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Carbon-13 Magnetic Resonance Chemical Shifts in Alkylbiphenyls[1]

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Carbon-13 NMR spectra were observed for the seventeen alkyl biphenyls. For the *meta*- and *para*-alkyl derivatives, the observed ring carbon-13 chemical shifts could be adequately understood in terms of the Karplus-Pople's formula by taking into account the hyperconjugative effect of the substituents. The observed chemical shifts of aliphatic carbon were in good agreement with the values of the corresponding alkylated benzenes within the limits of experimental error. For the *ortho*-derivatives, the conformation of substituents in the hindered biphenyls was particularly discussed in relation to the observed alkyl carbon-13 chemical shifts. In the cases of 2,2′-dimethylbiphenyl and 2,2′,6,6′-tetramethylbiphenyl, the chemical shifts of methyl carbons at the *ortho*-position revealed a high field shift of about 1 ppm, but that of 2,4,6-trimethylbiphenyl indicated only 0.4 ppm. The different shifts of the *ortho*-methyl carbons in the two cases suggested a spece interaction between the two methyl groups. This interaction may arise an orbital overlap between the methyl groups, which were considered to approach one another to take the *cis*-conformation.

Interest in the molecular structures of numerous biphenyl derivatives has often been focused on their stereochemistry. In particular, the substituents at the *ortho*-positions may cause a large steric effect; hence, two phenyls in *ortho*-substituted biphenyl derivatives are incapable of taking a planar structure in a solution. Regarding the conformation of the phenyl groups in the *ortho*-alkylated biphenyl, Suzuki[2] has already proposed a correlation between the rotation angle of the two planar phenyl groups and the wavelength of the ultraviolet obsorption maxima. Furthermore, Mislow *et al.*[3] and Ōki *et al.*[4] have also reported that a similar relationship holds between the twisted angle of biphenyls and the NMR chemical shifts of the alkyl protons at the *ortho*-position. In this case, the chemical shifts of the alkyl protons were reasonably explained in terms of an increased diamagnetic shielding effected by the ring current of the rotating phenyl groups. In the case of NMR studies of aromatic protons, however, the assignment of their chemical shifts becomes more or less difficult because of the superimposed structures caused by the various spin-spin couplings of the ring protons. In this work, the carbon-13 NMR measurement of both ring and the alkyl carbon-13 were carried out for the seventeen alkylbiphenyls, and the hyperconjugative and steric effects due to the higher alkyl groups were investigated.

The observed ring carbon-13 chemical shifts are discussed in terms of the Karplus-Pople's formula, taking into account the hyperconjugative effect of the substituents. Finally, the conformation of the hindered biphenyls is considered in relation to the observed alkyl carbon-13 chemical shifts.

Experimental

Each alkylated biphenyl was synthesized and identified in the manner reported in previous papers.[5-7] Samples containing carbon-13 in its natural abundance, 1.1%, were dissolved in tetrahydrofuran (THF). The carbon-13 magnetic resonance spectra were recorded using a JNM-4H-100 type NMR spectrometer at 25 MHz. A JNM-IS-100 proton decoupler was used in order to enchance the carbon-13 signal due to the nuclear Overhauser effect and to remove the splitting due to the spin-spin coupling between carbon-13 and proton spins.[8] Benzene was used as the external primary reference for the ring carbon-13 chemical shifts in biphenyl, and the shift of the β-carbon of THF was taken as the internal secondary reference. For the aliphatic carbon-13 chemical shifts of the alkyl group, cyclohexane was used as the primary reference.

Results and Disusssion

Chemical Shifts of Aromatic Ring Carbon Para- *or* Meta-*Alkylated Biphenyls.* The aromatic carbon-13 NMR spectrum of 4,4′-diethylbiphenyl is shown in Fig. 1. The observed spectrum consists of four lines; their integrated intensity ratios are about 1 : 1 : 2 : 2, which easily distinguishes $\Delta\sigma_1$ and $\Delta\sigma_4$ from $\Delta\sigma_2$ and $\Delta\sigma_3$.[9]

The chemical shift of each aromatic carbon-13 is calculated according to the additivity rule[10] based on the experimental values of both biphenyl and ethylbenzene, and the observed $\Delta\sigma_i$ value is assigned to each ring carbon, with reference to the results of the

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[1] Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2] H. Suzuki, This Bulletin, **32**, 1350, 1357 (1959); *ibid.*, **33**, 109 (1960).

[3] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, **86**, 1710 (1964).

[4] M. Ōki, H. Iwamura, and N. Hayakawa, This Bulletin, **37**, 1865 (1964).

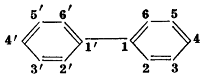
[5] K. Ishizu, H. Hasegawa, H. Chikaki, H. Nishiguchi, and Y. Deguchi, *Kogyo Kagaku Zasshi*, **68**, 1522 (1965).

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

[7] K. Ishizu, Y. Inui, K. Mukai, H. Shikata, and H. Hasegawa, *ibid.*, **43**, 3956 (1970).

[8] E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).

[9] The general sturcture of a biphenyl is



where $\Delta\sigma_1$, $\Delta\sigma_2$, $\Delta\sigma_3$, and $\Delta\sigma_4$ indicate both the positions and the chemical shifts.

[10] G. B. Savitsky, *J. Phys. Chem.*, **67**, 2723 (1963).

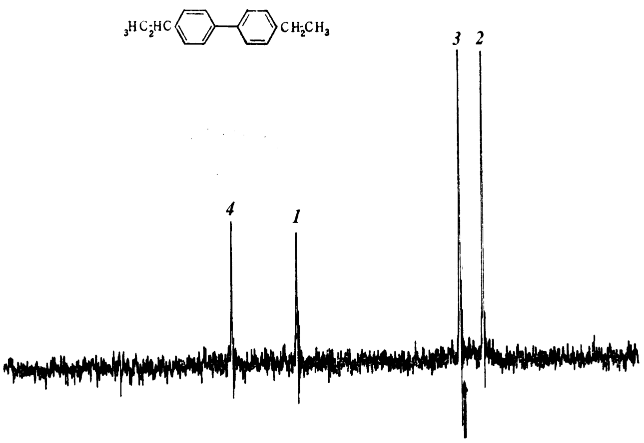


Fig. 1. The aromatic carbon-13 NMR spectrum of 4,4′-diethylbiphenyl. (Solvent: THF).

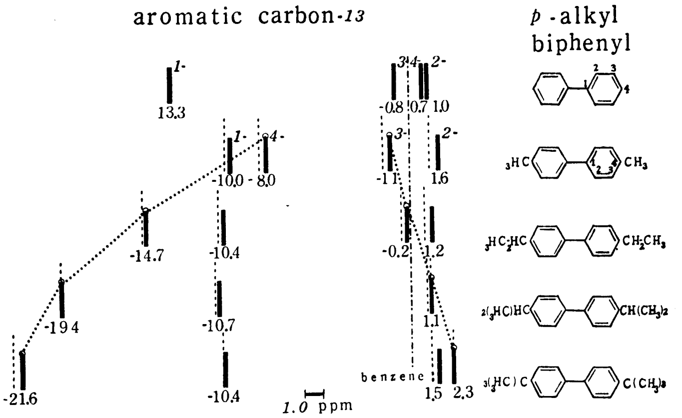


Fig. 2. The observed values and the calculated results of the aromatic carbon-13 chemical shifts for the *para*-alkylated biphenyls.[11] (Solvent: THF).

additivity calculations.

The observed and the calculated values of the aromatic carbon-13 chemical shifts for the *para*- and *meta*-alkylated biphenyls are summarized in Figs. 2 and 3. A satisfactory agreement can be seen between the observed values of the carbon-13 chemical shifts and those predicted by the additivity calculations.

In all cases, the hyperconjugative effect gives rise to a drastic lower-field shift for the ring carbon atoms ($\Delta\sigma_4$ and $\Delta\sigma_3$) bonded to the alkyl groups in the order of $CH_3 < CH_3CH_2 < CH(CH_3)_2 < C(CH_3)_3$. At the same time, an alternative higher-field shift of the next neighboring carbon atoms of the alkyl groups can be observed; that is, in the case of 4,4′-dialkylbiphenyl, the ring carbons at the *meta*-position reveal a chemical shift in the directions oppòsite to the chemical shift of the *para*-positions.

This is probably due to the *ortho-para* conjugation or to the inductive effect of the alkyl groups. The large value of the chemical shift at the *para*-position in the *meta*-alkylated biphenyl is a result of this effect being enhanced by the neighboring two alkyl groups.

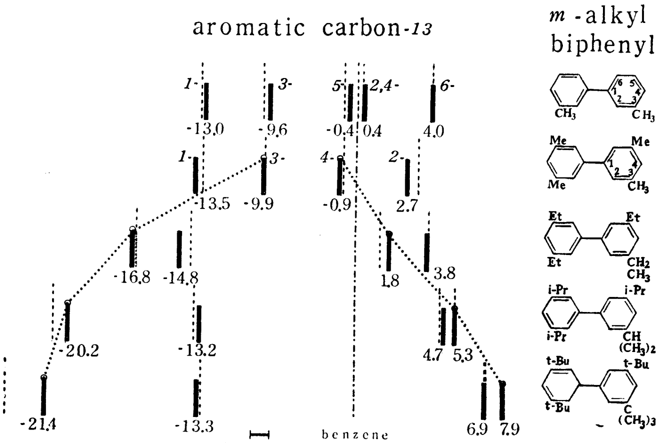


Fig. 3. The observed values and the calculated results of the aromatic carbon-13 chemical shifts for the *meta*-alkylated biphenyls.[11] (Solvent: THF).

HMO Calculation of Carbon-13 Chemical Shifts in Aromatic Ring Carbon. In order to put the present experimental results on a more rigorous theoretical base, the aromatic carbon-13 chemical shifts ($\Delta\sigma_i$) were calculated using the Karplus and Pople's equation[12] expressed as follows; $\Delta\sigma_{i\mathrm{PPM}} = (86.7 + 46.0\lambda_H)(\rho - 1) + 46.0(F - 0.399)$, where both the π-electron density (ρ) and the free valence (F) were calculated by the HMO method, and where the contribution due to the λ_H (polarity parameter of the C–H bond) is disregarded. For the treatment of the methyl group in the HMO calculation, we used two different models, the inductive (I) and the hyperconjugative models (II).

In the inductive model, any conjugative effect of the methyl group is disregarded, and the carbon to which the methyl group is attached is made somewhat more electropositive. The values of the Coulomb integral of these carbons, α_{CH_3} is estimated to be $\alpha_{CH_3} = \alpha - 0.2\beta$.

The hyperconjugation model has been proposed by Coulson and Crawford[13]; in it a linear combination of the hydrogen 1*s* orbitals is taken to give the pseudo π-orbital conjugating with the ring system. The parameters used in the HMO calculation of the methyl group ($>C_1-C_2\equiv H_3$) are;

$$\alpha_2 = \alpha - 0.1\beta, \quad \alpha_{H_3} = \alpha - 0.5\beta$$

$$\beta_{C_1-C_2} = 0.7\beta, \quad \beta_{C_2\equiv H_3} = 2.5\beta.$$

The results of 4,4′-dimethylbiphenyl, 3,3′-dimethylbiphenyl, and 3,3′,5,5′-tetramethylbiphenyl are given in Table 1. It may be seen that the hyperconjugative model gives a more or less satisfactory prediction of the aromatic carbon-13 chemical shift, except for the *para*-position of the 3,3′,5,5′-tetramethylbiphenyl, although the tendency of the observed chemical shift

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[11] Bold lines indicate the observed chemical shifts of the aromatic carbons and dotted lines correspond to the values of the chemical shifts calculated on the basis of the assumption of additivity rule. The chemical shifts are indicated such that positive ppm is to high field (to the right hand in each figure) of the shift from that of the carbon atoms of benzene (0 ppm) as an reference.

[12] M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

[13] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, **1953**, 2052 (1953).

Table 1. The observed and calculated aromatic carbon-13 chemical shift of 4,4′-dimethylbiphenyl, 3,3′-dimethylbiphenyl and 3,3′,5,5′-tetramethylbiphenyl (ppm)

4,4′-Dimethylbiphenyl

Position	Obsd	Calculated		
		Additivity	Inductive	Hyperconjugative
1	−10.0	−10.3	−11.1	−12.3
2	+1.6	+1.8	+1.8	+1.7
3	−1.1	−1.5	+2.6	+0.7
4	−8.0	−8.4	−6.1	−7.4

3,3′-Dimethylbiphenyl

Position	Obsd	Calculated		
		Additivity	Inductive	Hyperconjugative
1	−13.0	−13.2	−12.7	−12.7
2	+0.4	+0.3	+4.6	+2.6
3	−9.6	−9.9	−6.8	−7.6
4	−0.4	0.0	+3.3	+1.4
5	−0.4	−0.7	−0.3	−0.2
6	+4.0	4.0	+3.4	+2.1

3,3′,5,5′-Tetramethylbiphenyl

Position	Obsd	Calculated		
		Additivity	Inductive	Hyperconjugative
1	−13.5	−13.5	−12.8	−12.7
2	+2.7	+3.3	+6.3	+3.0
3	−9.9	−9.8	−7.0	−8.0
4	−0.9	−0.7	+6.0	+2.3

can also be qualitatively understood using the inductive model. It is interesting to see how the tendency of the observed ring carbon-13 chemical shift can be understood in terms of the HMO calculation for higher alkylated biphenyls.

For the sake of simplicity, we carried out the HMO calculation taking the Coulomb integral of the aromatic carbon, α_R, bonded to the higher alkyl group (R), $\alpha_R=\alpha-\delta\beta$.

The relation between the calculated carbon-13 chemical shift and the value of δ is plotted in Fig. 4 and Fig. 5.

In the case of the *para*-derivatives (Fig. 4), the theoretical value of the aromatic carbon-13 chemical shift of the *para*-position ($\Delta\sigma_4$) shows an increased lower-field shift with an increment of δ, while, conversely, a higher-field shift is predicted for the *meta*-position. The tendency of the observed ring carbon-13 chemical shift resulting from the higher alkyl substitution is also well explained for *meta*-derivatives (Fig. 5) in terms of the inductive parameter, which increases in the order of methyl, ethyl, isopropyl, and *t*-butyl groups.

These calculations thus support the idea that the hyperconjugative effect not only gives drastic lower-field shifts for the ring carbon atoms bonded to the alkyl groups, but also results in an auxiliary alternative shift on the next-nearest ring carbon atoms.

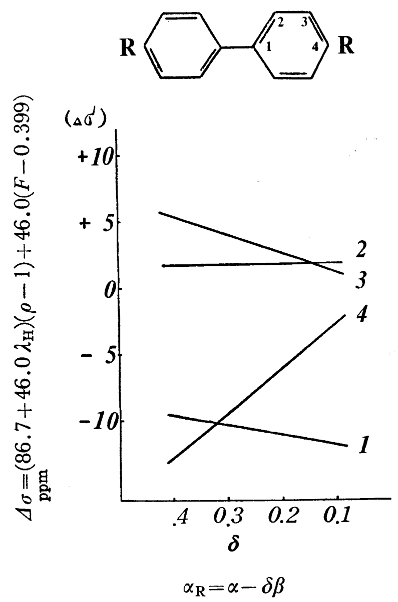

Fig. 4. The relation between the HMO carbon-13 chemical shift and the value of δ in 4,4′-dialkylated biphenyls.

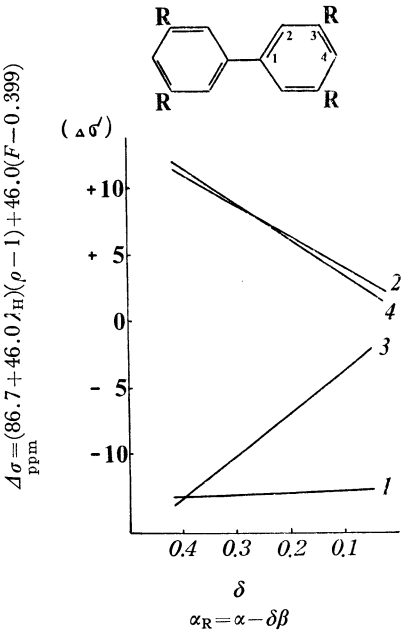

Fig. 5. The relation between the HMO carbon-13 chemical shift and the value of δ in 3,3′,5,5′-tetraalkylated biphenyls.

Ortho-alkylated Biphenyls. The observed chemical shifts of the ring carbons in several *ortho*-substituted biphenyls are given in Table 2. The analysis of the spectra of *ortho*-derivatives is much more difficult than *para*- or *meta*-derivatives, because we cannot make a quantitative assignment using the additivity rule such as was done for the *para*- and *meta*-derivatives. The HMO calculations of the aromatic carbon-13 chemical shift were carried out for the 2,2′,6,6′-tetramethylbiphenyl, where the Coulomb integrals of the *ortho*-ring carbon atoms were taken as $\alpha-0.2\beta$ and were the resonance integral of the 1–1′ bond was estimated to be

TABLE 2. THE OBSERVED AROMATIC CARBON-13 CHEMICAL SHIFT OF 2,2'-DIALKYLATED BIPHENYL

Substrate	Position 1	2	3	4	5	6
2,2'-dimethylbiphenyl	−13.2	−7.2	−1.7	−1.2	+2.3	+0.9
2,2'-diethylbiphenyl	−12.7	−13.6	−1.7	−0.1	+2.7	+0.5
2,2'-diisopropylbiphenyl	−12.3	−18.6	+3.0	−1.7	+3.0	+0.4
2,2'-di-*t*-butylbiphenyl	−12.8	−18.0	+4.2	−4.3	+1.4	−0.6

TABLE 3. THE OBSERVED AND CALCULATED AROMATIC CARBON-13 CHEMICAL SHIFT OF 2,2',6,6'-TETRAMETHYLBIPHENYL

Position	Obsd	Additivity	Calculated $\theta=0°$	30°	45°	60°
1	−11.7	−14.7	−8.2	−7.0	−5.2	−2.6
2	−7.2	−8.0	−4.8	−5.2	−5.9	−6.3
3	+0.3	+1.5	+4.5	+4.5	+4.6	+4.6
4	+0.8	+0.7	+0.7	+0.5	+0.2	−0.1

There are large discrepancies between the observed values and those calculated; however, this will probably means that the contribution of the σ orbital should be taken into account.

$\beta\cos\theta$ as a function of the twisting angle (θ) of the two phenyl rings. The results are shown in Table 3. The calculations of the chemical shifts by the foregoing inductive model, however, could not be related to the observed values in the same manner as the *meta*- and *para*-alkylated biphenyls were. Therefore, these assignments are only qualitative.

Chemical Shifts of Aliphatic Carbon. The chemical shifts of aliphatic carbon-13 atoms for *para*-, *meta*-, or *ortho*-alkylated biphenyls are presented in Figs. 6—9. In the cases of *para*- or *meta*-alkylated biphenyls, the observed chemical shifts of the aliphatic carbon agree with the values of the corresponding alkylated benzenes within the limits of experimental error. In the case of *ortho*-alkylated biphenyls, such as 2,2'-dimethylbiphenyl (II) and 2,2',6,6'-tetramethylbiphenyl (III)

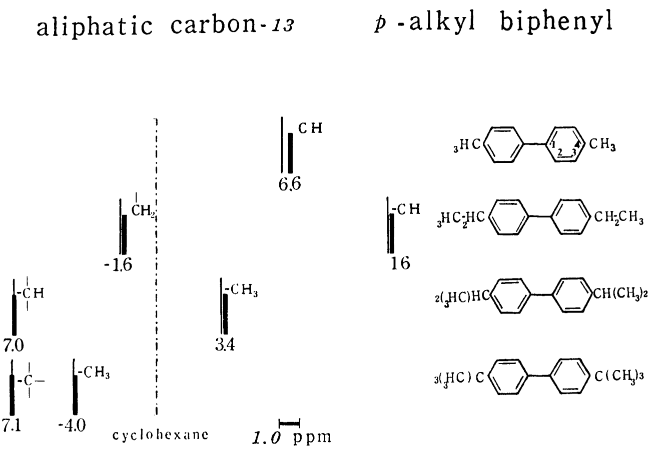

Fig. 6. The observed values of aliphatic carbon-13 chemical shifts for the *para*-alkylated biphenyls.[14] (Solvent: THF)

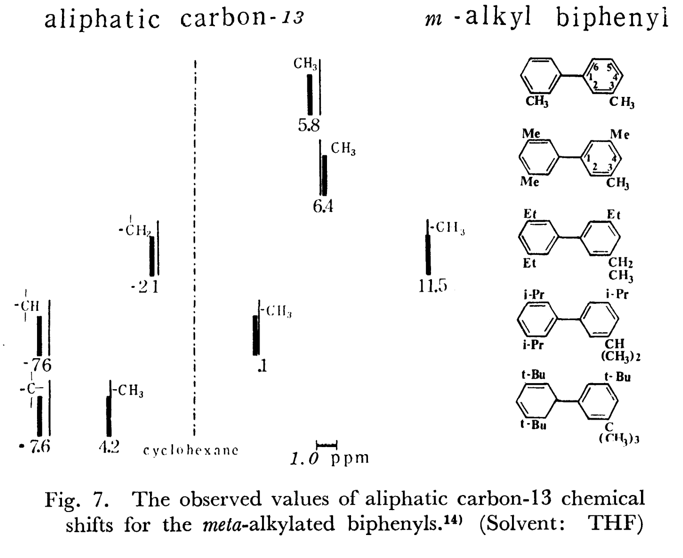

Fig. 7. The observed values of aliphatic carbon-13 chemical shifts for the *meta*-alkylated biphenyls.[14] (Solvent: THF)

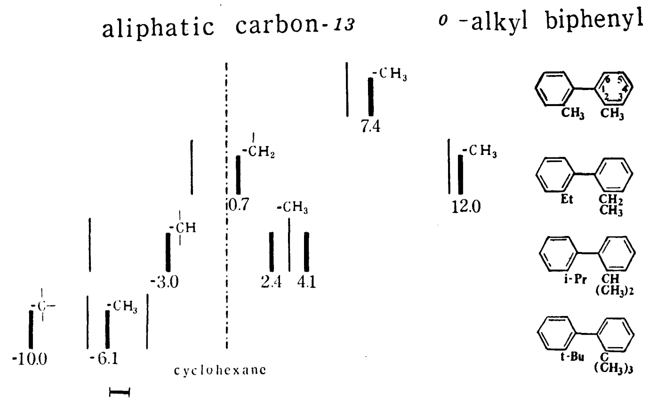

Fig. 8. The observed values of aliphatic carbon-13 chemical shifts for the *ortho*-alkylated biphenyls.[13] (Solvent: THF).

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[14] The bold lines indicate the observed chemical shifts and the narrow lines indicate those of aliphatic carbons in alkylated benzene. The chemical shifts were indicated in units of positive ppm to high field (to the right hand in each figure) taking the shift of the carbon atoms of cyclohexane (0 ppm) as a reference.

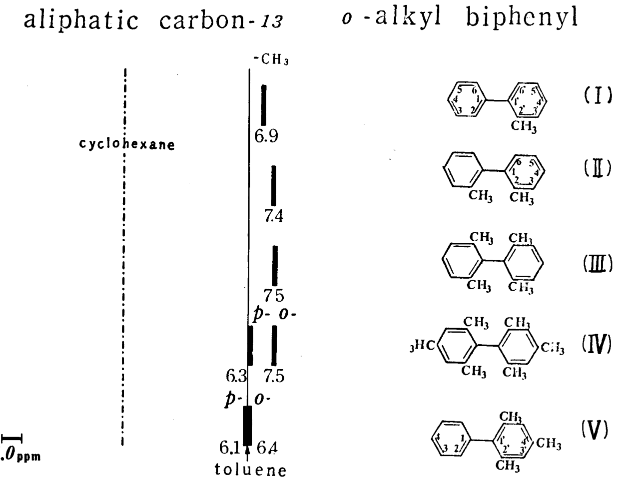

Fig. 9. The observed values of aliphatic carbon-13 chemical shifts for the *ortho*-methyl biphenyls. (Solvent: THF).

in Fig. 9, however, the chemical shifts of the methyl carbons shows a field shift higher by about 1 ppm than that of the corresponding toluene.

A similar higher-field shift is noted in the methyl protons, as is shown in Fig. 10; that is, the proton chemical shifts in the *ortho*-methyl groups also increase by about 0.4 ppm, thus exceeding the value for the methyl protons of toluene. These facts have already been understood in terms of the effect of the ring current[15] induced by the rotating biphenyl group[3,4]. It should be noticed, however, that a similar explanation is not always valid in all cases of the present investigation; a definite difference in the chemical shifts of carbon-13 NMR at the *ortho*-methyl groups is explicitly observed between the 2,4,6-tri-

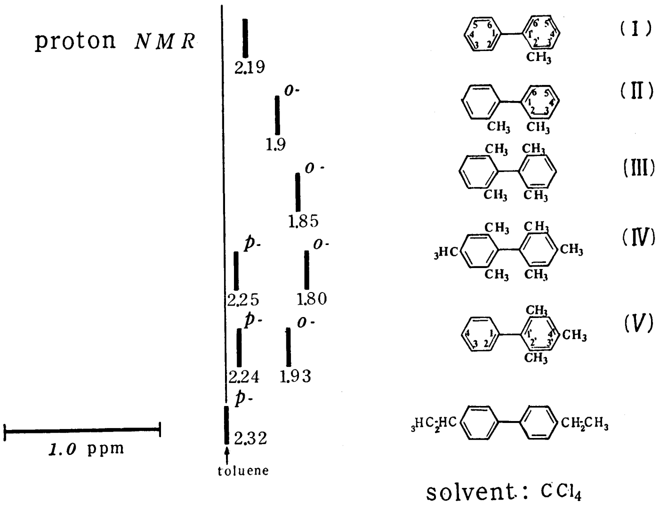

Fig. 10. The observed values of aliphatic proton chemical shifts for the *ortho*-methyl biphenyls. (Solvent: CCl_4).

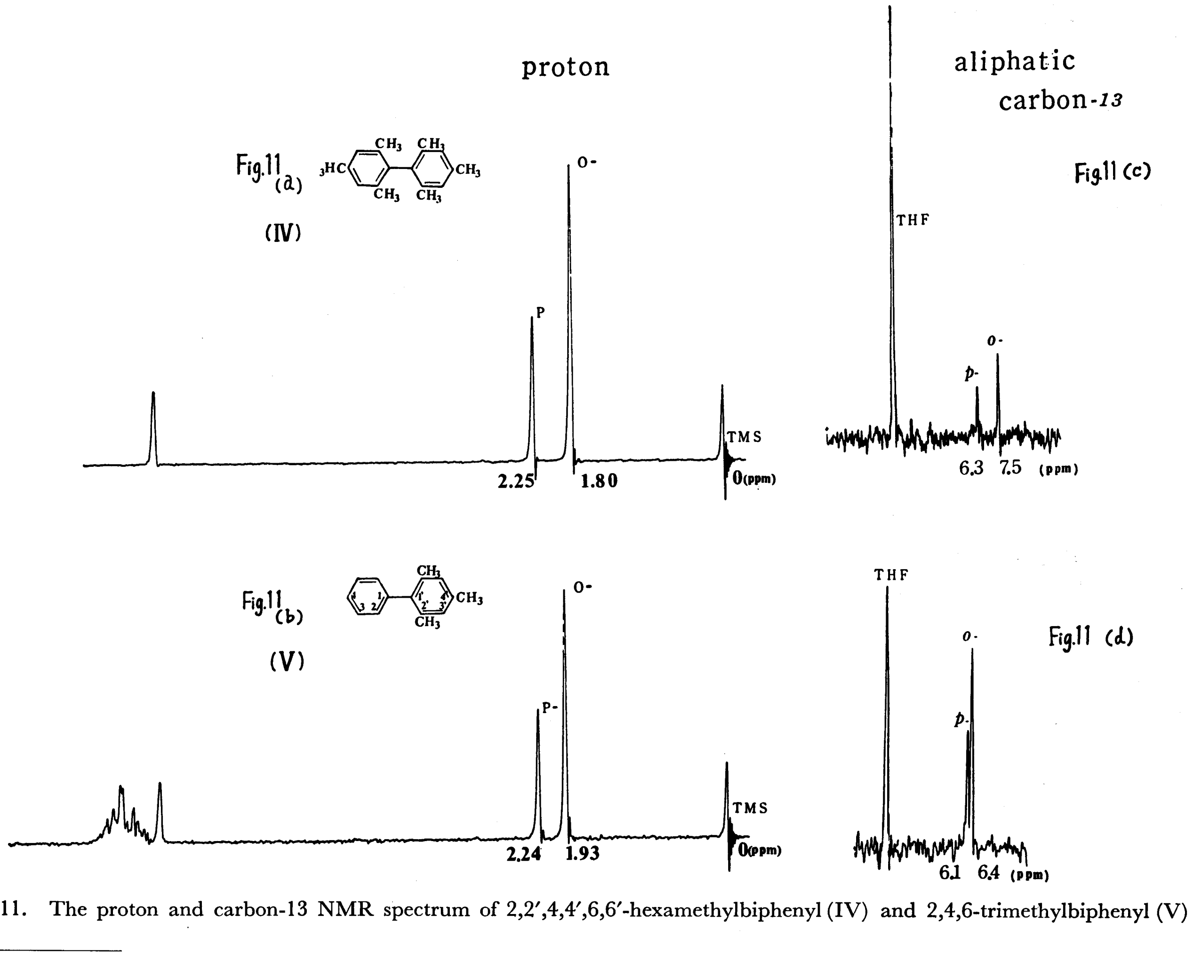

Fig. 11. The proton and carbon-13 NMR spectrum of 2,2′,4,4′,6,6′-hexamethylbiphenyl (IV) and 2,4,6-trimethylbiphenyl (V).

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[15] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

methylbiphenyl (V) and the 2,2′,4,4′,6,6′-hexamethylbiphenyl (IV), as is shown in Figs. 11-c and d. The results of these anomalous carbon-13 chemical shifts cannot be explained only on the basis of the ring-current model, since the effect of the ring current can be expected to be nearly the same in both cases.

On the basis of the present results, one may speculate that the difference in the chemical shifts of the *ortho*-methyl groups is responsible for that in the short-range interaction across the neighboring 2,2′-dimethyl groups. If this is the case, the interaction may arise from an orbital overlap between the methyl groups, which will approach one another to take the *cis*-conformation, because, in the case of V, one cannot expect such interactions. On the other hand, for IV two pairs of *ortho*-methyl groups can be accessible through a rotation around the central C–C bond of the biphenyl ring. From this point of view, the chemical shifts of the aliphatic carbon-13 of the other 2,2′-substituted derivatives cited in Fig. 8 may be reasonably understood by assuming a space interaction between the two alkyl groups. The present results for carbon-13 NMR lead to the assumption that the 2,2′-alkyl biphenyls are likely to take the *cis*-conformation rather than the *trans*-form, as was previously proposed by Suzuki.[2] If the two methyl groups in the molecular structure of II have the *trans*-conformation, the chemical shifts for the methyl groups will have values near the chemical shift which V indicates.

We are grateful to Miss Keiko Suzuki for her HMO calculations.