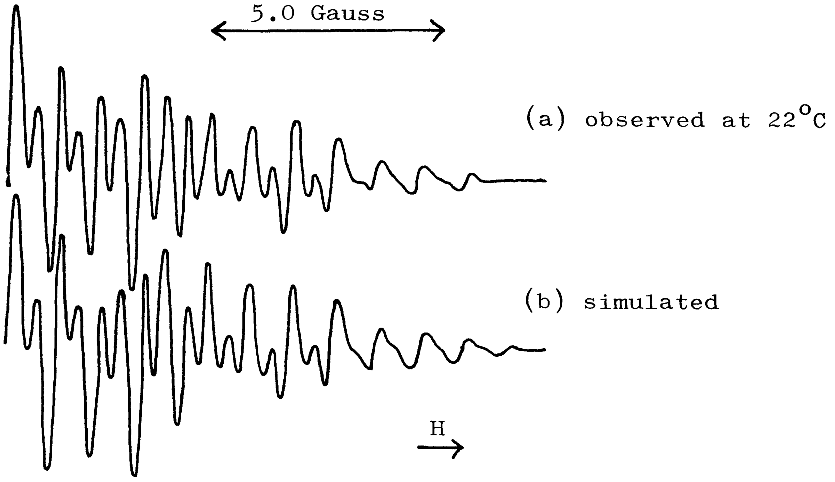


Fig. 1. ESR spectra of radical anion of PhC reduced with potassium.

ESR spectra of the radical anion of PrC at various temperatures are shown in Fig. 2(a). The spectra exhibit remarkable line width alternation and their hyperfine structure is interpretted on the basis of the spectral shape under over-modulation,[2)] as a result of coupling with four magnetically equivalent protons. The four protons must

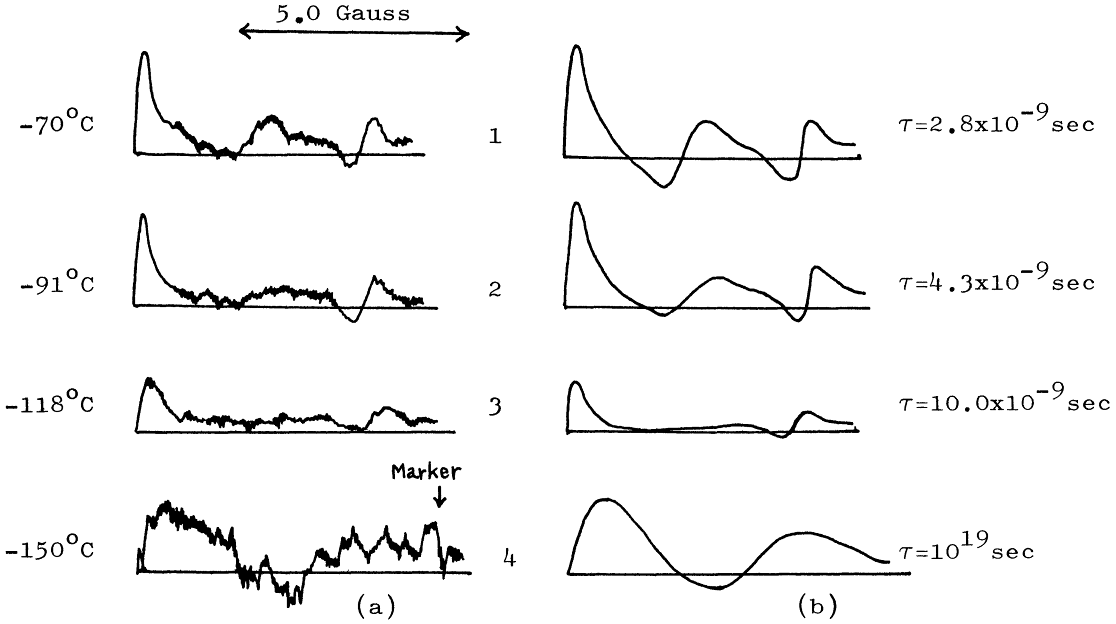
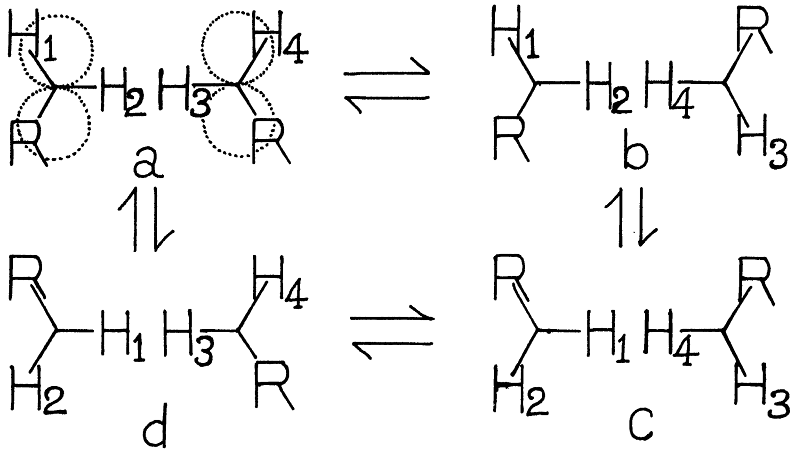


Fig. 2(a). ESR spectra of radical anion of PrC reduced with potassium at different temperatures.
(b). Simulated spectra, corresponding to (a).

be β-protons of n-propyl groups attached to carbon atoms at 5- and 6-positions, because no other nuclei with a spin quantum number of 1/2 have the possibility to couple strongly with electron spin. Line width alternation can be ascribed to the hindered internal rotation of two n-propyl groups. At -150°C, the solvent THF freezes and ESR spectra turn to broad three lines with the intensity ratio of about 1:2:1 as shown in Fig. 2(a-4). As the temperature increases, the spectra return back to the ones in Fig. 2(a-1~3). The whole change including the line width alternation is completely reversible. Appearence of broad three lines is explained to be due to the fact that rotation being suppressed, two n-propyl groups are fixed in such a way that two of the four β-protons do not couple or couple negligebly with electron spin.

A question is what kind of hindered rotation is occurring in the radical anion of PrC. The first problem is to decide stable conformations for two n-propyl groups each possessing two β-protons. They are the following ones. Two H-atoms and an ethyl group are projected on the plane perpendicular to the C_{β}-C_5 bond and $C_{\beta'}$-C_6 bond. a and c are cis-type and b and d are trans-type conformations.



The reason why one of two β-hydrogen atoms is placed in the plane containing three-membered ring is that the coupling of only two β-protons were observed in the spectrum at -150°C (Fig. 2(a-4)). All other conformations conceivable can be elliminated for the reason of a strong steric hindrance between two R(ethyl)-groups.

The occurrence of isomerization written above requires, however, that the plane of three-membered ring and that of five-membered ring must be twisted to each other, because the steric interaction between chlorine atom of the latter and R of propyl group is significant. It is quite reasonable to assume such a situation because the free rotation around the C_7-C_8 bond in 1-formyl-5,6-di-n-propylcalicene has already been reported to occur at higher temperature from the analysis of NMR data.[3] This is also supported by spin density calculation (see below).

A model system for the line width alternation similar to the above isomerization has been treated theoretically by Carrington.[4] Therefore, ESR spectra given in Fig. 2(a) were simulated according to his method which enables us to evaluate correlation times of rotation τ. For simulation, cis- and trans-types were assumed to have the same correlation time τ. It was further assumed that $a_\beta^{H_1} = a_\beta^{H_4}$ and $a_\beta^{H_2} = a_\beta^{H_3}$ for cis-(a)-type and that $a_\beta^{H_1} = a_\beta^{H_3}$ and $a_\beta^{H_2} = a_\beta^{H_4}$ for trans-(b)-type, where $a_\beta^{H_i}$ refers to the hyperfine coupling constant of the ith β-proton. The condition for the occurrence of line width alternation i.e., the following relationship and other similar ones

$$(a_\beta^{H_1} + a_\beta^{H_2}) \text{ for } \underline{a} \text{ conformation} = (a_\beta^{H_1} + a_\beta^{H_2}) \text{ for } \underline{b} \text{ conformation}$$

are expected to hold in the present case. The simulated spectra are given in Fig. 2(b). For simulation, 24.0 and 4.0 gauss were found to be the best values of $a_\beta^{H_1}$ and $a_\beta^{H_2}$ respectively and a certain small amount of absorption was added to the center line. This may suggest the existence of some other radical species in this system. The same values of $a_\beta^{H_1}$ and $a_\beta^{H_2}$ and the addition of the same amount to the central line also explain the spectrum observed at -150°C (Fig. 2(b-4)) if an appropriate line width and a τ value large enough are assumed. Suitable τ values to simulate ESR spectra change from 1×10^{-8}sec at -120°C to 3×10^{-9}sec at -50°C. As shown in Fig. 3, the plot of log $(1/\tau)$ against the reciprocal of absolute temperature gives a good straight line.5) From the slope we obtain an activation energy of 1.6_5 kcal/mole for potassium reduction and 1.4_1 kcal/mole for sodium reduction. These values correspond to the potential barrier for cis-trans isomerization.

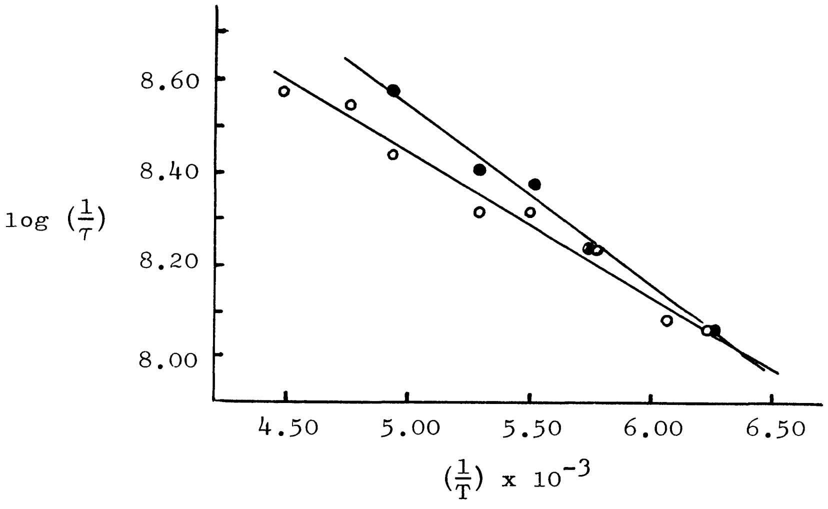


Fig. 3. Plot of log $(1/\tau)$ against 1/T.

● Potassium reduction

○ Sodium reduction

To understand the hyperfine structure, the unpaired spin density was calculated by a simple LCAO-MO method and by McLachlan's method based on LCAO-MO. The results for radical anion of PhC are listed in Table 1. As a Q_C-value in McConnell's equation, 29.0 gauss was found to be the best value. As for radical anion of PrC, the spin densities only on 5- and 6-carbons are concerned with the hyperfine structure. To estimate them the following equation was employed which have been used in success for the calculation of the coupling constant of β-protons,

$$a_{\beta}^{H} = \rho_{C}^{\pi} \cdot B \cos^{2} \theta \qquad (B = 45 \pm 6 \text{ gauss}^{6)})$$

where ρ_{C}^{π} is the spin density in the P_z orbital of the contiguous π-carbon atom and θ is the angle between P_z orbital and the C-H bond both projected on a plane perpendicular to the C-C axis. Using this equation and assuming $\langle \cos^{2}\theta \rangle_{av} \doteqdot 1/2$ for a short τ value, we obtain $a_{\beta}^{H_1} + a_{\beta}^{H_2} = 28.0$ gauss and $\rho_{C_5}^{\pi} = \rho_{C_6}^{\pi} = \rho_{C}^{\pi} = 0.62 + 0.10$. The too large value of ρ_{C}^{π} is due naturally to the underestimation of $\langle \cos^{2}\theta \rangle_{av}$. At any rate, there is no doubt that almost all the spin is localized on carbon atoms of 5- and 6-positions.

Table 1. Unpaired spin densities for radical anion of PhC.

position	obs.		calc.	
	Na red.	K red.	LCAO-MO	McLachlan
1	——	——	0	-0.005
1-Cl	——	——	0	-0.001
2	——	——	0	-0.004
2-Cl	——	——	0	-0.001
7	——	——	0	-0.032
8	——	——	0	-0.003
5	——	——	0.192	0.265
p'	——	——	0.047	0.015
o	0.100	0.097	0.075	0.094
m	0.035	0.033	0.006	0.027
p	0.115	0.110	0.098	0.115

$\alpha_{Cl} = \alpha_{C} + 1.8\beta$

$\beta_{Cl} = 0.8\beta$

$\alpha_{C'} = \alpha_{C} + 0.18\beta$

$\lambda = 1$ (McLachlan's parameter)

In calculating the spin densities of radical anion of PrC, it has been found that they depend in a specific way on the angle between the plane containing three-membered ring and that containing five-membered ring $\gamma (90^{\circ} > \gamma \geq 0^{\circ})$. In addition, they depend on the parameters of hyperconjugation. Using the parameters written below,[7] the simple LCAO-MO

$$C_{5(\text{or } 6)} \overset{0.9\beta}{\text{———}} \underset{\alpha - 0.1\beta}{C_{\beta}} \overset{2.5\beta}{\equiv\equiv} \underset{\alpha - 0.5\beta}{H_{2}R}$$

calculation gave for $\gamma \geq 45^{\circ}$ $\rho_{C}^{\pi} \approx 0.43$ and McLachlan's calculation gave for $\gamma \geq 45^{\circ}$

$\rho^{\pi}_{C} \approx 0.51$. However for $\gamma = 0^{o}$, the value of $\rho^{\pi}_{C} = 0.10$ (LCAO) and 0.12 (McLachlan), which is inconsistent with the experimental value. It is to be added that the calculated spin densities for radical anion of PhC are found to be independent of γ.

To sum up, the phenomena of line width alternation found in the spectra of radical anion of PrC originate from the existence of rather large n-propyl groups in two adjacent carbons which restricts their free rotations. The values of activation energy of ~1.5 kcal/mole are plausible as the potential barrier for rotation of n-propyl groups.6) It is highly plausible that the plane of three-membered ring and that of five-membered ring are twisted to each other to some extent. Otherwise a large spin density at 5- and 6-carbon could not be accounted for.

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