with the two downfield peaks and the two upfield peaks coinciding with the downfield and upfield doublet lines of the AB spectrum, respectively (see Figure 5). Using the notation of ref 17, the intensity ratio of line 3 to line 4 for the AB spectrum and the ratio of lines 5 + 6 to lines 7 + 8 for the AB_2 spectrum are identical to order $(J/\Delta\nu)^2$ (eq 12 and 13).

For the spectra considered, $J/\Delta\nu = 0.16$ so that the error is $\lesssim 0.4\%$ and we can treat the doublet as arising from nearest neighbor coupling only with very little error. (Note: these ratios are the inverse of the ratios given in the text.)

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(1) This work performed under the auspices of the U.S. Atomic Energy Commission.
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(23) For ^{13}C nuclei not directly bonded to hydrogens, ^{13}C–^{13}C dipolar relaxation can contribute significantly to T_1. As a result, the Overhauser enhancements for the singlet will be greater than that for the multiplets due to three spin effects. The relative intensities of the singlet and multiplet lines will then not reflect the labeling probabilities in the decoupled spectrum. However, accurate values can be obtained by examining the coupled spectrum for these carbons. A preliminary study of these effects has been submitted to *J. Magn. Reson.*

Carbon-13 Nuclear Magnetic Resonance. ^{13}C Shieldings and Spin–Lattice Relaxation Times in Chlorinated Biphenyls

Nancy K. Wilson

Contribution from the National Institute of Environmental Health Sciences, Research Triangle Park, North Carolina 27709.

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Abstract: Carbon-13 shieldings were measured for 25 chlorinated biphenyls. For 13 of these, the ^{13}C assignments of the protonated carbons were confirmed by selective proton decoupling. The effects of chlorine substitution on the ^{13}C shieldings could be approximately predicted using additive parameters obtained from chlorobenzene and 2-, 3- and 4-chlorobiphenyl data. Marked deviations from the predicted substituent effects occur when chlorines are ortho on the same ring or in 2 and/or 6 positions on both rings. The effects of a chlorine substituent are significantly transmitted through eight covalent bonds. Spin–lattice relaxation times were measured for the protonated carbons in several biphenyls. The relaxation is dominated by the carbon–hydrogen dipole–dipole interaction, which results in maximum nuclear Overhauser enhancements. The relaxation times are related to the rotational barriers about the interring bond.

Polychlorinated biphenyls (PCBs) are of considerable current interest because of their ubiquitous distribution and their remarkable persistence in the natural environment. Investigations centering about their identification in complex mixtures and their biological interactions have been numerous.[1] Several biological studies have indicated that certain PCB isomers are preferentially concentrated in living organisms. Evaluation of the potential health hazards associated with this class of compounds therefore clearly requires knowledge of the characteristics of specific PCB isomers.

Nuclear magnetic resonance, as an analytical tool sensitive to molecular structure, electronic charge distributions, and molecular interactions, is useful for discrimination between the many PCB isomers[2-4] and for study of the different potentials of these isomers for interactions in biological systems. Certain NMR parameters such as ^{13}C spin–lattice relaxation times can be interpreted in terms of molecular motion[5,6] and stereochemistry. Knowledge of the NMR parameters may thus allow more meaningful examinations of the biological effects of PCBs.

Proton NMR data at 220 MHz for a large number of PCBs have been reported,[3] as well as some data at 60 MHz.[4] Detailed analyses of the ^1H spectra of symmetrically substituted dihalobiphenyls[7] as well as several earlier studies of proton chemical shifts and substituent effects on these in halobiphenyls[8] are in the literature. Proton NMR in nematic liquid crystalline solvents has been used to investigate the conformation of 3,5,3′,5′-tetrachlorobiphenyl[9] and of 4,4′-dichlorobiphenyl,[10] but the first of these studies unrealistically predicts a single rigid conformation at room temperature. Fewer ^{13}C NMR studies of biphenyls have been published. Carbon-13 data for ten symmetrically substituted chlorinated biphenyls have been reported and related to trends in charge density distributions calculated by the CNDO/2 method.[2]

Recently, ^{13}C NMR data for some halobiphenyls including two additional chlorinated biphenyls have been published, together with the results of examinations of the spin-lattice relaxation of 4,4′- and 2,2′-dichlorobiphenyl.[11] Other studies include two of alkylbiphenyls,[12] one of which[13] relates inflections in the temperature dependence of the T_1 values to motional differences resulting from rotational hindrance by ortho-ortho′ alkyl substituents, and several of biphenyl itself[14-16] and 3- and 4-bromobiphenyl.[17]

In this paper we report the ^{13}C shieldings for 25 chlorinated biphenyls, the protonated carbon assignments for 13 of which have been confirmed by selective proton decoupling. Substituent parameters describing the effects of chlorine substitution on the ^{13}C shieldings have been measured. Deviations from the shieldings predicted with these parameters assuming additivity of substituent effects are discussed in terms of the steric interactions of ortho or ortho-ortho′ substituents. Spin-lattice relaxation times, T_1 values, for the protonated carbons in several of the chlorinated biphenyls were measured. The effects of molecular motion and steric hindrance to rotation about the interring bond on the measured T_1 values are discussed. Some abortive attempts to calculate the rotational barriers about this bond using the CNDO/2 method[18] are mentioned briefly.

Experimental Section

Biphenyl and its 4-chloro-, 4,4′-dichloro-, 2,2′-dichloro-, and 2,4,5,2′,5′-pentachloro derivatives were obtained commercially. The remaining PCBs were synthesized in these laboratories. All were characterized by sharp melting points and no impurities were evident in the ^{1}H NMR spectra. Details of the syntheses are reported elsewhere.[19]

Samples for proton NMR analysis were approximately 2.5 mol % solutions in chloroform-d or in 3,3-dimethylpentane to which a small amount of tetramethylsilane, TMS, was added. The ^{13}C samples were approximately 0.6 M solutions in 1,2-dibromoethane-d_4 containing a few drops of TMS. Samples for some of the relaxation time measurements were degassed using five or six freeze-pump-thaw cycles on a vacuum line and sealed under vacuum.

All NMR spectra were obtained on a Varian XL-100-12 spectrometer with Fourier transform and a 16K 620/L computer. Proton spectra at the 5 mm probe ambient temperature of 28° were collected using a 1000-Hz sweep width and an acquisition time of 4.0 sec. Initial ^{13}C spectra were obtained at an ambient temperature of 40° in an 8 mm probe, using 4000-Hz sweep widths and an acquisition time of 1.0 sec. More precise internal aromatic carbon shielding measurements were made with an 800-Hz sweep width and a 5.0-sec acquisition time. Assignments of the protonated carbon resonances for those PCBs whose ^{1}H spectra had been previously determined were made by selective (single frequency) proton decoupling. An internal deuterium lock was used, except for experiments in 3,3-dimethylpentane, for which an internal proton lock and continuous wave (CW) operation were employed. All chemical shifts are reported on the δ scale, relative to internal TMS.

Spin-lattice relaxation times were measured using the standard inversion-recovery $[-T-180°-\tau-90°-]_n$ pulse sequence,[20,21] or with the Freeman-Hill modified version,[22] $[-T-90°-T-180°-\tau-90°]_n$. A sweep width of 500 Hz, an acquisition time of 1.6 sec, and a 111 μsec 90° pulse, corresponding to $\gamma H_1 = 2250$ Hz, were used. The waiting period between experiments, T, was set to be at least $5T_1$. The T_1 values were extracted from the inversion-recovery data by two-parameter (S_0, T_1) least-squares fitting of the exponential decay curve

$$S = S_0[1 - 2\exp(-\tau/T_1)] \tag{1}$$

where S is the signal amplitude at time τ and S_0 is the limiting equilibrium amplitude.

Nuclear Overhauser enhancement (NOE) measurements were made by comparison of the integrals of the coupled to the noise-decoupled ^{13}C spectra or by suppression of the NOE by gating the decoupler off during the long delay between pulses, and on only during the data acquisition.[14]

Table I. Proton Chemical Shifts of Several Chlorinated Biphenyls[a]

	δ, ppm				
Substitution	H-2	H-3	H-4	H-5	H-6
2,2′^{b,c}		7.252	6.869	6.907	7.006
3,3′^{b,c}	7.270		7.064	6.846	6.922
4,4′^{c}	7.402	7.466		7.466	7.402
2,4,2′,4′^{c}		7.510		7.319	7.183
2,5,2′,5′		7.399	7.321		7.266
2,6,2′,6′^{c}		7.448	7.330	7.448	
3,4,3′,4′^{c}	7.618			7.514	7.358
3,5,3′,5′^{c}	7.589		7.589		7.589
2,3,4,2′,3′,4′				7.461	7.087
2,3,6,2′,3′,6′			7.390	7.494	
2,4,5,2′,4′,5′		7.621			7.364
2,4,6,2′,4′,6′^{c}		7.468		7.468	
3,4,5,3′,4′,5′	7.536				7.536
2,4,5,2′,5′		7.596			7.353
		7.411^{d}	7.335^{d}		7.236^{d}

[a] At 28°; 2.5 mol % in chloroform-d, except as noted. [b] Approximately 3.5 mol % in benzene-d_6. [c] From ref 2. [d] For the 2′,5′-disubstituted ring.

Table II. Proton Coupling Constants for Several Chlorinated Biphenyls[a]

	J, Hz									
Substitution	23	24	25	26	34	35	36	45	46	56
2,2′^{b,c}					8.1	1.3	0.4	7.5	1.7	7.7
3,3′^{b,c}		2.1	0.5	1.8				8.0	1.0	7.9
4,4′^{c}	8.4		0.4	2.3		2.3	0.4			8.4
2,4,2′,4′^{c}						1.9	0.4			8.2
2,5,2′,5′					8.8		0.6		2.1	
2,6,2′,6′^{c}					8.1			8.1		
3,4,3′,4′^{c}			0.4	2.1						8.4
2,3,4,2′,3′,4′										8.4
2,3,6,2′,3′,6′								8.3		
2,4,5,2′,4′,5′							≤0.2			
2,4,5,2′,5′							≤0.2			
					9.5^{d}		0.8^{d}		2.1^{d}	

[a] At 28°; 2.5 mol % in chloroform-d, except as noted. [b] Approximately 3.5 mol % in benzene-d_6. [c] From ref 2. [d] For the 2′,5′-disubstituted ring.

All variable temperature and T_1 measurements were made with a 5-mm variable temperature probe and the Varian temperature controller. With 50:50 benzene-benzene-d_6 having a copper-constantan thermocouple centered in the sample, full noise-decoupling power raised the equilibrium sample temperature by approximately 2° with cooling gas flowing through the probe at 15 scfh, and the controller maintained this temperature within ±0.5° at the receiver coil and within ±1.5° over the ca. 3 cm depth of the sample. For each experimental spectrum, the probe temperature was measured before and after the run and the two results were averaged.

Results and Discussion

Proton NMR Parameters. The proton chemical shifts and coupling constants for several of the chlorinated biphenyls studied are presented in Tables I and II. Influences on these have been discussed in some detail elsewhere[2,3,7] and will not be treated further here. The individual proton resonance frequencies obtained from the ^{1}H spectra were used to irradiate specific protons selectively while obtaining the ^{13}C spectra and thus allow unambiguous assignment of the protonated carbon resonances in these biphenyls.

spectra and thus allow unambiguous assignment of the protonated carbon resonances in these biphenyls.

Carbon-13 Shieldings. Although the total range of the ^{13}C shieldings for the PCBs is only 16 ppm, distinct resonances were observed for most of the individual carbons, and the spectra of the individual isomers are sufficiently different that the ^{13}C spectra serve as a ready means of determination of the degree and pattern of chlorine substitution. Figure 1 illustrates this point with the ^{13}C spectra of biphenyl and its three monochloro derivatives. These spectra represent averages of 264 to 735 transients obtained in a total experiment time of 1.8 hr with 6% (w/v) samples.

As shown previously,[2] the ^{13}C assignments for biphenyls which can reasonably be expected to have free rotation about the interring carbon-carbon bond at room temperature can be approximately predicted assuming additivity of substituent effects and values of these effects obtained from data on chlorinated benzenes.[23,24] The selective decoupling experiments provided confirmation of these predictions for the protonated carbons in several cases. Spin-lattice relaxation times, discussed later in this paper, were also helpful in making assignments. Quaternary carbons were first assigned on the basis of their relative intensities. Since the dipole-dipole mechanism is a major relaxation mechanism for these carbons, although not the only one, the relative NOE values of their resonances reflect the relative distances to the nearest protons, because of the r^{-6} dependence of the NOE.[25] The intensity relationships in partially relaxed spectra provide additional information since for carbons with the same NOE and same effective rotational correlation time, the T_1 value for a carbon with two nearest neighbor protons will be half that for a carbon with one neighboring proton with the same carbon-proton distance.[17,26]

With the considerations outlined above, the ^{13}C spectra for biphenyl and 2-, 3-, and 4-chlorobiphenyl were assigned. These shieldings are given in Table III. Employing these data, values were obtained for the effects of a chlorine substituent on the ^{13}C shieldings of biphenyl, which are summarized in Table IV. For comparison, the effects of chlorine substitution in benzene are included in the table. There are similarities in substituent effects between the biphenyls and benzene, most pronounced for the chlorinated carbon and the carbon para to it, and closest for 4-chlorobiphenyl. The resemblance of substituent effects in 4-chlorobiphenyl to those in chlorobenzene is expected, since earlier work[2] has shown that substituent effects on both ^{13}C shieldings and calculated electronic charge distributions in similar systems (monosubstituted benzenes and 4,4′-disubstituted biphenyls) are much the same, and point to resonance as the predominant factor in determination of the ^{13}C shieldings in these compounds. However, it was shown previously that small differences in ^{13}C shieldings between PCB isomers could best be related to small differences in the σ charge densities[2] and no doubt relative bond orders for freely rotating chlorinated biphenyls. Thus it is not surprising that for the 2-chloro and 3-chloro compounds, significant differences remain. The effects ortho to the chlorine are larger than anticipated, and are in the direction opposite to that anticipated from benzene data at C-1 and C-4, which would be most affected by the resonance interactions with the second ring. At positions meta to the chlorine substituent, the effects are qualitatively in agreement with the benzene results. An interesting aspect is the occurrence of a substituent effect at all carbons except C-3, -5, -3′, and -5′ in 4-chlorobiphenyl and C-3′ and -5′ in 3-chlorobiphenyl. In the case of C-4′ of 4-chlorobiphenyl, this amounts to transmission of a significant substituent effect through *eight* covalent bonds.

For a number of aromatic hydrocarbon systems, it has been shown that the effects of substituents on the ^{13}C shieldings are approximately additive.[27] For some freely rotating symmetric chlorinated biphenyls, additive parameters from benzene data predicted ^{13}C shieldings reasonably well.[2] With the chlorine substituent effects on biphenyl from Table IV, a better test of additivity relationships in chlorinated biphenyls is possible. These parameters were used to predict, on the basis of additivity, all the ^{13}C shieldings in the 22 remaining PCBs. A comparison of the observed to the predicted substituent effects is presented in Figure 2. The agreement is best for those PCBs which have no ortho (2, 2′, 6, or 6′) substituents and which therefore have essentially free relative rotation of the two rings. For all PCBs having one ring unsubstituted or with only a 4-chlorine, the shieldings of C-3 and C-5 and of C-2 and C-6 are equivalent for this ring, implying free relative rotation at ambient temperatures for biphenyls without ortho-ortho′ interactions. Larger deviations are evident with increased hindrance to this rotation, with increased ortho-ortho′ substitution, and are especially pronounced at C-1 and C-1′. These larger discrepancies are anticipated on the basis of an increased preferred interring dihedral angle with increased ortho-ortho′ substitution, resulting in decreased resonance interaction between the two rings and electronic distributions less similar to that in biphenyl. The deviations from the predictions are predominantly upfield for both C-1,1′ and C-2,2′ in 2,2′-chlorine-substituted PCBs. Considered with the known preference of the 2,2′-dihalobiphenyls for a syn conformation,[28] these results suggest that the same mechanism may operate to produce these discrepancies in the hindered biphenyls as in other hindered aromatic compounds with steric compression resulting from an ϵ interac-

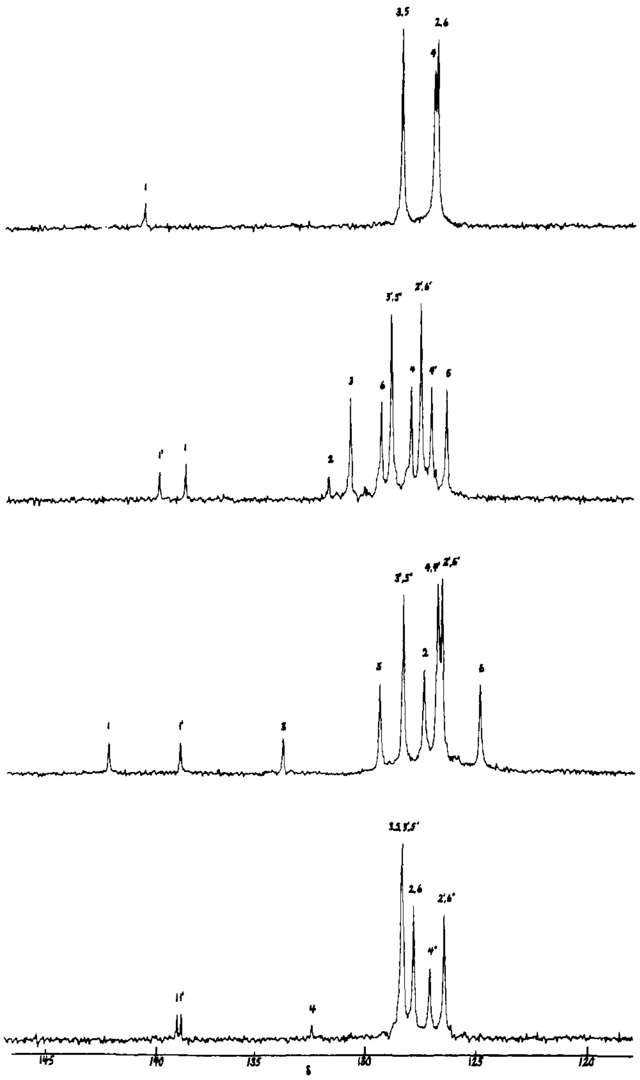

Figure 1. Proton-noise-decoupled ^{13}C spectra of biphenyl, 2-chlorobiphenyl, 3-chlorobiphenyl, and 4-chlorobiphenyl in 1,2-dibromoethane-d_4.

Table III. ^{13}C Shieldings of Several Chlorinated Biphenyls[a]

Chlorine substitution	δ, ppm C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′
Nil	140.60	126.75	128.37	126.87	128.37	126.75	140.60	126.75	128.37	126.87	128.37	126.75
2	138.50	131.75	130.81	127.95	126.28	129.34	139.75	127.44	128.85	126.98	128.85	127.44
3	142.15	127.31	133.86	126.68	129.43	124.71	138.77	126.50	128.29	126.68	128.29	126.50
4	138.93	127.86	128.41	132.73	128.41	127.86	139.13	126.43	128.41	127.11	128.41	126.43
2,2′[b]	137.6	132.8	130.7	128.7	126.0	128.9	137.6	132.8	130.7	128.7	126.0	128.9
3,3′[b]	140.7	127.4	134.2	126.8	129.6	124.8	140.7	127.4	134.2	126.8	129.6	124.8
4,4′[b]	137.5	127.7	128.5	132.9	128.5	127.7	137.5	127.7	128.5	132.9	128.5	127.7
2,6	136.00	134.15	127.55	128.42	127.55	134.15	138.72	127.43	128.87	127.43	128.87	127.43
3,4	140.29	128.35	132.07	130.60	130.04	125.77	137.69	126.28	128.35	127.54	128.35	126.28
2,4,2′,4′	135.2	133.8	131.5	134.2	126.6	129.0	135.2	133.8	131.5	134.2	126.6	129.0
2,5,2′,5′	137.70	131.14	130.29	129.17	131.64	130.09	137.70	131.14	130.29	129.17	131.64	130.09
2,6,2′,6′[b]	134.4	134.3	127.4	129.8	127.4	134.3	134.4	134.3	127.4	129.8	127.4	134.3
3,4,3′,4′[b]	137.8	128.3	132.5	131.8	130.4	125.7	137.8	128.3	132.5	131.8	130.4	125.7
3,5,3′,5′[b]	140.4	125.1	134.9	127.9	134.9	125.1	140.4	125.1	134.9	127.9	134.9	125.1
2,3,4,5	140.34	130.60	132.98	130.97	131.18	129.37	136.74	127.74	128.43	127.95	128.43	127.74
2,3,5,6	141.80	131.35	131.15	129.36	131.15	131.35	136.42	127.93	128.19	127.93	128.19	127.93
2,3,4,5,6	139.80	132.36	136.33	132.26	136.33	132.26	131.23	128.10	128.25	128.15	128.25	128.10
2,4,5,2′,5′	136.50	131.50	130.56	133.00	(132.22)[c]	129.61	137.19	130.72	131.73	130.37	(132.00)	130.46
2,3,4,5,6,2′	137.28	132.36	135.26	132.36	135.26	132.36	131.28	133.00	(129.84)	129.20	126.70	(129.72)
2,3,4,5,6,3′	138.25	133.79	137.77	132.85	137.77	133.79	131.42	128.48	132.10	128.48	129.52	126.66
2,3,4,5,6,4′	138.57	134.09	134.65	132.74	132.18	134.09	131.42	128.49	129.87	132.18	128.49	129.87
2,3,4,2′,3′,4′	136.99	131.71	133.02	133.62	127.74	128.34	136.99	131.71	133.02	133.62	127.74	128.34
2,3,6,2′,3′,6′	136.00	132.66	132.30	130.56	127.98	131.35	136.00	132.66	132.30	130.56	127.98	131.35
2,4,5,2′,4′,5′[b]	135.3	130.7	131.7	133.9	131.9	130.6	135.3	130.7	131.7	133.9	131.9	130.6
2,4,6,2′,4′,6′	132.2	135.0	127.8	134.9	127.8	135.0	132.2	135.0	127.8	134.9	127.8	135.0
3,4,5,3′,4′,5′[b]	136.6	126.4	134.2	133.6	134.2	126.4	136.6	126.4	134.2	133.6	134.2	126.4

[a] Approximately 0.6 *M* in 1,2-dibromoethane-d_4 at 40°. Where δ is given to 0.01 ppm, the precision is ±0.04 ppm, otherwise it is ±0.1 ppm. [b] From ref 2. [c] Similar values in parentheses may be interchanged.

Table IV. Observed Chlorine Substituent Effects on ^{13}C Shieldings of Biphenyl[a]

Substituent	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,6′	C-3′,5′	C-4′
2-Cl	−2.10	5.00	2.44	1.08	−2.09	2.59	−0.85	0.69	0.48	0.11
3-Cl	1.55	0.56	5.49	−0.19	1.06	−2.04	−1.83	−0.25	−0.08	−0.19
4-Cl	−1.67	1.11	0.04	5.86	0.04	1.11	−1.47	−0.32	0.04	0.24
1-Cl (on benzene)[b]	6.2	0.4	1.3	−1.9	1.3	0.4				

[a] In ppm ±0.03 ppm; positive values denote downfield shifts. [b] From ref 6.

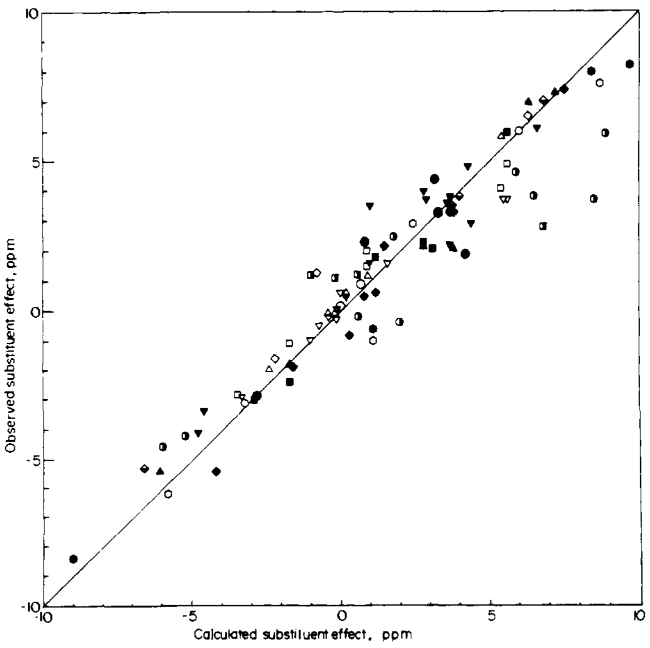

Figure 2. The observed substituent effects on the ^{13}C shieldings of PCBs relative to biphenyl vs. those substituent effects calculated assuming additivity: (○) 4,4′-Cl_2; (□) 3,4,3′,4′-Cl_4; (△) 3,3′-Cl_2; (▽) 3,4-Cl_2; (◇) 3,5,3′,5′-Cl_4; (●) 2,5,2′,5′-Cl_4; (■) 2,2′-Cl_2; (▲) 2,4,2′,4′-Cl_4; (▼) 2,4,5,2′,5′-Cl_5; (◆) 2,6-Cl_2; (⬡) 2,6,2′,6′-Cl_4; (⬢) 2,4,6,2′,4′,6′-Cl_6; (◑) 2,3,6,2′,3′,6′-Cl_6; (◈) 2,4,5,2′,4′,5′-Cl_6; (◧) 2,3,5,6-Cl_4.

tion, e.g., the "bay" interaction in 4,5-disubstituted phenanthrenes,[29] which results in shifts of the C-4, -5, -12, and -13 resonances to higher field. However, for 2,2′-dichlorobiphenyl itself, there is very little effect evident; therefore other factors must also contribute significantly, the rate of rotation (or the average dihedral angle at a given temperature) being one obvious contributor. Lowering the temperature should increase the proportion of 2,2′-dichlorobiphenyl in the preferred syn conformation, and thus result in a shift of the ^{13}C shieldings of C-1,1′ and C-2,2′ toward higher field, if the "bay" interaction mechanism is operative. These resonances do indeed shift toward higher field: at −90°, both C-1,1′ and C-2,2′ resonances are 0.6 ppm upfield from their positions at 40°; the shifts of the other carbons are smaller and in the opposite direction, 0.3 and 0.2 ppm for C-6,6′ and C-5,5′, respectively, or negligible.

Deviations from the ^{13}C shieldings predicted employing additivity are very pronounced for biphenyls having ortho chlorines on the same ring, and rotational hindrance amplifies these deviations. The buttressing effect of 3,3′-chlorines on the 2,2′-chlorine substituents undoubtedly prevents distortion of the C–C–Cl bond angles, thus raising the rotational barrier and leading to further discrepancies from the additivity predictions based on a freely rotating model. The chlorine-bearing carbons tend to be more shielded than predicted; however, clear trends are not discernible.

Carbon-13 Spin-Lattice Relaxation Times. Several relaxation mechanisms are known to contribute to the spin-lattice relaxation of ^{13}C nuclei. For the chlorinated biphenyls at ambient temperatures, only two of these mechanisms,

Table V. ^{13}C Spin–Lattice Relaxation Times of Protonated Carbons in Several Chlorinated Biphenyls[a]

Chlorine substitution	T_1, sec									
	C-2	C-3	C-4	C-5	C-6	C-2′	C-3′	C-4′	C-5′	C-6′
Nil	4.2	4.1	2.4	4.1	4.2	4.2	4.1	2.4	4.1	4.2
Nil[b, c]	5.2	5.4	3.4	5.4	5.2	5.2	5.4	3.4	5.4	5.2
2		2.7	1.9	2.8	2.6	3.0	3.0	2.1	3.0	3.0
2[c]		3.4	2.8	3.3	3.2	3.6	4.0	2.5	4.0	3.6
3	2.3		1.8	2.4	2.3	2.9	2.8	1.8	2.8	2.9
4	3.3	3.3		3.3	3.3	3.3	3.3	1.8	3.3	3.3
2,2′		2.3	1.9	2.3	2.3		2.3	1.9	2.3	2.3
2,6		2.0	1.5	2.0			2.3	1.5	2.3	
2,3,5,6			1.5				1.5		1.5	
2,6,2′,6′		1.9	1.6	1.9			1.9	1.6	1.9	
2,4,5,2′,5′[c]		2.6			2.9		3.1	4.4		2.7
2.3,6,2′,3′,6′			1.6	1.9				1.6	1.9	
2,3 4,5,6						1.5	1.5	1.3	1.5	1.5
2,3,4,5,6,2′							0.9	1.2	0.8	0.9
2,3,4,5,6,3′						0.95		0.95	0.96	0.92
2,3,4,5,6,4′						1.8	1.8		1.8	1.8

[a] Approximately 0.6 *M* in 1,2-dibromoethane-d_4 at 40°, unless otherwise indicated. Samples not degassed. [b] From ref 14. [c] In chloroform-*d*.

spin–rotation and internuclear dipole–dipole interactions, are expected to make significant contributions, and for the protonated carbons, dipole–dipole relaxation should predominate.[5,6,30] Measurements of the NOE have shown that ^{13}C–^{1}H internuclear dipolar interactions completely dominate the spin–lattice relaxation of the protonated carbons in biphenyl itself.[14] For overall isotropic molecular reorientation, the dipolar contribution to T_1, essentially due to the directly bonded protons, is

$$1/T_1 = N\hbar^2\gamma_C^2\gamma_H^2r^{-6}\tau_{\rm eff} \qquad (2)$$

where N is the number of protons directly bonded to the carbon, γ_C and γ_H are the magnetrogyric ratios of ^{13}C and ^{1}H, r is the C–H internuclear distance, and $\tau_{\rm eff}$ is the effective correlation time for rotational reorientation.[26] Protons not directly bonded to the carbon have little effect on T_1 because of the r^{-6} dependence. If anisotropic motion or internal reorientation occurs, the differing effective correlation times may produce unequal values of $1/NT_1$ for the different protonated carbons. These effects have been amply demonstrated in several systems[5,6] including biphenyl, where slower tumbling perpendicular to the long axis of the molecule results in more effective dipolar relaxation and hence a shorter T_1 for the para than for the ortho and meta carbons.[14,15] Similarly, 3- and 4-bromobiphenyl[17] and 4,4′- and 2,2′-dichlorobiphenyl[11] exhibit T_1 values suggestive of anisotropic molecular motion.

The T_1 values for the protonated carbons in 13 chlorinated biphenyls, obtained for nondegassed samples at the probe ambient temperature, are given in Table V. Degassed samples of the 2-, 2,2′-, 3-, 2,6,2′,6′-, 2,6-, 4-, and 2,4,5,2′,5′-chlorinated isomers and biphenyl itself gave T_1 values identical to those in the table within the experimental error of approximately 10%, indicating that relaxation by dissolved oxygen is insignificant for the protonated carbons. The measured NOE (η) for these carbons was 2.0 with a standard error of 0.14 in each isomer examined. Since the theoretical maximum value of η is 1.988 for completely dipole-dipole relaxation, other mechanisms do not make an experimentally significant contribution to the relaxation of these carbons at ambient temperatures. Thus the ^{13}C–H relaxation times may be interpreted at least qualitatively in terms of the motional characteristics described by the $\tau_{\rm eff}$ of eq 2.

A comparison of these relaxation times for a group of PCBs is given in Figure 3. A slower change of the ^{13}C–H bond vector with respect to the applied field axis results in a longer $\tau_{\rm eff}$ and a shorter T_1 value. Thus the larger T_1 observed for the ortho (2,6,2′,6′) and meta (3,5,3′,5′) carbons of biphenyl compared to that for the para (4,4′) carbons reflects, as previously noted in a different solvent,[14,15] preferred (faster) rotation about the longitudinal axis of the molecule.[31] Similar preferred rotation about the 4–4′ major axis can be inferred from the T_1 values for C-4 and C-4′ of all the PCBs in the figure. In each case these are shorter than the T_1 values for the protonated carbons lying off this axis. Relative internal rotation of the two rings is also apparent from a comparison of T_1 for the ortho and meta carbons in the substituted to the unsubstituted rings of the 2-Cl, 3-Cl, and 2,6-Cl$_2$ isomers. Rotation of the ring having the greater moment of inertia about the long axis is slower, leading to shorter T_1 values for these carbons. Rotational hindrance due to interaction with solvent molecules will be somewhat greater for the substituted ring and will also contribute to reduction of T_1 for this ring. The moment of inertia of the 4-Cl isomer about the long axis is the same for both rings and likewise the off-axis T_1 values are the same. For PCBs with all ortho positions chlorine substituted, the essentially isotropic molecular motion shown by the nearly equal T_1 values at the meta and para positions is consistent with a high degree of steric hindrance to rotation about the interring bond.

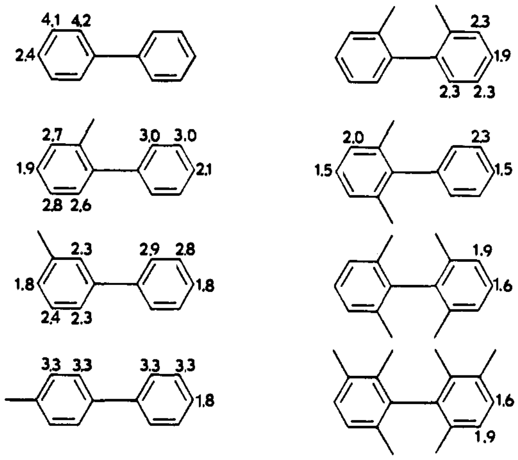

Figure 3. Spin-lattice relaxation times (in seconds) of the protonated carbons in some chlorinated biphenyls.

A group of PCBs having one ring fully chlorinated is shown in Figure 4. The T_1 values given for the isomer with the second ring unsubstituted may indicate some preferential rotation about the longitudinal axis; however, the motion appears to be nearly isotropic. For the 3′-Cl isomer isotropic motion is apparent, and the data for the 2′-Cl isomer indicate motion slightly preferred about an axis approximately perpendicular to the 4–4′ axis.

Some investigators at these laboratories have been engaged in studies of binding of PCBs to rat blood plasma lipoproteins. This binding should cause a severe drop in the rate of molecular reorientation of the PCB because of the large molecular weight of the lipoprotein, with an accompanying increase in $\tau_{\rm eff}$

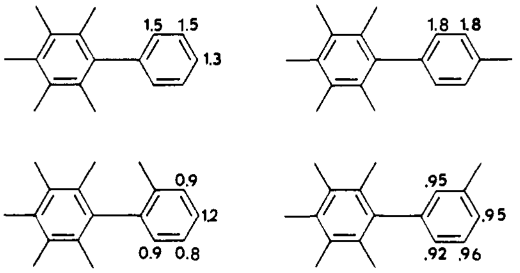

Figure 4. Spin-lattice relaxation times (in seconds) of the protonated carbons in some chlorinated biphenyls.

Table VI. Temperature Dependences of the ^1H Chemical Shifts of Some Chlorinated Biphenyls[a]

Chlorine substitution	Slope of shift vs. $1/T$ plot (Hz °K × 10^{-3}) for proton no.				
	2	3	4	5	6
3,3'	−2.4		−0.23	0.0	0.0
2,4,2',4'		0.15		1.3	0.67
2,4,5,2',4',5'		0.58			2.7
2,6,2',6'		0.0	0.0	0.0	
2,4,6,2',4',6'		0.0		0.0	

[a] From +70 to −110° in 3,3-dimethylpentane.

and a decrease in T_1.[5] Radioactive tracer data indicate that 2,4,5,2′,5′-pentachlorobiphenyl binds to the lipoprotein.[32] The T_1 values of the PCB protonated carbons, ca. 3-4 sec in deuteriochloroform, dropped to ca. 100 msec in micellar suspensions of PCB-lipoprotein in D_2O. The extreme fragility of the lipoprotein prevented the lengthy experiments necessary to obtain precise T_1 measurements for the bound PCB; however, the large drop in the magnitude of T_1 supports the postulate of binding. With singly labeled ^{13}C-enriched PCB isomers, relaxation times should provide useful complements to biological studies.

Other Approaches. Some other approaches to the investigation of rotational barriers in chlorinated biphenyls were utilized. The temperature dependences of the PCB ^1H chemical shifts were measured in an inert solvent, 3,3-dimethylpentane. These are summarized in Table VI. Those proton shifts which changed with temperature showed a small linear temperature dependence over the entire range 70 to −110°. The data suggest that for PCBs with no ortho chlorines or with one ortho chlorine on each ring, relative rotation of the rings is still fairly rapid at −110°. On the basis of known rotational barriers in other biphenyl derivatives,[33] this would be consistent with anticipated rotational barriers of ca. 1-4 kcal/mol for the non-ortho-substituted PCBs and of ca. 9 kcal/mol or less for the ortho-ortho′-substituted PCBs. The ^1H spectra of biphenyls with all four ortho positions chlorine-substituted exhibit no temperature dependence. These PCBs may be "locked" into one minimum energy conformation.

In the course of work on the relationships of PCB ^{13}C shieldings to calculated electron charge densities,[2] potential energy vs. interring dihedral angle calculations for two PCBs were carried out by the CNDO/2 method.[34] Unfortunately, these gave unrealistically large rotational barriers and unrealistically small minimum energy preferred dihedral angles, ca. 230 kcal/mol and 31° for 2,6,2′,6′-tetrachlorobiphenyl and 132 kcal/mol and 24° for 2,2′-dichlorobiphenyl. Although these are qualitatively consistent with the NMR data, i.e., a very large barrier is predicted for the 2,6,2′,6′ isomer, and from ^{13}C shielding vs. charge density correlations[2] the appropriate syn conformation for the 2,2′ isomer is indicated, further refinements in the method are obviously needed before it can be confidently applied to problems of this type.

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