BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2932—2936 (1973)

ESR Studies of the Cation Radicals Produced by $SbCl_5$ Oxidation of Some Biphenyls with *ortho*- and *para*-Dialkyl Substituents

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(Received February 8, 1973)

The cation radicals of some alkylbiphenyls such as 4,4′-bitolyl, 4,4′-di-*t*-butylbiphenyl, and 2,2′, 4,4′, 6,6′-bimesityl, were generated by $SbCl_5$ oxidation in CH_2Cl_2. The ESR observation was carried out, and the Q values of the methyl and *t*-butyl were estimated based on either the theoretical spin density or the experimentally-determined spin density from the ^{13}C-hyperfine splitting. The Q value of the methyl in the cation radical was found to be 1.5 times that for the anion radical. The *t*-butyl groups of the cation radical also showed a much larger Q value than that for the anion radical. The perturbation of the spin density due to the steric hindrance was investigated with reference to the prediction of the McLachlan's MO calculations carried out for the hindered biphenyl. The experimentally-determined spin density derived from the Q value established for the *para*-derivative can be adequately interpreted on the assumption that the planar character of the biphenyl would be much reduced, contrary to the tendency found for the anion radicals. This effect suggests that a different delocalization of the unpaired electron may be expected between the cation and the anion radical: that is, the unpaired electron brings about a fair bonding on the central 1–1′ bond in the anion radical, but an antibonding for the cation radical, because the odd π-orbital of the cation has its node between the central 1–1′ bond.

The oxidation of aromatic hydrocarbons with $SbCl_5$ in CH_2Cl_2 is now one of the standard methods for preparation of the cation radicals in solution.[1] There have been numerous ESR studies of the aromatic cation radicals, which have often provided a useful test of molecular orbital theories. In the previous papers, we have reported several studies of the alkyl biphenyl anion radicals;[2–5] we hoped to compare the alkyl proton splitting with that of the cation radicals in order

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2) K. Ishizu, This Bulletin, **36**, 938 (1963).
3) K. Ishizu, *ibid.*, **37**, 1093 (1964).
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to demonstrate the importance of the hyperconjugation mechanism in these derivatives. The ESR studies of the *ortho*-derivatives would be attractive, because the conformational change in the biphenyl ring can be elucidated by an investigation of the steric hindrance observed for the cation radical and the anion radical.

In the present paper, we wish to report the results of ESR studies of the cation radicals generated by the usual $SbCl_5$ oxidation of some alkyl biphenyls, such as 4,4′-bitolyl, 4,4′-di-*t*-butylbiphenyl, and 2,2′, 4,4′,6,6′-bimesityl. The alkyl proton splitting was determined and the splitting parameters, Q^R, of the methyl and *t*-butyl groups were calculated on the basis of McLachlan's spin density for the ring carbon atoms. The twisting angle between the two phenyls was estimated with reference to the theoretical spin density of the hindered biphenyl. The experimentally-determined spin density for the cation radical was compared with that for the anion radical, and we will present new experimental evidence that the presence of the unpaired electron in the frontier orbital actually plays an important role in causing a large modification of the conformation of biphenyl.

Experimental

Materials and ESR Samples. 4,4′-bitolyl, (mp 121—122 °C), 4,4′-di-*t*-butylbiphenyl, (mp 198—199 °C), and 2,2′, 4,4′, 6,6′-bimesityl (mp 102—103 °C) were synthesized by Ullman reactions in the manner described bofore.[4] Commercial-grade dichloromethane was dried over P_2O_5 and fractionally distilled. Antimony pentachloride purchased from Nakarai Chemicals Ltd was used without further purification. About a 10% solution of $SbCl_5$ was prepared using CH_2Cl_2 as the solvent and it was stocked in a refrigerator. The materials (*ca.* 2 mg) were placed in a reaction tube (1) and 1 ml of the 10% $SbCl_5$ solution was mixed with 5 ml of CH_2Cl_2 in the side arm tube (11), shown in Fig. 1. The inside of the reaction tube was evacuated, and the reaction tube (1) was placed in liquid N_2; then $SbCl_5$ and CH_2Cl_2 were distilled into the reaction tube (1), which was placed in an aceton-dry ice bath after the removal of the oxidizing agent. As the frozen reaction mixture was melted in an aceton-dry ice bath, the oxidation of the materials proceeded smoothly and the reaction mixture began change in color from deep-blue to blue-green for the *para*-derivatives and to yellow for the *ortho*-derivatives.

The radical solution thus prepared was inserted in a precooled ESR cell, and the ESR spectra were recarded at −40—70 °C. The ESR apparatus employed here was JEOL ME-3X spectrometer operating with a 100 kHz magnetic-field modulation. The magnetic field was calibrated by means of the ring proton hyperfine coupling constant of the perylene cation radical prepared in concentrated sulfuric acid.

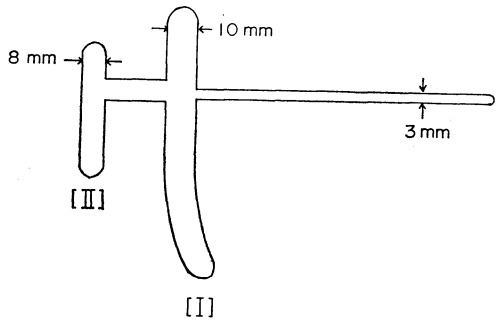

Fig. 1. The reaction vessel and the ESR cell.

Results and Discussion

4,4′-Bitolyl. The spectrum of the 4,4′-bitolyl cation radical observed at −50 °C is shown in Fig. 2. The ESR signal intensity was rapidly depressed when the observing temperature was brought to −30 °C. The largest septet splitting (8.79 Gauss) was easily assigned to those of methyl protons (a_4^H), and the quintet splitting (2.64 Gauss) was ascribed to the *ortho*-ring protons (a_2^H) taking into account McLachlan's MO calculation of the spin density. The *meta*-proton splitting could not be detected in the observed spectrum. The hyperfine coupling constants of each proton thus determined are; $a_4^{CH_3}=8.79$, $a_2^H=2.64$, and $a_3^H<0.03$ Gauss.[6] These values are nearly comparable with those of the cation radical generated by the XeF_2 oxidation of toluene.[7] Besides the proton hyperfine structure, three kinds of ^{13}C-hyperfine splitting were recorded, as is shown in Fig. 3. We found that the absolute values of these hyperfine coupling constants are much like those of the *ortho* (a_2^C)-, the *meta* (a_3^C)-, and the *para* (a_4^C)-ring carbon atoms of the 3,3′,5,5′-tetra-*t*-butylbiphenyl anion radical, as has already been reported,[8] but the splitting of a_1^C, was not resolved in the present case. The ^{13}C hyperfine splittings were assumed to be as follows; $a_2^C=1.83$, $a_3^C=-3.59$, and $a_4^C=8.47$ Gauss.

4,4′-Di-t-butyl Biphenyl. The ESR spectrum of 4,4′-di-t-butylbiphenyl, shown in Fig. 4, was observed in the temperature range of −70 °C to −60 °C. Besides the *ortho*-proton splitting of 2.67 Gauss, one may see the t-butyl proton splitting (0.38 Gauss), which is three times larger than that of the anion radical.[9] The proton hyperfine coupling constants thus estimated are $a_2^H=2.67$ and $a_4^{t\text{-}But}=0.38$ Gauss.

Bimesityl. The ESR spectrum of the cation radical, given in Fig. 5-a, was recorded at −55 °C.

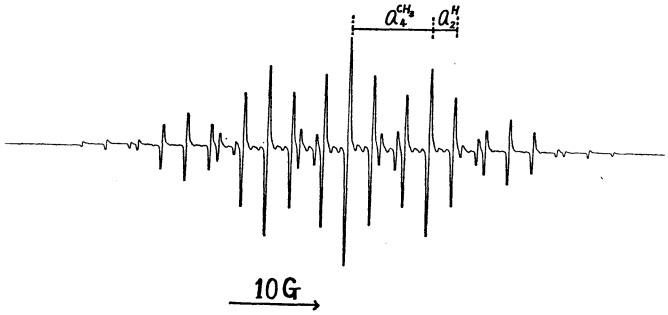

Fig. 2. The ESR spectrum of 4,4′-bitolyl cation radical observed at −50 °C.

6) The maximum resolution of the ESR spectrometer.
7) M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Amer. Chem. Soc.*, **72**, 5096 (1970).
8) K. Ishizu, Y. Inui, K. Mukai, H. Shikata, and H. Hasegawa This Bulletin, **43**, 3956 (1970).
9) M. D. Curtis and A. L. Allred, *J. Amer. Chem, Soc.*, **87**, 2554 (1965).

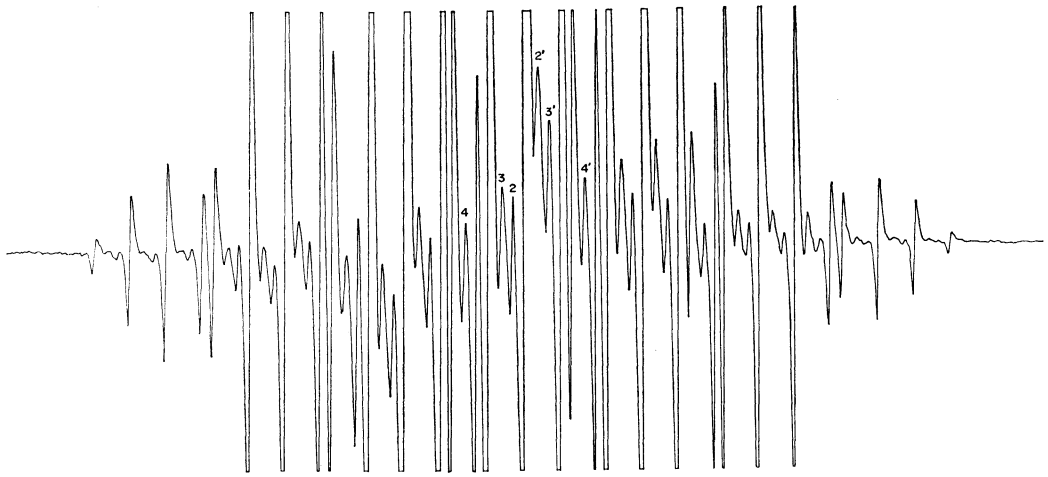

Fig. 3. The ^{13}C-splitting of the ring carbon atoms of 4,4'-bitolyl cation radical. The figures denote the ring position.

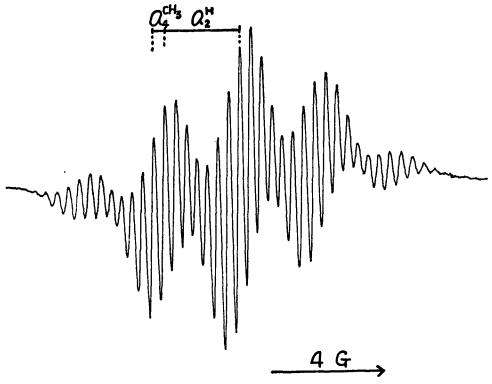

Fig. 4. The ESR spectrum of 4,4'-di-*t*-butylbiphenyl cation radical observed at −70 °C.

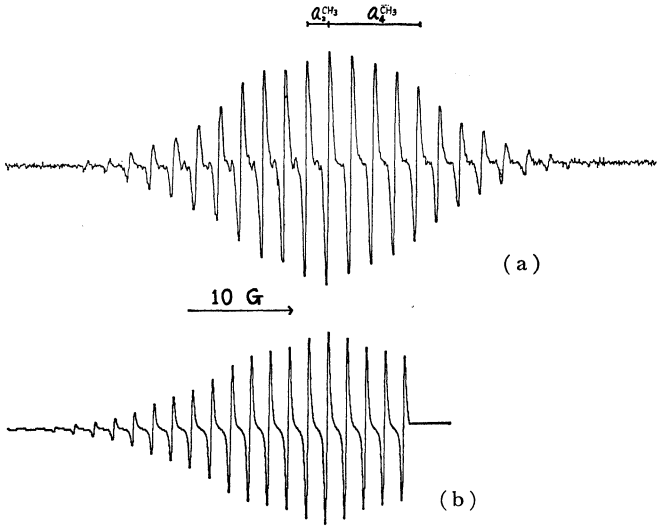

Fig. 5. a) The ESR spectrum of 2,2',4,4',6,6'-bimesityl cation radical observed at −60 °C.
b) The computer simulated spectrum.

The bimesityl cation radical is fairly stable for a continuous observation of the ESR spectrum for about 4 hr, but the cation radicals of the other *ortho*-methyl biphenyls, such as 2,2'-bitolyl and 2,2',6,6'-bixylyl, were not successfully generated. The hyperfine structures of the observed spectrum can be well analyzed in terms of the septet splitting of the *para*-methyl protons (8.79 Gauss) and of the *ortho*-methyl proton splitting (2.19 Gauss). The computer-calculated spectrum, shown in Fig. 5–b, is in good agreement with the observed spectrum. Under the higher resolving conditions, the ring proton splitting of the *meta*-position, a_3^H was measured to be 0.13 Gauss. The hyperfine coupling constants thus determined are $a_2^{CH_3}=2.19$, $a_3^H=0.13$ and $a_4^{CH_3}=8.79$ Gauss.

Biphenyl and the Other Alkylbiphenyl. Biphenyl was dissolved in CH_2Cl_2 and treated with $SbCl_5$ in the same manner. The resulting blue solution showed a strong ESR absorption split into eleven equally-spaced hyperfine lines (2.12 Gauss). The hyperfine structure of the spectrum was, however, identical with that for the 4,4'-dichlorobiphenyl cation radical previously reported.[7] The 4-chlorobiphenyl also gave the same ESR spectrum of dichlorobiphenyl. The 3,3',5,5'-tetra-methylbiphenyl and the 3,3',5,5'-tetra-*t*-butylbiphenyl afforded poorly-resolved ESR spectrum, but we failed to detect the ESR absorptions of the alkylbiphenyls, such as 4,4'-diethylbiphenyl and 4,4'-di-isopropylbiphenyl.

Table 1. The observed hyperfine coupling constants of the alkyl biphenyl anion and cation radicals (Gauss)

		$a_2^H, a_2^{CH_3}$	a_3^H	a_4^R
4,4'-Bitolyl	Anion	2.66	0.51	5.63
	Cation	2.64		8.79
4,4'-Di-*t*-butyl Biphenyl	Anion	2.64	0.60	0.10[9]
	Cation	2.67		0.38
2,2', 4,4', 6,6'-Bimesityl	Cation	2.19	0.13	8.79

Hyperconjugation of the Alkyl Group. McLachlan's MO calculations of the spin density were carried out for 4,4'-bitolyl using two different models, the inductive and the hyperconjugative models. In the inductive model, the Coulomb integral of the ring-carbon atoms

Table 2. Theoretical and experimental spin density for the 4,4′-bitolyl anion and cation

Position	1	2	3	4	CH_3
Anion					
Inductive	0.1272	0.1189	−0.0316	0.1982	
Hyperconjugative	0.1259	0.1046	−0.0170	0.1885	0.0141
Experimental		0.1033	−0.0187	0.2011[a]	
Cation					
Inductive	0.1297	0.0931	−0.0090	0.2021	
Hyperconjngative	0.1242	0.0946	−0.014	0.1955	0.0192
Experimental		0.0939	0.0172	0.1945[b]	

a) $Q^{CH_3}=-27$ Gauss was used. b) Estimated from the a_3^C and a_4^C values, based on the Karplus and Fraenkels formula.

neighboring the methyl group, α_{CH_3}, was estimated to be $\alpha_{CH_3}=\alpha-0.2\beta$. The Coulson-Crawford parameters were used for the hyperconjugation model of the methyl groups ($>C_1-C_2\equiv H_3$) as follows; $\alpha_2=\alpha-0.1\beta$, $\alpha_{H_3}=\alpha-0.5\beta$, $\beta_{C-C}=0.7\beta$, $\beta_{C\equiv H_3}=2.5\beta$.[10] McLachlan's parameter was taken as $\lambda=1.1$ everywhere. Based on the observed values of the ring-proton splitting (a_i^H), the experimental values of the spin density (ρ_i^π) were calculated based on the Colpa-Bolton's formula, expressed as follows;

$$a_i^H = Q_{CH}^H \rho_i^\pi \pm K_{CH}^H [\rho_i^\pi]^2$$

where the negative sign is applicable to the cation, and the positive sign, to the anion radicals, and where the parameters were taken as $Q_{CH}^H=-27$ Gauss and $K_{CH}^H=-12$ Gauss. Both the experimental and theoretical values of the spin density (ρ_i^π) are summarized in Table 2,

It has been well known that the methyl protons of the cation radical usually give a much larger splitting than those of the anion radical, and this effect has been accepted as being straightfoward evidence supporting the importance of the hyperconjugation mechanism in the methyl group.[12] The methyl proton splitting of the 4,4′-bitolyl cation radical is indeed 1.5 times larger than that for the anion radical, as may be seen in Table 1.

In the case of the cation radical, however, the ρ_4^π can not be derived from the methyl proton splitting, because the Q^{CH_3} value has not been widely established. In the present works, the experimental values of ρ_3^π and ρ_4^π were estimated from the ^{13}C-hyperfine splitting constant, a_3^C, a_4^C using the Karplus-Fraenkel formula:[13]

$$a_i^C = (S^C - \sum_{i=1}^{3} Q_{C_iX_i}^C)\rho_i^\pi - \sum_{i=1}^{3} Q_{X_kC_i}^C \rho_k^\pi$$

where $S^C=-12.7$ Gauss, the contribution from the 1s electron of C_i; where $Q_{C_iX_k}^C$ ($Q_{C_iH}^C=19.5$, $Q_{C_iC_k}^C=14.4$ Gauss), the $\sigma-\pi$ interaction parameter produced by the ρ_i^π on the C_i atom bonded to sp^2-hybridized ring carbon atoms, and where $Q_{C_kC_i}^C=-13.9$ Gauss represents a polarization from the neighboring sp^2-carbon atom. The parameters ($Q_{CC'}^C=30.0$, $Q_{C'C}^C=-20.9$ Gauss) for a sp^2-hybridized carbon bonded to the sp^3-carbon of the methyl group (C′) are referred to the value calculated by Strauss and Fraenkel.[14]

By substituting these parameters into the equation, the following equations were derived, neglecting the spin density on the methyl carbon at the *para*-position:

$$a_3^C = 35.5\rho_3^\pi - 14.4(\rho_2^\pi + \rho_3^\pi)$$

$$a_4^C = 46.1\rho_4^\pi - 28.8\rho_3^\pi$$

Using the experimental value of ρ_2^π obtained from the ring-proton splitting, ρ_3^π and ρ_4^π were thus calculated to be $\rho_3^\pi=0.0172$ and $\rho_4^\pi=0.1945$, which showed an excellent agreement with the theoretically-calculated values shown in Table 2.

The methyl-proton splitting parameter, Q^{CH_3}, was calculated to be 43.5 Gauss on the basis of the calculated value, assuming an inductive model of hyperconjugation. It can also be estimated to be 45.2 Gauss on basis of the experimental spin density, ρ_4^π, as determined from the ^{13}C-hyperfine splitting.

Of interest is the comparison of the *t*-butyl proton splitting, $Q^{t\text{-But}}$, which is tentatively estimated using the theoretical spin density calculated by the inductive model for the methyl group.

The $Q^{t\text{-But}}$ value for the cation radical (1.88) is about four times that for the anion radical (0.50).

Steric Hindrance of the Biphenyl Cation Radical. Molecular orbital calculations of the spin density were carried out for hindered models of the 2,2′,4,4′, 6,6′-bimesityl cation radical, assuming that the value of the resonance integral between the central 1–1′ bond varies with the function of the twisting angle, θ, of the two phenyls; that is, $\beta_{11'}=\beta\cos\theta$.

In Fig. 6, we show the dependence of the twisting angle, θ, on the theoretical spin density at the ring carbon atoms. The calculation results of both the inductive and hyperconjugative models suggested that the steric hindrance may cause a large depression in the spin density at the *ortho*-position (ρ_2^π), but may have scarcely any effect on the *para*-position (ρ_4^π). Therefore, either the degree of the depression in ρ_2^π or the increment in ρ_4^π/ρ_2^π would also be a good measure for estimating the degree of the steric hindrance, as has been described before.[3,4] According to the MO calculation, there is a possibility that the negative

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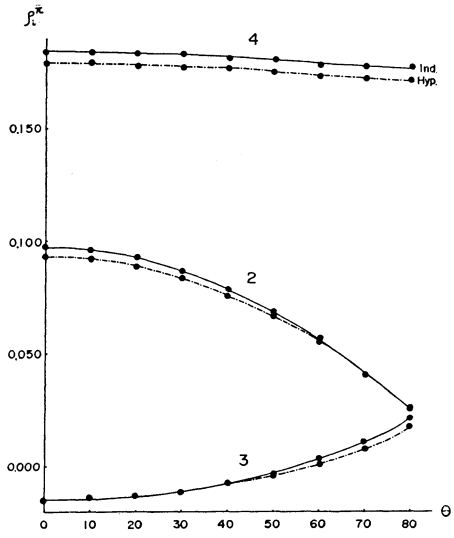

Fig. 6. Dependence of theoretical spin density of ring carbon atoms on twisting angle θ between the phenyl rings in 2,2′,4,4′,6,6′-bimesityl cation radical.
—●—●— calculation using the Inductive model (Ind)
—●—● calculation using the hyperconjugation model (Hyp).
The numbers represent the positions on the biphenyl ring.

spin densities at the *meta*-position, ρ_3^π, change to positive sign with an increase in the steric effect.

We have, however, disregarded the effect on the *meta*-position, because the observed *meta*-proton splitting is too small for us to qualify the steric effect on the basis of the present ESR observations. The experimental spin densities of the ρ_2^π and ρ_4^π/ρ_2^π values were calculated using the Q^{CH_3} value estimated for the p,p'-bitolyl cation radical; that is, $\rho_2^\pi=0.050$, $\rho_4^\pi=0.2021$, and $\rho_4^\pi/\rho_2^\pi=4.40$. Unfortunately, the ESR observation of the 2,2′,4,4′,6,6′-bimesityl anion radical has never been successfully achieved. However, for the 2,2′,6,6′-bixylyl anion radical, these values were already known to be $\rho_2^\pi=0.082$ and $\rho_4^\pi/\rho_2^\pi=2.30$.[4] Furthermore, the ρ_2^π of the anion radicals of the *ortho*-alkyl derivatives hitherto studied have been coincidently close to this value, and the ratios of ρ_4^π/ρ_2^π lay together in the range from 2.30 to 2.50.[2,4,5]

A large discrepancy in the ρ_2^π and ρ_4^π/ρ_2^π values can be seen between the cation and the anion radical. This suggests that the more stronger steric hindrance may work on the cation radical rather than on the anion radical.

According to the MO calculation, the twisting angle of the two phenyls would be around 70° in this cation radical, rather close to the values for the neutral molecules,[15], while it is assumed to be 45°~50° for the anion radicals of hindered alkylbiphenyls. In order to explain the different planar characters of the biphenyl observed for the cation and the anion radical, the bonding character between the central 1–1′ bond may be considered in terms of the partial bond order in the frontier molecular orbital of each ion radical.

In the case of the anion radical, the conjugation between the two phenyl rings may be enhanced by the presence of the unpaired electron, which has a positive bond order between the central 1–1′ bond in the π_{n+1} molecular orbital. The similar enhanced planar character of biphenyl reported for the excited triplet state of *ortho*-methyl derivatives[16,17] has also been interpreted in terms of the delocalization of the unpaired electron across the two phenyl rings.

On the contrary, the unpaired electron occupies the molecular orbital in the case of cation radicals, and the conjugation of the two phenyls may be strongly reduced, just as in the neutral molecules, because the wave function has the node and there is a negative bond order between the 1–1′ bonds in these molecules.

The numerical calculations were carried out on the FACOM 230—60 at the Data Processing Center, Kyoto University.

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