Paramagnetic Resonance of Radicals of Some Aromatic Vinyl Compounds. II

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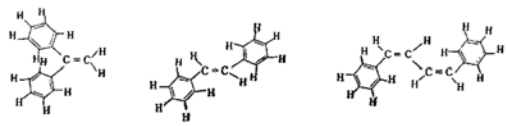
In the preceding paper[1] the results of the paramagnetic resonance of radicals of styrene, α-methylstyrene and *p*-methylstyrene were described. Here the results of the paramagnetic resonance of radicals of 1, 1-diphenylethylene, stilbene and 1, 4-diphenylbutadiene will be described and will be discussed in connection with the problem of the process of the polymerization of these compounds.

Experimental

The measurements of paramagnetic resonance of the above radicals were performed at room temperature by using the same apparatus as that being described in the preceding paper and the samples were also prepared by the same method as that described in the preceding paper.



1-1 Diphenylethylene — Stilbene — 1-4 Diphenylbutadiene

Fig. 1.

Results and Discussion

1,1-Diphenylethylene (DPE). — Two spectra have been observed in the 1, 1-diphenylethylene (DPE) radical in the tetrahydrofuran solution with its concentration of $10^{-3}\sim10^{-4}$ M under different conditions of the sample. In the DPE radical produced by method I described in section 2 of the preceding paper, many lines were observed as shown in Fig. 2.

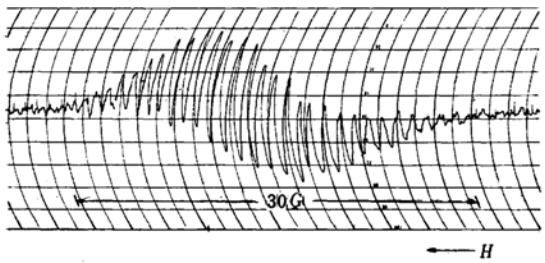


Fig. 2. Paramagnetic resonance spectrum of 1-1 diphenylethylene radical.

We tried to explain the observed spectrum through the following spin Hamiltonian,

$$\mathcal{H}=g\beta\boldsymbol{H}\boldsymbol{S}+\sum_{i=1}^{4}A_o\boldsymbol{I}_{oi}\boldsymbol{S}+\sum_{i=1}^{4}A_m\boldsymbol{I}_{mi}\boldsymbol{S}+\sum_{i=1}^{2}A_p\boldsymbol{I}_{pi}\boldsymbol{S}+\sum_{i=1}^{2}A_\beta\boldsymbol{I}_{\beta i}\boldsymbol{S} \qquad (1)$$

where the first term describes the Zeeman energy and $\boldsymbol{I}_o$, $\boldsymbol{I}_m$, $\boldsymbol{I}_p$ and $\boldsymbol{I}_\beta$ describe the spin of the proton in the *ortho*-, *meta*-, *para*- and β position respectively, and the suffix i given under the spins of the proton $\boldsymbol{I}$ shows a different position in the same site with respect to the symmetry of the molecule. Although the observed spectrum is so complicated that we can not analyze it definitely, the following values of the parameters, g, A_o, A_m, A_p and A_β, in the above spin Hamiltonian seem to fit best with the observed spectrum: $g=2.002$ $A_p=A_p\sim6$ gauss, $A_m\sim1$ gauss, $A_\beta\sim3$ gauss. However, some ambiguities are left in these values except in the case of g. The calculated spectrum is shown in Fig. 3, where several lines at both sides apart from the center are assumed not to be observed owing to their weak intensities. The above analysis indicates that the magnetic center corresponding to the observed spectrum is the unpaired electron in the DPE monomer anion.

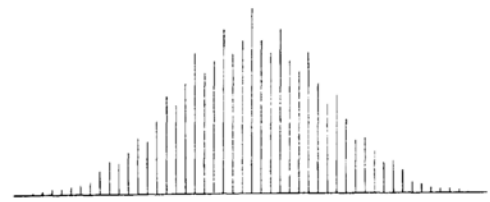


Fig. 3. The calculated spectrum of 1-1 diphenylethylene anion.

According to McConnell[2] the hyperfine splitting constant is proportional to the unpaired electron density on the carbon atom adjacent to the proton in the aromatic hydrocarbon. From the above hyperfine splitting

1) K. Morigaki, K. Kuwata and K. Hirota, This Bulletin, 33, 952 (1960).

2) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); H. M. McConnell and D. B. Chesnut, ibid., **28**, 107 (1958).

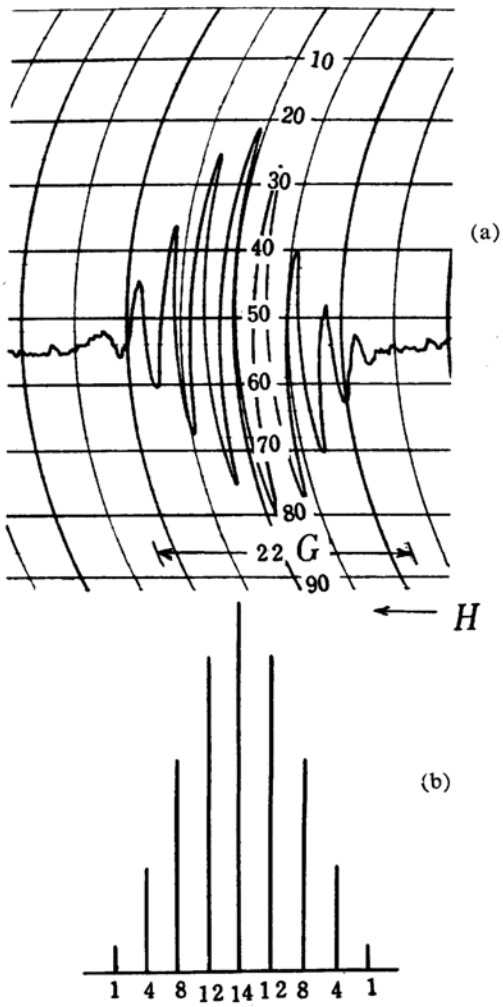


Fig. 4. (a) Paramagnetic resonance spectrum of 1-1 diphenylethylene radical.
(b) The calculated spectrum of 1-1 diphenylethylene radical.

constant in Eq. (1) the unpaired electron densities of the DPE monomer anion at each carbon atom in the aromatic ring can be derived, i. e., they are given in ratio as follows:

$$\rho_o : \rho_p : \rho_m = 6 : 6 : 1$$

where ρ_o, ρ_p and ρ_m give the unpaired electron densities on the carbon atom adjacent to the *ortho*-, *para*- and *meta*-hydrogen atom respectively.

On the other hand, the simple LCAO-MO calculation gives the normalized unpaired electron densities the following values,

$$\rho_o = 0.05521, \quad \rho_p = 0.07813, \quad \rho_m = 0.00622$$

or

$$\rho_o : \rho_p : \rho_m = 8.9 : 12 : 1$$

The observed spin densities on the *ortho*- and *para*-carbon atoms are smaller than those expected from the simple LCAO-MO calculation. The normalized unpaired electron density on the β-carbon atom given by the simple LCAO-MO calculation is given by $\rho_\beta = 0.3856$. In spite of the large value of the electron density on the β carbon atom, the observed hyperfine splitting is half as much as that corresponding to the unpaired electron densities on the *para*- and *ortho*- carbon atoms. This means that there is a marked difference between the cases of the β-proton and the ring proton in the proportionality constants connecting the unpaired electron density to the hyperfine splitting. However, the origin of the small proportionality constant for the hyperfine splitting at the β-proton has not been found.

Another spectrum, as shown in Fig. 4 (a), was observed in the sample of DPE which has been kept at 110°C for two days after the observation of the first spectrum shown in Fig. 2. The change of the spectrum coming from the heat-treatment of the sample is drastic and is accompanied with that of its color from dark yellow to green. This indicates that the DPE radical was changed into another kind of radical through the heat-treatment. From the following analysis of the observed spectrum the magnetic center corresponding to the second spectrum seems to be identified with the unpaired electron being localized around the end of the anion of the DPE polymer as shown in Fig. 5.

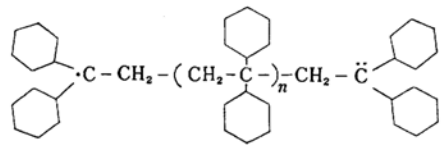


Fig. 5. Structural formula for 1-1 diphenyl polymer anion.

The observed spectrum can be explained by the following spin Hamiltonian,

$$\mathcal{H} = g\beta \boldsymbol{H}\boldsymbol{S} + \sum_{i=1}^{4} A_o \boldsymbol{I}_{oi}\boldsymbol{S} + \sum_{i=1}^{4} A_m \boldsymbol{I}_{mi}\boldsymbol{S} + \sum_{i=1}^{2} A_p \boldsymbol{I}_{pi}\boldsymbol{S} \qquad (2)$$

with $g = 2.0026 \pm 0.0005$, $A_p = 5.4 \pm 0.5$ gauss, $A_o = 2.7 \pm 0.3$ gauss and $A_m \sim 0$ gauss. Although two kinds of hyperfine interaction with four equivalent protons are indistinguishable from each other in the resonance experiment, it is assumed in the above assignment from the theoretical point of view that the hyperfine interaction with the *ortho*-protons will be stronger than that with the *meta*-protons. A pattern of the spectrum is constructed from the above spin Hamiltonian with the parameters given above

as shown in Fig. 4 (b). This spectrum consists of nine lines with relative intensities of 1 : 4 : 8 : 12 : 14 : 12 : 8 : 4 : 1. The relative intensities of each component in the calculated spectrum are in good agreement with the observed ones of 1 : 4 : 8 : 12.5 : 14 : 12.5 : 7.5 : 3.8 : 1. If the line widths of each component are attributed to the unresolved hyperfine interaction due to the four *meta*-protons, the coupling constant A_m is given by the value of about 0.7 gauss.

The above model of the magnetic center is similar to the diphenylmethyl radical concerned with the part on which the unpaired electron is localized. The calculation of the spin densities of the π-electrons on the carbon atoms in the diphenylmethyl radical performed by using the Pauling-Wheland valence-bond theory shows that the spin densities of the π-electrons on the *para*-, *ortho*- and *meta*-carbon atoms are given as follows (See Appendix):

$$\rho_p = 0.2790, \quad \rho_o = 0.2732, \quad \rho_m = -0.1483.$$

The spectrum constructed on the basis of the above spin densities, as shown in the appendix, is slightly different from the observed spectrum. The relative spin densities obtained from the above analysis of the observed spectrum are not in agreement with the calculated ones. The actual situation of distribution of the π-electrons in the DPE polymer radical will not be so simple as the case of diphenylmethyl. Indeed the DPE polymer forms a bending chain, so the two benzene rings in which the unpaired electron is to be localized may not be on the co-plane. However, it has not been clear at the present stage whether the above difference between the observed spectrum and the calculated one shows that the magnetic center corresponding to the observed paramagnetic resonance may not be the unpaired electron in the DPE polymer radical.

Stilbene. — A resonance line without any structures was observed in the stilbene radical in tetrahydrofuran solution with its concentration of $10^{-3} \sim 10^{-4}$ M (Fig. 6). It has the maximum separation of thirteen gauss in the derivatives of the absorption line and the *g*-factor of 2.002. This result indicates that the hyperfine structure can not be resolved because many protons contribute to the hyperfine splitting. This situation is consistent with the simple LCAO-MO calculation of the unpaired electron density in the stilbene anion. The stilbene radical in tetrahydrofuran with its concentration of 10^{-1} M showed a Lorentzian-shaped line with the line width of 1.8 gauss.

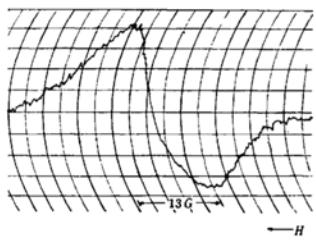


Fig. 6. Paramagnetic resonance spectrum of stylbene radical.

1,4-Diphenylbutadiene.—In a sample including the radical of 1,4-diphenylbutadiene prepared by method I, a resonance spectrum with unresolved h. f. s., which extends in the region of the magnetic field of about thirty-four gauss with $g = 2.00$, has been observed as shown in Fig. 7. But it has not been investigated in detail.

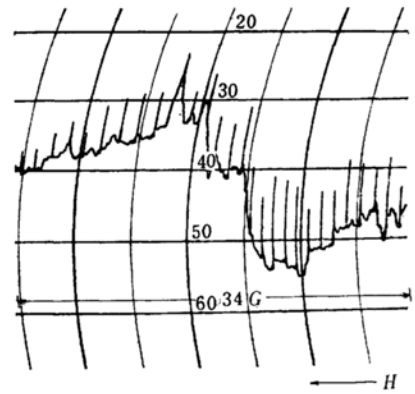


Fig. 7. Paramagnetic resonance spectrum of 1,4-diphenylbutadiene radical.

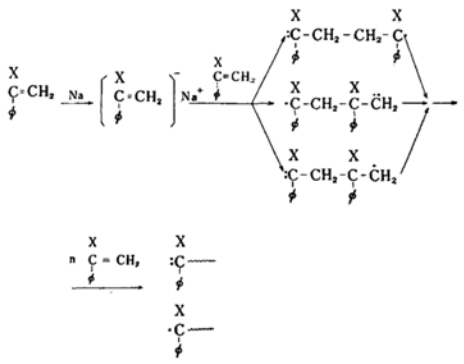
Discussions on the Process of Polymerization

As described in the preceding paper, the pattern of the paramagnetic resonance spectra of radicals of styrene and *p*-methylstyrene depends sensitively on the degree of polymerization. In the latter substance changes of pattern and intensity of the paramagnetic resonance with time have been clearly observed. In the former samples three kinds of spectra have been observed, according to the conditions of preparation of the radicals. In the preceding paper the situations under which the polymerization of styrene and its derivatives proceeds were discussed by considering the above results.

In the case of DPE radicals, when a renewed reaction of DPE adducts, which had shown many resonance lines, with the sodium metal was performed by keeping the sample at 100°C for two days, another new spectrum was observed, which was considered to be coming from the hyperfine interaction of the unpaired electron being localized around the end molecule of DPE polymer, probably with a

low degree of polymerization, with its protons.

From these results it may be considered that polymerization is initiated through the process in which the monomer of the aromatic vinyl compound forms a bond between itself and the α- or β-carbon atoms of the radical anion to grow into the polymer. This situation can be described in the following formula.



where X means H, CH_3 or $\phi(=C_6H_5)$.

The process of polymerization of the aromatic vinyl compounds has been studied through the optical absorption spectroscopy[3]. In order to confirm the above model of the process of polymerization, further experiments will be necessary.

Summary

Paramagnetic resonance absorption of the radicals of 1, 1-diphenylethylene, stilbene and 1, 4-diphenylbutadiene in tetrahydrofuran solution was investigated at room temperature. In diphenylethylene (DPE) radicals two kinds of spectra were observed corresponding to two states of the radicals; one is the DPE monomer anion and the other the DPE polymer anion. In connection with the experimental results in the case of styrene, α-methylstyrene and *p*-methylstyrene described in the preceding paper, the process of polymerization of some aromatic vinyl compounds was discussed.

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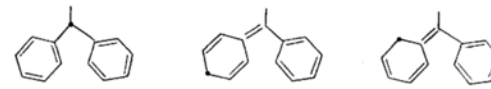
3) K. Hirota, K. Kuwata, H. Togawa and S. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 602 (1958); K. Kuwata, to be published in This Bulletin.

Appendix

Spin Densities in the Diphenylmethyl Radical

Spin densities of π-electrons on carbon atoms in the diphenylmethyl radical are calculated by using valence-bond theory. Valence-bond theory has been so far applied also to calculations of spin densities on carbon atoms in the triphenylmethyl radical by Brovetto and Ferroni[4] and in the perinaphthenyl radical by McConnell and Dearman[5] in good agreements with the experimental results. Therefore, valencebond theory is adequate to calculate the spin densities of π-electrons in these odd-alternant hydrocarbon radicals.

Valence-bond structures for calculation of the spin densities of π-electrons on carbon atoms in the diphenylmethyl radical can be divided into three groups shown in Fig. 8. To these three groups belong the 4, 4, 8 independent wave functions for the unpaired electron on the methylic carbon atom, and the *para*- and the *ortho*-carbon atoms of the benzene ring respectively. All functions related to Dewar structures will be neglected.



φ_1 φ_2 φ_3

Fig. 8.

With a linear combination for the φ_{ik} the wave function Ψ in the ground state can be constructed in such a way as to minimize the total energy of electrons. Then, Ψ is given by the following equation,

$$\Psi = \sum_i C_i \sum_k \varphi_{ik} \tag{A1}$$

The total Hamiltonian fo the π-electrons under the existence of the external magnetic field is:

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 \\ \mathcal{H}_1 &= g\beta \boldsymbol{HS} \\ \mathcal{H}_2 &= -(8\pi/3) g\beta g_N \beta_N \sum_k \boldsymbol{I}_k \boldsymbol{S} \delta(\boldsymbol{r}_e - \boldsymbol{r}_k) \end{aligned} \tag{A2}$$

where $\mathcal{H}_0$ means the kinetic energy and the Coulomb potential energy of the electrons; $\mathcal{H}_1$ is Zeeman energy in which the external magnetic field and the electronic spin are described by $\boldsymbol{H}$ and $\boldsymbol{S}$ respectively, $\mathcal{H}_2$ is the hyperfine interaction energy coming from the Fermi type contact hyperfine interaction between the electron and the *k*th-proton with

4) P. Brovetto and S. Ferroni, *Nuovo Cimento*, **5**, 142 (1957).

5) H. M. McConnell and H. H. Dearman, *J. Chem. Phys.*, **28**, 51 (1958).

the nuclear spin I_k, β and β_N are the electronic and nuclear Bohr magnetrons respectively, and g and g_N are the electronic and nuclear g-factors and $\delta(\boldsymbol{r}_e-\boldsymbol{r}_k)$ means the Dirac delta function for the distance between the electron and the kth-proton. In the above Hamiltonian the dipolar interaction between the electron and the proton is neglected, because it is averaged out not to contribute to the paramagnetic resonance spectrum by a tumbling motion of the molecule in the solution.

After some computations the minimum energy W of the Hamiltonian $\mathcal{H}_0$ is given in the following equation,

$$W=Q+4.7046\alpha \qquad \text{(A3)}$$

where Q means the Coulomb integral and α the single exchange integral.

Corresponding to the state with the minimum energy, the wave function in the ground state is given as follows:

$$\Psi=0.1572\varphi_1+0.1341\varphi_2+0.1312\varphi_3 \qquad \text{(A4)}$$

The matrix element of the hyperfine interaction $\mathcal{H}_2$ is calculated by using the Brovetto-Ferroni method as applied to triphenylmethyl. By using Eq. (A1) the matrix element $\langle\Psi|\mathcal{H}_2|\Psi\rangle$ is given in the following equation,

$$\langle\Psi|\mathcal{H}_2|\Psi\rangle=\sum_{ij}c_ic_j\sum_{kl}\langle\varphi_{ik}|\mathcal{H}_2|\varphi_{il}\rangle \qquad \text{(A5)}$$

The matrix elements $\langle\varphi_{ik}|\mathcal{H}_2|\varphi_{il}\rangle$ can be calculated in a similar way to the case of triphenylmethyl.

$$\langle\Psi|\mathcal{H}_2|\Psi\rangle=-(8\pi/3)g\beta g_N\beta_N A \times[0.2790I_{zp}-0.1483I_{zm}+0.2732I_{zo}]\cdot S_z \qquad \text{(A6)}$$

where I_{zp}, I_{zm} and I_{zo} mean the component along the external magnetic field of the total spin of the protons in the *para*, *ortho* and *meta* position of the benzene ring respectively, and A is the factor which depends on the strength of the $\sigma-\pi$ interaction.

The magnetic field H corresponding to the transition $\Delta S_z=\pm1$, $\Delta I_z=0$ in the experiment using the microwave with the frequency ν is given by the following equation

$$H=h\nu/g\beta+(8\pi/3)g_N\beta_N A \times[0.2790I_{zp}-0.1483I_{zm}+0.2732I_{zo}] \qquad \text{(A7)}$$

Then, the paramagnetic resonance spectrum can be constructed by Eq. (A7) as shown in Fig. 9, where only the upper part of the spectrum corresponding to the value of H larger than $h\nu/g\beta$ is given, because the spectrum is symmetrical with respect to the value of the magnetic field $H=h\nu/g\beta$.

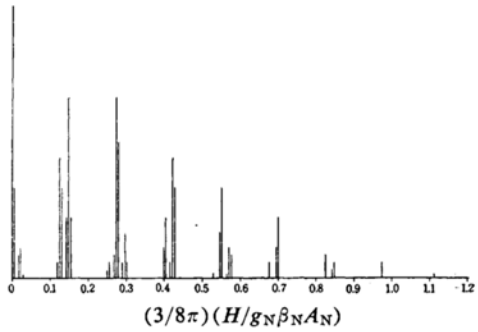


Fig. 9. The calculated spectrum of diphenylmethyl radical.

A comparison of the above calculated spectrum with the observed one in the DPE radical shows some differences as shown in Fig. 9. Though the observed spectrum consists of nine lines, more lines should be expected from the results of the calculation. Especially, the fifth line from the central one, which has about half the intensity in comparison with the fourth line in the calculated spectrum, should be observed from the experimental condition of our spectrometer. The origin of the above differences between the theoretical spectrum and experimental one is discussed in the text.