Carbon-13 Nuclear Magnetic Resonance Studies of Biphenyl Derivatives II. FT-NMR of Halobiphenyls[1)]

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The natural-abundance ^{13}C NMR spectra of the *ortho-* or the *para*-halobiphenyls were obtained by the pulse Fourier transform NMR (FT–NMR). For the *para*-derivatives, the observed chemical shifts of the C_1, C_2, and C_3-positions gave an excellent linear dependence on the electronegativity of the substituents. The dependence for the C_4-position, which showed a deviation from the linear plot, may be due to the heavy atom effects. The additivity of the chemical shifts holds also for the *ortho*-derivatives except for the cases of the bridgehead carbons, the C_1 and C_1'-positions. In particular, the observed chemical shifts of the C_2, C_3, and C_4 positions for 2,2′,6,6′-tetrachlorobiphenyl showed a good agreement with the predicted values, whereas a large discrepancy can be seen between the observed and the assumed values for the C_1 and C_1' positions. The effects on the chemical shifts due to the steric hindrance are discussed by comparison with the results of the hindered alkylbiphenyls. The temperature dependence of the spin-lattice relaxation time was investigated for 4,4′- and 2,2′-dichlorobiphenyls. The activation energies of the molecular reorientation are negligibly small at the C_1, and C_4-positions for the *para*-derivative, but the *ortho*-derivatives have higher values at these positions, indicating anisotropy for the molecular motion.

The recent greater facility of ^{13}C FT-NMR spectroscopy has promised to better results from structural and dynamic studies of organic molecules. In particular, the measurements of the spin-lattice relaxation time (T_1) can yield useful information about molecular motion.[2,3)] In the present work, ^{13}C FT NMR measurements were carried out on 4,4′-dihalobiphenyls, 4-halobiphenyls and several *ortho*-substituted chlorobiphenyls. The substituent effects of halogen atoms were studied in terms of the electronegativity of the substituents. The effects on the chemical shifts due to the steric hindrance were investigated on the basis of the additivity calculation and compared with the results of the previous works on the hindered alkylbiphenyls.[4)] The spin-lattice relaxation times of the ring carbons were measured for 4,4′-dichlorobiphenyl and 2,2′-dichlorobiphenyl, and the activation energies of the molecular reorientation were estimated from the temperature dependence of the spin-lattice relaxation time. The activation energies for the C_1 and C_4 positions were negligibly small, and those for C_2 and C_3 showed nearly the same value in the case of the *para*-derivative. This means that the molecule is likely to rotate around the long axis of biphenyl. In the case of the *ortho*-derivative, however the activation energy values increased at both C_1 and C_4 positions, suggesting that a molecular motion may be greatly hindered in the direction of the long molecular axis. The D_2O used for the NMR lock was also filled outside the spherical tube. The concentration of the samples used for the T_1 measurements was adjusted so as to make a 30% solution in THF. The reproducibility of the T_1 values was better than 10%.

Experimental

All the ^{13}C NMR spectra were recorded with a JEOL PS/PFT-100 spectrometer equipped with a Fourier transform operation at 25.15 MHz under a complete proton decoupling. Benzene was used as the external reference, and the chemical shifts were measured within limits of experimental error of about 0.1 ppm. The following materials were synthesized and recrystallized from ethanol (the physico-chemical indices are given): 4-fluorobiphenyl (mp 74.2—75 °C), 4-chlorobiphenyl (mp 72—72.5 °C), 4-bromobiphenyl (mp 79.5—80 °C), 4-iodobiphenyl (mp 112—113 °C), 4,4′-difluorobiphenyl (mp 88—89 °C), 4,4′-dichlorobiphenyl (mp 149—150 °C), 4,4′-dibromobiphenyl (mp 162—163 °C), 4,4′-diiodobiphenyl (mp 199—202 °C), and 2,2′-dichlorobiphenyl (mp 58—59 °C). The 2,2′,6,6′-tetrachlorobiphenyl and 2,6-dichlorobiphenyl were purchased from the Japan chromatograph Co., Ltd. The purity of the material was checked by means of the proton NMR spectra. The samples were prepared as approximately a 10—30% solution in tetrahydrofuran (THF).

The measurements of the spin-lattice relaxation time (T_1) were carried out using the Inversion Recovery Method[5)] and the Progressive Saturation Method.[6)] The pulse width was 20 μs for 90° pulse in all the experiments. In these experiments, spherical tubes, which were placed in standard tubes, were employed to reduce the inhomogenity of the external field (H_0) and the rf field (H_1).

Results and Discussion

The ^{13}C NMR spectra of 4,4′-difluorobiphenyl and 4,4′-dichlorobiphenyl observed at room temperature are given in Fig. 1. The spectra can be easily analyzed on the basis of the predictions of additivity calculations.[7)] An extra splitting of the ^{19}F ($I=1/2$) nucleus can be seen in Fig. 1, where the magnitude of the spin-spin coupling constant alters as a function of the distance between the ^{13}C and ^{19}F nuclei. The calculated chemical shifts of 4,4′- and 4-halobiphenyls, summarized in Table 1, are in satisfactory agreement with the observed values. In order to study the substituent effects in the *para*-derivatives, plots were made between the observed chemical shifts and the electronegativity. As is shown in Fig. 2, the plots for C_1 and C_3 give straight lines, indicating that they are positive-dependent on the absolute value of the electronegativity, conversely, those for the C_2 and C_4 positions show a

Table 1. The ^{13}C chemical shifts of 4,4′-dihalobiphenyl and 4-halobiphenyl (ppm)

4,4′-Dihalobiphenyl		C-1	C-2	C-3	C-4				
H	Observed	−13.1	1.3	−0.5	1.1				
F[a]	Observed	−8.4	−0.4	12.7	−37.0				
	Predicted	−8.8	−0.5	12.7	−33.8				
Cl	Observed	−10.3	−0.1	−0.8	−5.4				
	Predicted	−11.3	−0.2	−0.7	−4.9				
Br	Observed	−10.7	−0.4	−3.8	6.4				
	Predicted	−11.7	−0.5	−3.7	6.9				
I	Observed	−16.6	−0.4	−9.9	34.9				
	Predicted	−12.2	−0.7	−9.7	34.9				
4-Halobiphenyl		C-1	C-2	C-3	C-4	C-1′	C-2′	C-3′	C-4′
F[b]	Observed	−9.4	−0.3	12.7	−34.5	−12.1	1.3	−0.8	0.9
	Predicted	−8.8	−0.4	12.4	−38.7	−13.1	1.3	−0.5	1.1
Cl	Observed	−11.3	−0.2	−0.7	−5.4	−11.5	1.4	−0.7	1.1
	Predicted	−11.3	−0.2	−0.7	−4.9	−12.1	1.3	−0.5	1.1
Br	Observed	−11.8	−0.9	−3.9	6.7	−12.2	0.3	−0.8	1.2
	Predicted	−7.7	−1.3	−4.8	7.6	−13.3	1.2	−0.8	1.0
I	Observed	−12.4	−0.5	−9.6	35.5	−11.7	1.6	−0.5	0.7
	Predicted	−16.6	−0.4	−9.9	34.9	−13.1	1.3	−0.5	1.1

The chemical shifts are indicated that positive is to high field (to the right side) from benzene.

a) $J_{C-F}=245$ Hz $J_{C-C-F}=22$ Hz $J_{C-C-C-F}=8$ Hz

b) $J_{C-F}=255$ Hz $J_{C-C-F}=21$ Hz $J_{C-C-C-F}=8$ Hz

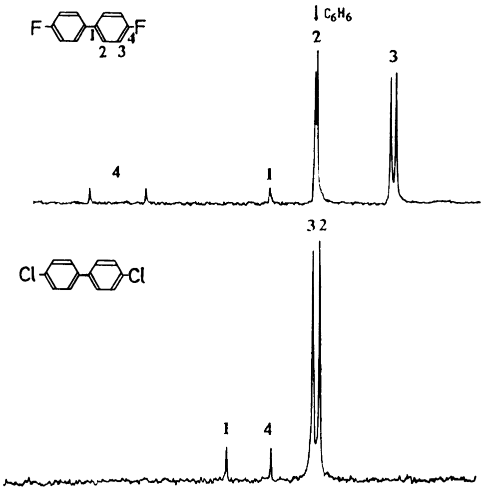

Fig. 1. ^{13}C FT-NMR spectra of 4,4′-difluorobiphenyl and 4,4′-dichlorobiphenyl.

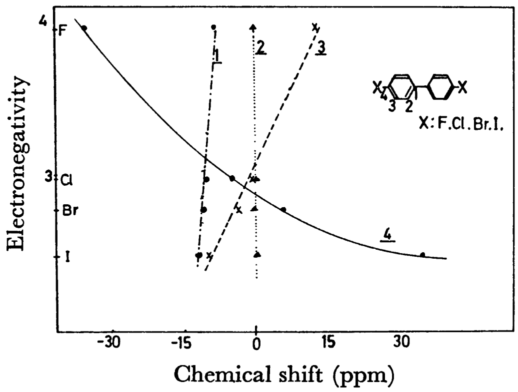

Fig. 2. Relation between the observed chemical shifts and the electronegativity of the substituents in 4,4′-dihalobiphenyls.

The electronegativity were taken from L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, New York (1940).

negative-dependence. Similar alternative effects of the substituents, which were previously confirmed by the proton NMR of the 4,4′-dihalobiphenyl, have also been reported in ^{13}C NMR studies of the alkylbiphenyls. The plots of the C_4-position only revealed a remarkable deviation from the straight line. This can probably be attributed to the heavy-atom effects of the halogen atoms.[8] It is of interest to compare the observed chemical shifts and predicted values in the *ortho*-derivatives, since the discrepancy between them may be attributed to the effect of a steric hindrance. In Table 2 we give the observed and the predicted ^{13}C

Table 2. The ^{13}C chemical shifts of 2,6-dichlorobiphenyl, 2,2′-dichlorobiphenyl and 2,2′,6,6′-tetrachlorobiphenyl

		C-1	C-2	C-3	C-4	C-1′	C-2′	C-3′	C-4′
2,6-Cl	Observed	−12.6	−6.9	−0.4	−1.8	−9.2	0.4	−1.6	0.2
	Predicted	−14.9	−7.0	−0.4	−1.7	−13.1	1.3	−0.5	1.1
		C-1	C-2	C-3	C-4	C-5	C-6		
2,2′-Cl	Observed	−10.5	−5.5	−3.4	−1.5	1.8	−1.5		
	Predicted	−13.3	−4.6	−0.7	−0.5	1.3	−0.2		
2,2′,6,6′-Cl	Observed	−7.2	−7.0	−0.3	−3.0				
	Predicted	−14.9	−7.6	−0.4	−3.0				

2,6-Cl: 2,6-dichlorobiphenyl 2,2′-Cl: 2,2′-dichlorobiphenyl 2,2′,6,6′-Cl: 2,2′,6,6′-tetrachlorobiphenyl chemical shifts of 2,2′-dichlorobiphenyl, 2,6-dichlorobiphenyl, and 2,2′,6,6′-tetrachlorobiphenyl. It is rather surprising that the additivity calculation gave more or less suitable results for the ring carbons, except for the values of the bridgehead C_1 and C_1' positions. Similar results for the proton NMR chemical shifts have previously been reported for 2,2′-dichlorobiphenyl.[9] This suggests that the anisotropic effect of the ring current is reduced by the large electronegativity of the halogen atoms. As can be seen in Table 2, however, the observed shifts of the C_1 and C_1' atoms show a remarkable deviation, shifting higher by about from 2.3 to 2.5 ppm in dichlorobiphenyl and by 7.7 ppm in 2,2′,6,6′-tetrachlorobiphenyl, exceeding the calculated values by the additivity rule. A similar large discrepancy between the observed and the predicted C_1 chemical shifts has already been demonstrated for hindered alkylbiphenyl. One may consider several cooperative mechanisms[10] which modify the chemical shift for the *ortho*-derivatives. The first is the perturbation of the π-bond order between the central C_1–C_1' bond or that of the charge density on the bridgehead carbon atoms due to the steric hindrance. In the present case, however, the first effect is not important, because the observed chemical shifts of the other position (C_2, C_3, C_4) are nearly the value calculated for the planar biphenyl. Recently, the importance of the short-range interaction has been demonstrated between non-bonded atoms which are accessibly located in hindered molecules.[4,11,12] In such a case, a large higher shift (a so-called compression shift) has been observed for the carbon atoms bonded to the carbon interacting together this shift is due to the electronic repulsion. No such effect can be seen for the *ortho*-carbon atoms of the present derivatives. This suggests that the two phenyls are almost perpendicularly twisted in the hindered halobiphenyls.[13] In such a case, these anomalous discrepancies in the C_1-chemical shift may be considered to result from some interaction between the chlorine and $2p_z$ carbon atomic orbitals, but a more rigorous explanation will need further investigations.

Carbon-13 Spin-lattice Relaxation Time. When analyzing ^{13}C spin-lattice relaxation time, three possible relaxation mechanisms may be considered. One is the chemical-shift anisotropy (CSA), and another is spin-rotation (SR) and ^{13}C–^{1}H dipole-dipole interactions.[2,14,15] The third mechanism is expected to be predominant for the protonated carbons. It has been relatively easy to observe the ^{13}C relaxation under complete proton decoupling.[16] In this case, if the rotational reorientation of the molecule is isotropic, the ^{13}C–^{1}H dipole relaxation contributes to the $1/T_1$ of all the protonated carbons to the same extent. The ^{13}C–^{1}H dipole-dipole relaxation becomes:

$$1/T_1 = K\{f(\omega_H-\omega_C)+3f(\omega_C)+6f(\omega_H+\omega_C)\} \qquad (3)$$

where:

$$f(\omega_i) = \tau_R(1+\omega_i^2\tau_R^2)^{-1} \qquad (4)$$

$$K = \hbar^2\gamma_H^2\gamma_C^2r^{-6} \qquad (5)$$

The τ_R is the rotational correlation time, r is the C–H distance, and γ_H and γ_C are the gyromagnetic ratios of the proton and carbon nuclei respectively. For all cases, we have $(\omega_C+\omega_H)\tau_R \ll 1$, and Eq. (3) can be reduced to the familiar results;

$$1/T_1 = \hbar^2\gamma_H^2\gamma_C^2\tau_R r^{-6} \qquad (6)$$

Equations (3)—(6) can be suitably modified, however, either when the rotational reorientation of the molecule is anisotropic or when an internal motion of the functional group must be considered.[15] If the anisotropic motion (τ_G) is much slower than the overall reorientation ($\tau_R(\tau_G \gg \tau_R)$), the relaxation time becomes identical to the suitably-modified Eq. (6). In this case, an internal motion has little effect on $1/T_1$, and τ_G can be estimated only with difficulty. On the other hand, however, if an anisotropic motion is much faster than the overall reorientation ($\tau_G \ll \tau_R$), the relaxation can be easily understood on the basis of Eqs. (3) and (6). One may thus expect that T_1 values do not depend on the correlation time for the overall reorientation, but will be affected by an internal motion. In the *para*-position, T_1 is shorter than those for the carbon atoms at the *ortho*- and the *meta*-positions as a result of the preferred rotation about the symmetry axis. The bulky substituents of benzene that are axially symmetric causes the T_1 *ortho*/T_1 *para* and T_1 *meta*/T_1 *para* ratios to become larger, while substituents without axial symmetry lead to these ratios approaching 1.0.[17] In rod-shaped molecules such as diphenyl diacetylene, the T_1 value for the *para*-carbons is five times shorter than the T_1 for the *ortho*- and *meta*-carbons.[2]

In order to see the motional anisotropy in the present biphenyl derivatives, the temperature dependence of the T_1 values was investigated for 4,4′-dichlorobiphenyl and 2,2′-dichlorobiphenyl.

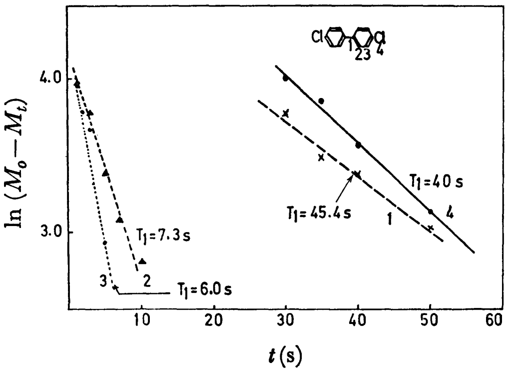

Fig. 3. Spin-lattice relaxation times of ^{13}C nuclei in proton decoupled 4,4′-dichlorobiphenyl.

The relaxation behavior of the ring carbons in 4,4′-dichlorobiphenyl is shown in Fig. 3.[18] The *ortho*-carbon relaxation of 4,4′-dichlorobiphenyl is nearly identical with that of the *meta*-carbons, since the anisotropic motion of this molecule dominates around the long biphenyl axis.

In general, the observed spin-lattice relaxation time T_1 can be divided into two contributions:

$$1/T_1 = (1/T_1)_D + (1/T_1)_0 \qquad (7)$$

where the first term is the contribution of the dipole-dipole interaction and where the second term includes those of all the other mechanisms, in which the spin-rotation mechanism and the chemical-shift anisotropy

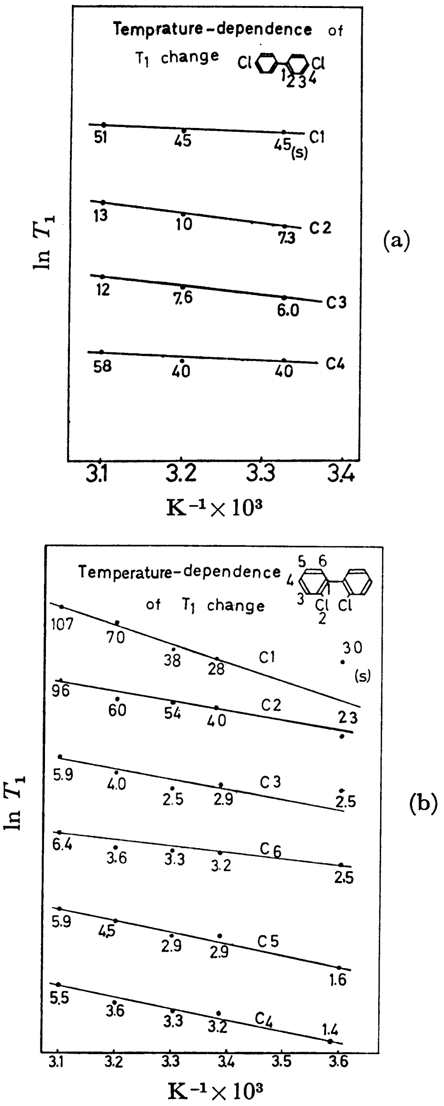

Fig. 4. Temperature dependence of the spin-lattice relaxation times for chloroderivatives.
a) 4,4′-dichlorobiphenyl, b) 2,2′-dichlorobiphenyl.

have been considered to be most important.[2)] If the contribution of the spin-rotation relaxation is really important, the temperature dependence on the relaxation time will show a tendency opposite to those due to the other relaxation mechanisms.[14)] At present, we have no strong experimental basis on which to characterize the relaxation mechanism of each carbon atom, but we have assumed that the dipole relaxation will be dominant for all carbon atoms; that is, $(T_1)_D \simeq T_1$, since the ^{13}C-resonance lines show nearly the same intensity ratio as that calculated from the numbers of the equivalent carbon atoms in the biphenyl ring. As is illustrated in Fig. 4, the T_1 curves show a temperature dependence of the Arrhenius type on the high-temperature side of their minima and the temperature dependence of τ_R is given by:

$$\tau_R = \tau_R{}^0 \exp (E_a/RT) \qquad (8)$$

where E_a is the activation energy for the molecule reorientation. The apparent activation energy can be calculated from the slope of the plot, as is summarized in Table 3. The E_a values of the C_2 and C_3 positions are almost equal, but those for C_1 and C_4 positions are all negligibly small in the case of the *para*-derivative. This indicates that the rotation of the moecule is overwhelmingly dominant around the long axis of biphenyl. On the other hand, the E_a values of both C_1 and C_4 positions become much higher than those of the other positions in the *ortho*-derivative. This indicates that the partial motion of the phenyl would be greatly modified by the steric hindrance, in particular around the long axis of biphenyl.

Table 3. Activation energy (kcal/mol)

	C1	C2	C3	C4	C5	C6
4,4′-Cl	—	5.1	5.6	—		
2,2′-Cl	9.8	5.7	6.3	8.1	6.0	5.8

4,4′-Cl: 4,4′-dichlorobiphenyl.
2,2′-Cl: 2,2′-dichlorobiphenyl.

The temperature dependence of the C_1 and C_3 positions, which changes the slope at around 10 °C, suggests some contribution from the other relaxation mechanisms. The spin-rotational relaxation is most probable, but detailed investigations are now under way.

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18) M_0 is the line intensity of longest pulse sequence ($t \simeq 4T_1$) and M_t is that of a given pulse interval (t) in the steady state. For any line, the quantity (M_0–M_t) was found to be an exponential function of t, and the time constant was given to the spin-lattice relaxation time.