ENDOR Studies in the Conformation of 3,3'- or 3,4'-Polymethylenebiphenyl Anion Radicals.

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(Received February 3, 1975)

The ENDOR spectra have been observed for the anion radicals of 3,3'- and 3,4'-polymethylenebiphenyl with various chain lengths. The hyperfine coupling constants of the ring protons of the 3,3'-derivatives are comparable with those of the reference derivative, *m,m'*-bitolyl, and the biphenyl ring is considered to take the planar conformation. When the chain length is shortened and the polymethylene chain increases its probability of being held on the biphenyl aromatic plane, strong through-space interactions are observed between the aromatic π and the polymethylene pseudo-π orbital. In 3,4'-polymethylenebiphenyl with shorter chain lengths, the coplanar phenyl rings are twisted out by the polymethylene span and the magnitudes of the spin densities at the *ortho*-position are reduced by the resonance inhibition between two phenyls. McLachaln's MO calculations predict that the twisting angles between the two phenyls are similar to the value reported for 2,2'-bitolyl anion radical. In contrast to the case of the 2,2'-bitolyl anion radical, however, a conformational change in biphenyl resulting from the delocalization of the unpaired electron is suppressed by a tight lock of the rotation of the phenyl groups in the polymethylene derivatives.

Polymethylenebiphenyls bridged by a suitable polymethylene chain at the 3,3'- or 3,4'-positions were synthesized, and the conformation of the diamagnetic neutral molecule was investigated by means of UV and NMR absorption spectroscopies.[1,2] The UV absorption parameters of the 3,3'-polymethylenebiphenyls indicated that the biphenyl rings are coplanar.

On the other hand, in the cases of the 3,4'-polymethylenebiphenyls, the polymethylene span prevents the biphenyl ring from having the coplanar conformation and inhibition of the resonance between the two phenyls was observed in the conjugation band of the UV absorption. In the previous studies of hindered biphenyl anion radicals, one of the present authors, K.I., proposed that the coplanar character of the biphenyl ring is enhanced by delocalizations of the unpaired electron.[3—5]

In the cases of the polymethylenebiphenyls, the rotation of each phenyl ring is tightly locked in certain conformations, thus, little conformational change could be expected due to the presence of the unpaired electron.

A comparative study of the steric hindrance with the anion radical of the 2,2'-alkylbiphenyl and that of the polymethylenebiphenyl is of considerable interest, since the rotation of the phenyl group can be partially allowed and since interchange between the *trans*- and *cis*-conformations may be possible in 2,2'-dialkylbiphenyls.

However, the ESR technique is not suitable for this study, because the hyperfine multiplets may be very complicated as a result of the lower molecular symmetry. Furthermore, the possibility of the long-range interaction of the polymethylene may give an additional complexity to the ESR hyperfine structures, as may be expected from the anomalous NMR shift of the polymethylene protons observed in the neutral molecules.[1]

In the present work, ENDOR studies were made for 3,3'-polymethylenebiphenyl (n=8 and 10) and 3,4'-polymethylenebiphenyl (n=9, 10, 11), bridged by different chain lengths (n).

The spin densities of the *ortho*- and *para*-positions were determined, and the degrees of the steric hindrance were estimated from McLachlan's MO calculations carried out for the twisted biphenyls. In addition, it was clearly demonstrated that the long-range interaction of the polymethylene group varies with both the chain lengths and the bridging positions.

Experimental

The synthesis and physicochemical properties of the materials used here were reported in the previous paper.[1] The radical anions were prepared by reduction with a potassium metal in DME (Dimethoxyethane), letting the reaction mixtures stand in a dry ice–acetone bath. The stability of the anion radicals depends strongly on the polymethylene chain lengths. In paticular, the radical anions of the 3,4'-polymethylene derivative with n=9 are stable only at temperatures lower than −70 °C. The ENDOR spectra were recorded by a JEOL-type ES-EDX-1 spectrometer under operating conditions similar to those described elsewhere.[6] The ESR intensities began to saturate at a microwave output of about 2 mw on the dial scale of the JES-ME-3 ESR spectrometer, and the ENDOR spectra were successfully recorded in the vicinity of −80 °C.

Results and Discussion

3,3'-Polymethylenebiphenyl. The ESR spectra of 3,3'-bridged polymethylene derivatives showed merely the broadened nine-line hyperfine structures; these structures were not further resolved into any lines, as may be seen in Fig. 1. The ENDOR spectra shown in Fig. 2, however, were resolved to show the details of complicated hyperfine couplings. The hyperfine coupling constants of the *ortho*- and *para*-protons, (a_2^H, a_6^H, and a_4^H) were easily identified with reference to the ENDOR spectrum of the *m,m'*-bitolyl anion radical. The hyperfine coupling constants assumed in the ESR measurement of the *m,m'*-bitolyl anion radicals were reconfirmed by the present work; the absolute values of the hyperfine coupling constant determined by ENDOR also gave an excellent agreement with the

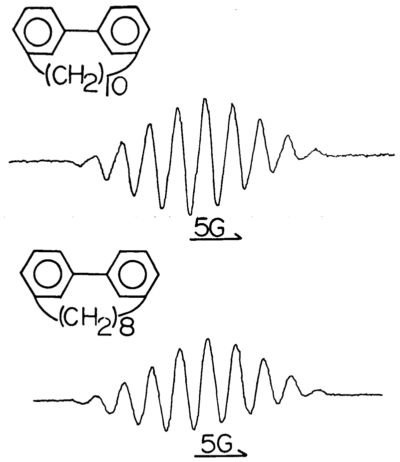

Fig. 1. ESR spectra of 3,3′-polymethylenebiphenyl anion radical recorded at −85 °C.

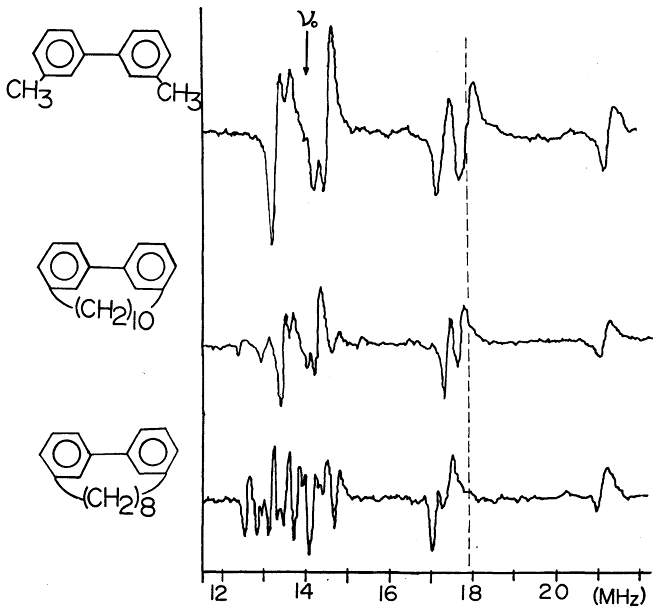

Fig. 2. Higher frequency halves of ENDOR spectra of 3,3′-bitolyl and 3,3′-polymethylenebiphenyl anion radicals. ν_0: free proton frequency.

results of the recent NMR measurements.7)

As compared with the ENDOR hyperfine structures of the *meta*-ring protons of the reference derivative, the polymethylene derivatives exhibited rather complicated structures around the free proton frequency.

Beside the β-proton splitting (0.15 gauss) and the ring-proton splitting (0.29 gauss) at the *meta*-position, the derivative with $n=10$ gave two extra splittings (0.58, 1.02 gauss); they probably resulted from the long-range interaction attributable to the polymethylene chain.

Similar long-range interactions attributable to long alkyls have already been demonstrated by the previous ENDOR study of the Banfield-Kenyon radical.8) More substantial evidence of the long-range interactions can be seen in the derivative with $n=8$. The multiple hyperfine structures composed of six different splittings cannot be explained without taking into account the contribution from the long-range interactions.

It is quite intersting that the polymethylene derivatives bridged by the shorter chain length ($n=8$) give strong long-range interactions. In the 3,3′-polymethylene derivatives, the polymethylene strain may force the polymethylene chain to take a coplanar structure with the biphenyl aromatic plane. Thus, the through-space interaction between the aromatic-π and the polymethylene pseudo-π orbital must be effectively enhanced in the derivatives bridged by shorter chain lengths.

The hyperfine coupling constants of the 3,3′-polymethylenebiphenyl anion radicals are summarized in Table 1. It may be seen that the magnitude of the *ortho*(a_2^H, a_6^H)- and *para*(a_4^H)-splittings for the 3,3′-polymethylene derivatives resembles that for the *m,m′*-bitolyl and biphenyl anion radicals. This means that the biphenyl ring probably takes the planar conformation in 3,3′-polymethylene derivatives.

3,4′-Polymethylenebiphenyl. The ESR spectra of the 3,4′-polymethylenebiphenyl anion radical are shown in Fig. 3.

Since the molecule has no symmetry, the ESR spectra are very complicated as a result of the overlap of the unresolved hyperfine components. The resolution of the ESR spectrum is reduced with an increase in the chain length; thus, the undecamethylene derivative exhibits no resolvable hyperfine structures. As one may expect from the ESR observation, the ENDOR spectrum of the derivative with $n=11$ exhibits the most complicated structures. As is shown in Fig. 4, more than eight hyperfine splittings were detected in the frequency region of the *meta*-ring and β-methylene protons, indicating the possibility of a long-range interaction due to the polymethylene group.

Contrary to the cases of the 3,3′-polymethylene derivatives, the number of the hyperfine lines is reduced with a decrease in the polymethylene chain length. A molecular model suggests that a part of the polymethylene chain located around the 4′-position separates

Table 1. Hyperfine coupling constant of 3,3′-polymethylenebiphenyl anion radicals (G)

Compound	Position			
	a_3^H, a_5^H, and a^R	a_2^H	a_6^H	a_4^H
3,3′-Bitolyl	(0.27 0.44)a)	2.43	2.81	5.22
	(0.27 0.49)b)	2.33	2.82	5.15
	(0.284 0.494)c)	2.37	2.78	5.25
Decamethylene	0.15 0.29 0.58 1.02	2.53	2.77	5.13
Octamethylene	0.11 0.21 0.37 0.48 0.57 0.76	2.43	2.61	5.22

a) ENDOR b) ESR c) NMR

Table 2. Hyperfine coupling constant of 3,4′-polymethylenebiphenyl anion radicals (G)

Compound	(a_3^R $a_{3'}^R$, a_5^H $a_{5'}^H$)	a_6^H	$a_{2'}^H$	$a_{6'}^H$	a_6^H	$a_{4'}^R$	$a_{4'}^H$
Nonamethylene	(0.08, 0.26, 0.45, 0.75)	1.54	1.72	2.30	2.68	3.71	4.97
Decamethylene	(0.07, 0.17, 0.31, 0.42, 0.67)	1.19	1.87	2.10	2.43	3.56	5.11
Undecamethylene	(0.05, 0.18, 0.38, 0.55, 0.59, 0.72, 1.00, 1.05)	1.88	2.16	2.62	2.86	3.56	4.93

Hyperfine coupling constants at the *ortho*- and the *para*-positions are assigned with reference to predictions of the MO calculations.

from the aromatic plane and becomes perpendicular to the 4′-substituted phenyl ring as the twist of the phenyl group increases. In this situation, the probability of the orbital overlap between the polymethylene group and the aromatic ring may be considerably reduced.

The four lines appearing in the frequency range from 16 MHz to 18 MHz are assigned to the absorption due to the *ortho*-protons, while the two lines at 19 MHz and 21 MHz are attributed to the splittings of the β-methylene ($a_{4'}^R$) and the ring (a_4^H), respectively both at the *para*-positions.

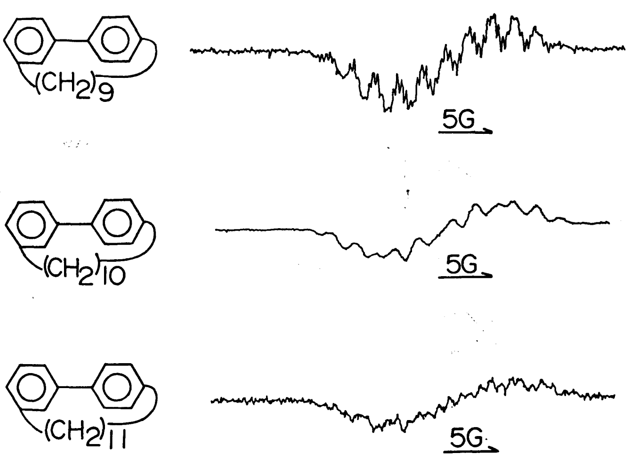

Fig. 3. ESR spectra of 3,4′-polymethylenebiphenyl anion radicals recorded at −85 °C.

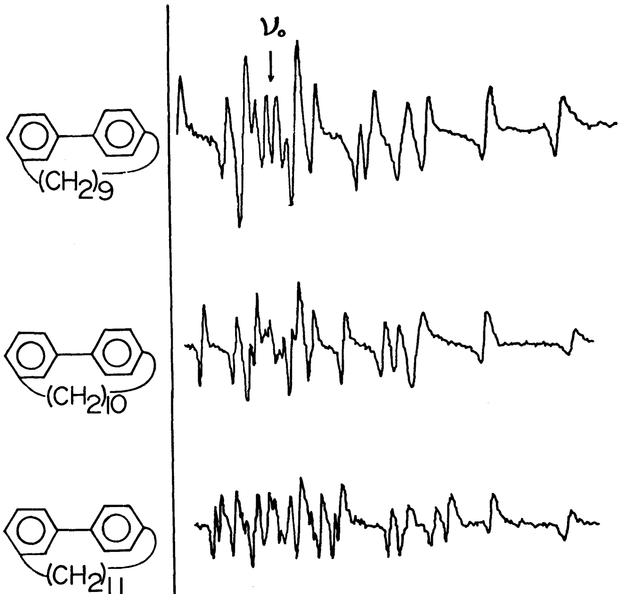

Fig. 4. Higher frequency halves of ENDOR spectra of 3,4′-polymethylenebiphenyl anion radicals.
ν_0: free proton frequency.

In the previous studies, an exceptionally hindered internal rotation of the alkyl chain was reported for the 4,4′-di-*n*-propylbiphenyl and 4,4′-polymethylenebiphenyl anion radicals, where a normal quintet splitting of the four methylene protons splits into two sets of triplet splittings.[9,10] A similar situation is probable for the present cases. Based on the observed methylene proton splitting ($a_{4'}^{\beta}$) and McLachlan's spin density ($\rho_{4'}^{\pi}$) at the 4′-position, the equilibrium dihedral angles, φ, of the β-methylene group were calculated tentatively, assuming McConnell-Heller's equation:[11]

$$a_{4'}^{\beta} = (B_0+B_2\cos^2\varphi)\rho_{4'}^{\pi} \tag{1}$$

Taking the B_0/B_2 ratio to be +0.06 with B_2=50 gauss,[12] the dihedral angles were estimated to be 48°, 49°, and 53° for n=9, 10 and 11 respectively.

If the segment motion of the β-methylene group is tightly locked, one of the two β-methylene protons may give rise to the splitting ($a_{4'}^{\beta}$) in the range from 16 MHz to 17 MHz, as one would expect from a similar calculation using $\varphi'=70$ °. In the present case, however, it is difficult to identify this splitting because of the overlap of the absorption with those of the *ortho*-protons observed in the same frequency region.

The experimental spin densities of the ring carbon ρ_i^{π}, were calculated from the ring proton splitting (a_i^H) using Copla-Bolton's equation:[13]

$$a_i^H = Q_{CH}(0)\rho_i^{\pi} - K_{CH}^H[\rho_i^{\pi}]^2 \tag{2}$$

where $Q_{CH}^H(0)=-27$ and $K_{CH}^H=-12$ gauss. The Coulomb integrals of the ring carbons attached to the methylene were estimated to be $\alpha_i=\alpha-0.2\beta$, and the resonance integral between the bridgehead carbons was taken to be $\beta_{11}=\beta\cos\theta$ as a function of the twisting angles (θ) of the phenyl groups. McLachlan's parameter, λ, is estimated to be 1.1 for any derivative. McLachlan's spin densities (ρ_2^{π}, $\rho_{2'}^{\pi}$, ρ_6^{π}, $\rho_{6'}^{\pi}$, and $\rho_{4'}^{\pi}$) of the derivative with n=11 indeed show an excellent agreement with the experimental values when the biphenyl ring is assumed to take the planar conformation, that is, when θ=0. On the other hand, the MO calculation carried out on the twisted biphenyls taking θ=50° gives results which account for the observed spin densities of the derivatives with n=9 and 10, as may be seen in Table 3.

In the UV absorption maxima of the conjugation band observed for the neutral molecules, the derivatives bridged by shorter chains (n=9 and 10) display a blue shift as compared with the UV absorption parameters of the derivative with a longer chain (n=11); that is,

TABLE 3. EXPERIMENTAL AND THEORETICAL SPIN DENSITIES OF POLYMETHYLENEBIPHENYLS

Chain length	Spin densities						Twisting angle
n	4	4′	2	6	2′	6′	θ
Exp. 9	0.202	—	0.104	0.058	0.066	0.088	
10	0.208	—	0.093	0.045	0.071	0.080	
Calcd.	0.216	0.157	0.139	0.048	0.082	0.082	50°
Exp. 11	0.200	—	0.111	0.071	0.101	0.102	
Calcd.	0.197	0.183	0.141	0.082	0.117	0.117	0°

TABLE 4. PARAMETERS OF THE STERIC HINDRANCE FOR POLYMETHYLENEBIPHENYLS

	ρ_p/ρ_o		ρ_p/ρ_o
Biphenyl	2.12	*o,o′*-Bitolyl	2.46[a)]
m,m′-Bitolyl	2.09	3,4′-Nonamethylene	2.28[b)]
3,3′-Decamethylene	2.04	3,4′-Decamethylene	2.52
3,3′-Octamethylene	2.19	3,4′-Undecamethylene	1.97

a) $Q^{\mathrm{H}}_{\mathrm{CH}_3}$ is estimated to be 28 G. b) $\rho^{\pi}_{4'}$ -values are estimated from the McLachlan's MO calculations. c) ρ_p/ρ_o values are calculated to be $\frac{(\rho^{\pi}_4+\rho^{\pi}_{4'})/2}{(\rho^{\pi}_2+\rho^{\pi}_{2'}+\rho^{\pi}_6+\rho^{\pi}_{6'})/4}$.

3,4′-nonamethylenebiphenyl ($\lambda_{\max}$=250 nm, ε=14500), 3,4′-decamethylenebiphenyl ($\lambda_{\max}$=248 nm, ε=16700) and 3,4′-undecamethylenebiphenyl ($\lambda_{\max}$=252 nm, ε=18800). The regular blue-shift of the absorption maxima from the undecamethylene to the nonamethylene derivative is accompanied by a decrease in the extinction coefficient. This can be understood in terms of the resonance inhibition resulting from the steric hindrance.

No detailed investigation of the structure of the neutral molecules has been reported, so the twisting angles, θ, of the two phenyls are assumed to be between the two values for biphenyls (θ=30°, $\lambda_{\max}$=247 nm, ε=18050) and 2-methylbiphenyls (θ=58°, $\lambda_{\max}$=235 nm, ε=10500).[14)]

The present calculations of the twisting angles in the anion radicals are more or less qualitative. Therfore, the ratios of the averaged spin densities at the *para*- and the *ortho*-positions, $\rho_p^{\pi}/\rho_o^{\pi}$, which have often been used as parameters to estimate the degree of the steric hindrance, are tentatively compared with those for the usual alkyl derivatives in Table 4.

It is very interesting that the values for the 3,4′-nona- and decamethylene derivatives are close to that for *o,o′*-bitolyl, while the value for the 3,4′-undecamethylene derivative is rather akin to those of biphenyl and the 3,3′-polymethylene derivatives. Since the twisting angles of the 2,2′-dialkylbiphenyl anion radicals are assumed to be around 45°, one may see that the MO prediction of the steric hindrance is also valid for the present derivatives. In addition, it may be speculated that the same magnitude of the steric hindrance can be assumed for both the neutral molecules and the anion radicals of the hindered polymethylenebiphenyls.

In contrast to this situation, it has been known that the biphenyl rings of the 2,2′-dialkylbiphenyl anion radicals are likely to increase in planar character because of a delocalization of the unpaired electron.

In 2,2′-dialkylbiphenyl, the rotations of the two phenyl groups are partially allowed, and the extra delocalization energy of the unpaired electron may compenasate for the repulsion energy between the two phenyls so as to increase the coplanarity of the biphenyl ring. On the other hand, the rotation of each phenyl group is tightly locked in the hindered polymethylene derivatives and the conformation of the biphenyl ring may be fixed in a certain twisting angle by the strong polymethylene strain.

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