ESR Studies of the Negative Ions of Biphenyl Derivatives. IV. Conformation of 4,4′-Polymethylenebiphenyl Anion Radicals

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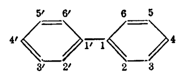
The electron spin resonance has been observed for anion radicals of 4,4′-polymethylene bridged biphenyls which have various lengths of the polymethylene chain, from the carbon number of $n=11$ to that of $n=16$. The relation between the chain length of the methylene bridge and the ring-proton splitting were studied in order to see how the polymethylene span brings on a strain in the biphenyl ring. The geometrical structures of the sp^3-hybrid bond of the β-carbons were investigated on the basis of the observed values of the β-proton splitting in each derivative. In the cases of both pentadeca and hexadeca derivatives, the magnitude of both the *ortho*- and the *meta*-ring proton splitting are comparable with those of the 4,4′-diethylbiphenyl anion radical, the open-chain model of the present derivatives. A rotation of the β-methylene sp^3-bond is forbidden in this case, however, and the coupling constants of the β-methylene protons no longer exhibit an equivalent value; that is, two of these C–H bonds are placed on a coplanar biphenyl plane, but the others are twisted out by about 30° from the $2p_z$ axis of the ring-carbon atom. When the number of the methylene groups is reduced from thirteen to twelve, the magnitude of the *ortho*-ring proton coupling constant is greatly reduced. The HMO calculations of the spin density were carried out. The observed tendency of the ring-proton splitting can be qualitatively understood on the assumption that the coplanar biphenyl ring may be modified by twisting the phenyl groups about the central 1-1′ bond rather than by slanting them together against the original aromatic plane. A strong beam of the polymethylene chain also causes a modification of the geometrical structure of the β-methylene sp^3 bond and results in a reduction of the β-proton coupling constant to a large extent.

Polymethylenebiphenyls in which a suitable length of the polymethylene chain is bridged at the 2,4′-, 3,4′-, or 4,4′-positions have recently been synthesized, and their conformation have been studied by UV and NMR absorption spectroscopy.[1–3)]

In the cases of the 4,4′-polymethylene derivatives, a molecular model suggests that at least thirteen methylene carbon atoms are necessary to set the bridge across the 4,4′-positions of the biphenyl ring without resulting in a strain in the molecule.

If the number of the methylene carbon atom is less than thirteen, the biphenyl ring is hard to held in the coplanar fashion. In this study, ESR observation has been carried out for the anion radicals of 4,4′-polymethylenebiphenyl, which have various numbers of polymethylene groups, from 11 to 16. The hyperfine coupling constants of either β-methylene or the ring proton are determined in order to elucidate the steric structure of these derivatives. The degree of the strain effected in the biphenyl ring could be estimated by a comparison of the values of the ring-proton splitting with those of 4,4′-diethyl biphenyl, an open-chain model of the present derivatives. The geometrical structure of the β-methylene carbons may be investigated on the basis of the measurement of the β-proton hyperfine coupling constant and its temperature dependence. The general structure of 4,4′-polymethylene biphenyl is given below;



Experimental

The materials used in this studies were synthesized by a process previously established before. The physico-chemical indexes of the materials are listed in Table 1.

TABLE 1. PHYSICO-CHEMICAL INDEXES OF THE MATERIALS

Number of polymethylene carbon n	11	12	13	14	15	16
Mp(°C)	86— 88	116— 117	101— 102.5	112.5— 114.5	128— 129	110— 111

4,4′-Diethylbiphenyl (mp 82.5°C) was synthesized by an Ullman reaction on *p*-iodo-ethylbenzene. The anion radicals were prepared in dimethoxyethane (DME) by reduction with a potassium mirror kept in an acetone–dry ice bath.

The green-colored paramagnetic solution gave a strong ESR absorption, and the anion radicals were stable enough for the observation of the ESR spectra at room temperature. The ESR spectra were recorded by a JEOL ME-3X spectrometer operating with a 100 kHz magnetic field modulation. The magnetic field was calibrated by a perylene cation radical prepared in concentrated sulfuric acid.[4)]

Results and Discussion

The Analysis of the ESR Spectra. The ESR spectrum of the 4,4′-hexadecabiphenyl anion radical recorded at −20°C is given in Fig. 1(a). One may easily determine the *ortho*- and the *meta*-proton hyperfine coupling constants ($a^H{}_2$ and $a^H{}_3$) by referring to those of the 4,4′-diethyl biphenyl anion radical, which have

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1) M. Nakazaki and S. Isoe, *Chem. Ind.* (London), **1965**, 224.

2) M. Nakazaki and K. Yamamoro, *ibid.*, **1965**, 486.

3) K. Yamamoto, T. Horikawa, and M. Nakazaki *Tetrahedron Lett.* **1969**, 4597.

4) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

already been reported.[5]

As for the β-proton splitting (a_4^{H}), however, neither the line intensity nor the total width of the spectrum were adequately explainable unless the non-equivalent values of the β-proton splitting were assumed; that is, a triplet splitting ($a_4^{\mathrm{H_A}}$) arises out of the two methylene protons, but that of the others ($a_4^{\mathrm{H_B}}$) vanishes to the order of the line width (200 m gauss).

The hyperfine coupling constants thus estimated are: $a_4^{\mathrm{H_A}}=7.00$, $a_4^{\mathrm{H_B}}<0.20$, $a_2^{\mathrm{H}}=2.62$, and $a_3^{\mathrm{H}}=0.46$ gauss. These values were confirmed by the computer calculation of the line intensity, as is shown in Fig. 1(b).[6] As the temperature is gradually elevated, the hyperfine structures began to change; the spectrum shown in Fig. 1(c) was recorded at room temperature. In this case, another triplet splitting, $a_4^{\mathrm{H_B}}$ was recognized in addition to $a_4^{\mathrm{H_A}}$, and the hyperfine structure could be understood well using the following hyperfine coupling components; $a_4^{\mathrm{H_A}}=6.51$, $a_4^{\mathrm{H_B}}=0.47$, $a_2^{\mathrm{H}}=2.60$, and $a_3^{\mathrm{H}}=0.47$ gauss. The computer-calculated spectrum shown in Fig. 1(d) also gives a good agreement with the observed spectrum. A similar temperature dependence of the β-proton splitting was observed for the 4,4′-pentadecamethylene derivative ($n=15$). When the number of the methylene group was reduced to $n=14$, the a_2^{H} value began to decrease, but the a_3^{H} value showed a slight increase. The triplet splitting of $a_4^{\mathrm{H_B}}$ was hidden in the line-width, and it was not possible to observe the temperature dependence in this case for the temperature range of $-50\sim+50$°C. In the case of $n=13$, a further decrease in the $a_4^{\mathrm{H_A}}$ value was noted, while either the a_2^{H} or the a_3^{H} values were almost comparable with those of tetradecamethylene biphenyl ($n=14$). Therefore, the critical length of the polymethylene chain for making a bridge between the 4,4′-position of the biphenyl without a strain resulting may be concluded to be $n=14$. The hyperfine coupling constants of both the *ortho-* or β-protons were strongly suppressed if the number of the methylene carbon atoms reduced to $n=12$, and further for the derivative of $n=11$.

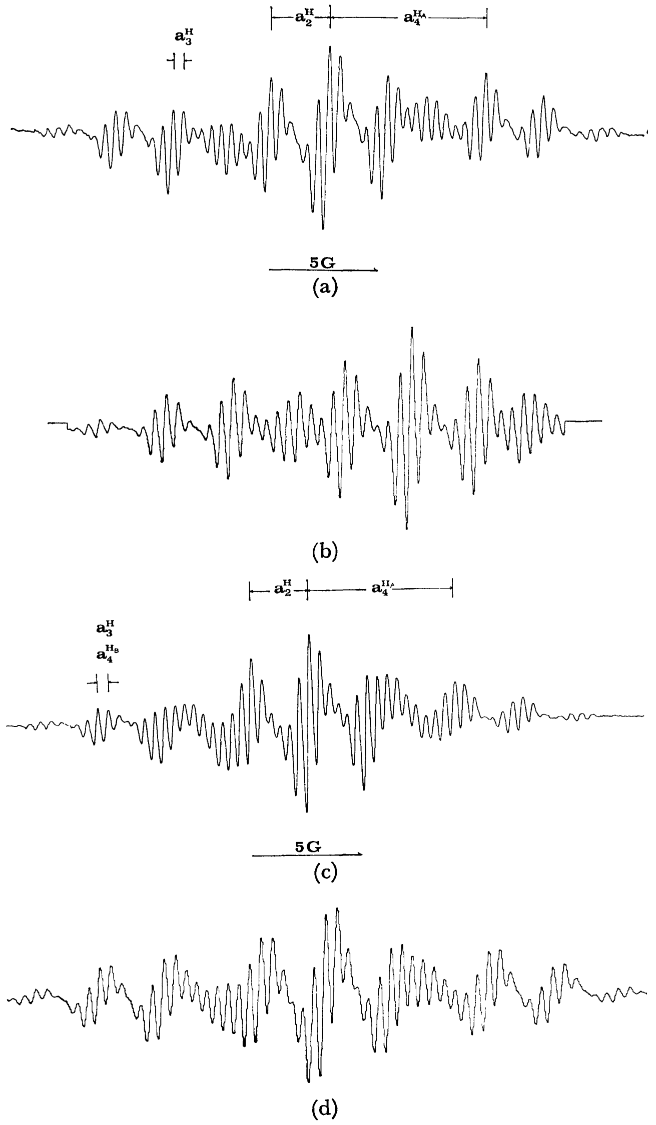

Fig. 1. 4,4′-Hexadecamethylenebiphenyl
a) ESR spectrum recorded at −20°C. b) computer simulated spectrum of (a). c) ESR spectrum recorded at room temperature. d) computer simulated spectrum of (c). A line shape is assumed to be as a Lorentzian with line width 0.2 gauss.

In Fig. 2(a), we show the ESR spectrum of 4,4′-dodecamethylenebiphenyl anion radical. The computer simulation of the spectrum again confirmed that the triplet splitting of $a_4^{\mathrm{H_B}}$ came to have the same magnitude of the line-width, as is shown in Fig. 2(b). The hyperfine coupling constants of the 4,4′-polymethylene biphenyl anion radical thus determined are summarized in Table 2. The relations between the hyperfine coupling constants and the number of polymethylene carbon atoms are plotted in Fig. 3.

The Ring-proton Splitting. It can be seen from Table 2 and Fig. 3 that the polymethylene strain actually serves to reduce the a_2^{H}, accompanied by a

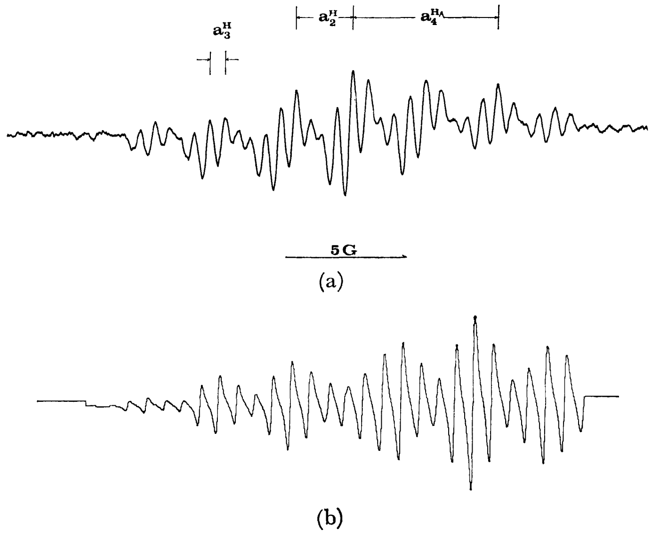

Fig. 2. 4,4′-Dodecamethylenebiphenyl
a) ESR spectrum recorded at +50°C. b) computer simulated spectrum of (a). A line shape is assumed to be as a Lorentzian with line width 0.3 gauss.

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[5] K. Ishizu, K. Mukai, H. Hasegawa, K. Kubo, H. Hishiguchi, and Y. Deguchi, This Bulletin, **42**, 2808 (1969).

[6] The computer calculations of the spectra were carried out using a JEOL JEC-5 spectrum computer.

Table 2. Proton hyperfine coupling constants of 4,4'-polymethylenebiphenyl anion radicals (gauss)

	a_2^H	a_3^H	a_4^H	a_4^H	Temp.(°C)
CH_3–	2.66	0.51	5.63	5.63	+25
C_2H_5–	2.68	0.51	3.99	3.99	0
n-C_3H_7–	2.68	0.48	3.62	3.15	−60
$-(CH_2)_{11}-$	2.18	0.63	5.49	—	0
$-(CH_2)_{12}-$	2.38	0.60	5.97	—	0
$-(CH_2)_{13}-$	2.58	0.52	6.16	—	0
$-(CH_2)_{14}-$	2.58	0.51	6.52	—	0
$-(CH_2)_{15}-$	2.67	0.45	6.54	0.45	0
	2.68	0.45	6.78	—	−20
$-(CH_2)_{16}-$	2.60	0.47	6.51	0.47	+25
	2.62	0.46	7.00	—	−20

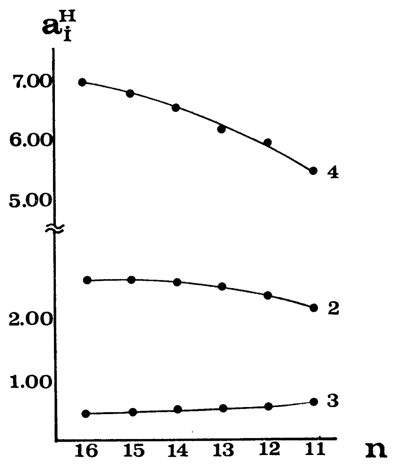

Fig. 3. The relation between the observed proton hyperfine coupling constant (a_i^H) and the number of the polymethylene groups (n), where the numeral represents the position (i) on the biphenyl ring.

slight increase in the a_3^H.

In order to explain the present results qualitatively, HMO calculations of the spin density were carried out on the assumptions that the polymethylene span modifies the structure of the coplanar biphenyl at the central 1-1' bond and that the axis of the $2P_z$ AO of each 1,1' ring carbon is either slanted (θ) or twisted (γ), as is shown in Fig. 4.

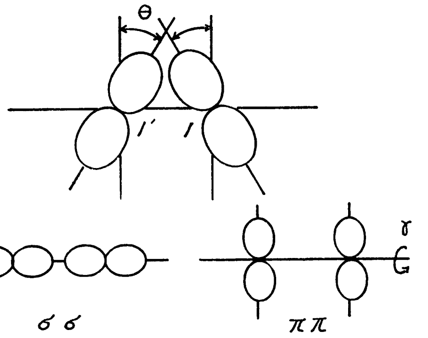

Fig. 4. $2P_z$ AO of the central 1, 1' ring carbons slanted or twisted by the polymethylene bridge.

The resonance integral between the 1-1' bond, $\beta_{11'}$, was calculated from the overlap integral, $S_{11'}$, as a function of both θ and γ; it may be expressed as follows.[7]

$$\beta_{11'} = \frac{S_{11'}/(1+S_{11'})}{S_{\pi\pi}/(1+S_{\pi\pi})}$$

$$\beta_{11'} = S_{\sigma\sigma}\sin^2\theta + S_{\pi\pi}\cos^2\theta\cos\gamma$$

The values of both the $S_{\sigma\sigma}$(0.3326) and $S_{\pi\pi}$(0.2186) integrals were used, referring to Kopineck's calculation,[8] where the bond distance of the C_1–C_1' bond was taken to be 1.539 Å.

For the sake of simplicity, the inductive parameter of the polymethylene group was rounded off to $\delta=-0.2$, taking into account that for methyl;[9] that is, the Coulomb integral of the *para*-position was estimated to be $\alpha_4=\alpha_4'=\alpha-0.2\beta$.

In Fig. 5, we show the relations between the theoretical spin density on the ring carbon atoms (ρ_i^π) and the twisting angle (γ), where the slanting angle (θ) is tentatively assumed to be 0, 15, and 30°.

As may be seen in Fig. 5, the spin density on the *ortho*-positions (ρ_2^π) shows a gradual increase, and that for the *meta*-positions (ρ_3^π), a decrease, with an increase in θ, contrary to the observed tendency of the spin density.

On the other hand, however, the HMO calculation gives an adequate explanation of the observed results, when the effect of the twisting of the phenyl rings (γ) is taken into account.

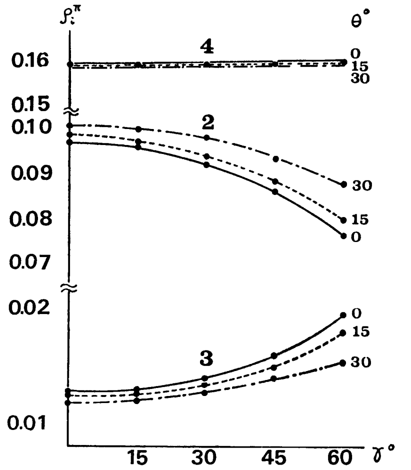

Fig. 5. Dependence of HMO spin density on the strain caused at the central 1-1' bond of the biphenyl ring.

It is noteworthy here that the spin density on the *para*-positions is not affected everywhere. Based on the present calculation, one may speculate that the polymethylene bridge causes a strain in the molecule by twisting the phenyl rings rather than inclining them against the original aromatic plane.

The Methylene Proton Splitting. The β-proton coupling constant has been calculated by the following equation, expressed as a function of the angle between the carbon-hydrogen bond and the axis of the ring carbon $2P_z$ orbital:

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[7] John D. Roberts "Notes on molecular orbital calculations" W. A. Benjamin, Inc, New York (1962), p. 82.

[8] H. J. Kopineck, *Z. Naturforsch.*, **5A**, 420 (1950).

[9] A. Streitweiser, Jr. "Molecular orbital theory for organic chemists" John Wieley & Sons, Inc. New Yorkk (1961), p. 131.

$$a_i^{H} = \langle Q \rangle \rho_i^{\pi}, \quad Q = B_0 + B\cos^2\varphi.^{10)}$$

In the case of the methyl derivative, the free rotation of the methyl group will average out the cosine term to $\langle \cos^2\phi \rangle = 1/2$, thus, the methyl-proton splitting is directly proportional, to the spin density, ρ_i^{π}, of the adjacent ring carbon atom, where the B_0 term is regarded as small in comparison with $B \approx 50$ gauss. According to this model, the ethyl proton splitting can also be well understood, assuming that $\langle Q \rangle$ is suppressed by about 25% by a restricted rotation of the ethyl group.

Recently, however, the fact of an exceptional hindered internal rotation of the alkyl group was demonstrated for the *n*-propyl derivative,[11] where it was recognized that a normal quintet splitting of the four β-protons fell into two sets of triplet splitting.

In the cases of the present derivatives, one may thus expect that a rotation of the β-methylene residue would be largely restricted not only by the large mass of the polymethylene chain, but also by its strong strain. This is indeed true, because the temperature dependence of the β-proton coupling constant has been found to be negligible for the derivatives of $n=11$—13, and the lack of the two-methylene-proton splitting in the observed spectra suggests that one of the CH bond is tightly fixed on the aromatic plane.

When the length of the polymethylene chain increases, the biphenyl ring recovers its coplanar fashion and the β-proton coupling constants can be calculated in the same manner as was used for the open-chain derivative. McLachlan's calculation ($\lambda = 1.0$) of the spin density was carried out for the open-chain derivative; ρ_4^{π} was thus estimated to be 0.195, taking the Coulomb integral of the *para*-positions to be $\alpha_4 = \alpha_4' = \alpha - 0.2\beta$. The β-proton coulping constants, $a_4^{H_A}$ and $a_4^{H_B}$, were calculated to be 7.30 gauss and zero respectively, when the β-methylene residue takes the conformation ($\varphi = 30°$), as is illustrated in Fig. 6.

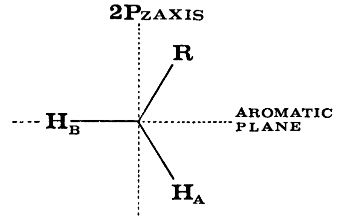

Fig. 6. The probable conformation of the β-methylene sp^3-bond in hexadecabiphenyl anion radical.

This must also be the case with the hexadecamethylenebiphenyl anion observed at −20°C. The occurrence of a small triplet splitting ($a_4^{H_B}$) observed at room temperature suggests that the torsional oscillation of the β-methyl residue is accelerated by thermal activation and that the sp^3-lobes of methylene group take a new equilibrium conformation.

Of interest is the magnitude of the β-proton splitting, which is lowered by the reduction of the chain length, for the MO calculation predicts that the spin density at the *para*-position will not be affected by a modification of the biphenyl ring.

The probably means that the polymethylene beam alters the conformation of the β-methylene sp^3 bond so as to reduce the orbital overlap between this hybrid orbital and $2P_z$ atomic orbital of the ring carbon atom. The beam is so strong that the freedom of the segment movement of the polymethylene is greatly suppressed, and the temperature dependence of the β-proton splitting is no longer observed in this case.

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10) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

11) F. Nemoto, K. Ishizu, and H. Hasegawa, *Chem. Lett.*, **1972**, 267.