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NUCLEAR MAGNETIC RESONANCE SPECTRA OF FIVE ISOMERS OF 1,2,3,4,5,6-HEXACHLOROCYCLOHEXANE

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Abstract—NMR parameters are determined by the complete analysis of the spectra for five isomers of 1,2,3,4,5,6-hexachloro-cyclohexane (BHC). Interesting correlations are found between the spin coupling constants and the chlorine atom configuration, which are interpreted by the conformational dependence of the electronegative substituents with repsect to the coupled protons, as well as the small changes in the dihedral angle due to ring distortion. Some elucidations are made about the magnetic anisotropy effect of C—Cl bonds on the proton chemical shifts, and it is suggested that all of the proton shifts in BHC isomers cannot be explained only by the anisotropy effect, even after the solvent effect is eliminated. Proton decoupled ^{13}C spectra of these compounds are also observed.

INTRODUCTION

NMR spectra of five isomers (α-, β-, γ-, δ- and ε-isomers) of 1,2,3,4,5,6-hexachlorocyclohexane (benzene hexachloride, BHC) were first studied by Lemieux *et al.* in 1958.[1] Their spectra were obtained at 40 MHz in dioxane and the general features of the chemical shift characteristic to each isomer were shown. Harris and Sheppard reported the spectral results of the γ- and δ-isomers,[2] where the low-temperature study of γ-isomer was made at 40 MHz in acetone solution, and an approximate value of the free energy for the ring inversion was estimated. At the same time the chemical shifts and the coupling constants of the δ-isomer in benzene solution were obtained from a 60 MHz spectrum by first-order analysis. In connection with the effect of the anisotropic magnetic susceptibility of C—Cl bond, Homer and Callaghan remeasured the chemical shifts of the β- and δ-isomers in dioxane.[3]

As is well known, except for the γ-isomer, benzene hexachlorides have a rigid ring structure. To each carbon atom are attached a chlorine and a hydrogen atom. Therefore BHC isomers are suitable compounds for investigating the anisotropy effect of the C—Cl bond on proton chemical shifts. While in the β-BHC all six protons are placed at axial positions so that they are all equivalent and give a single line spectrum, other isomers have three or four different types of protons and they interact complicatedly with spin coupling. However, no study has been made of the spin coupling constants, although they would surely provide information on ring structure.

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structure, complete spectral analysis is necessary to determine the chemical shifts as well as the spin coupling constants.

In a previous paper we made a complete analysis of β-BHC for the ^{13}C-satellite spectrum in ^{1}H resonance and the undecoupled ^{13}C spectrum obtained by Fourier transform spectroscopy.[4] In the present paper the proton resonance parameters are determined for the other BHC isomers, and the anisotropy effects of C—Cl bond on the proton chemical shifts discussed. At the same time interesting correlations are found between the spin coupling constants and the chlorine atom configuration. Proton-decoupled ^{13}C spectra of these compounds are also observed.

RESULTS

The PMR spectra of the α-, δ-, and ε-BHC are shown in Figs 1, 2, and 3, respectively. Fig. 4 shows the low temperature spectrum of γ-BHC (at about −50°) which gives a single line at room temperature due to ring inversion. At the bottom of the figures the calculated spectra are shown. Agreement of the observed and the calculated spectra are satisfactory, but in γ-BHC the line width of the observed spectrum is rather broad so that the reliability of the obtained parameters is not so good as that of the other

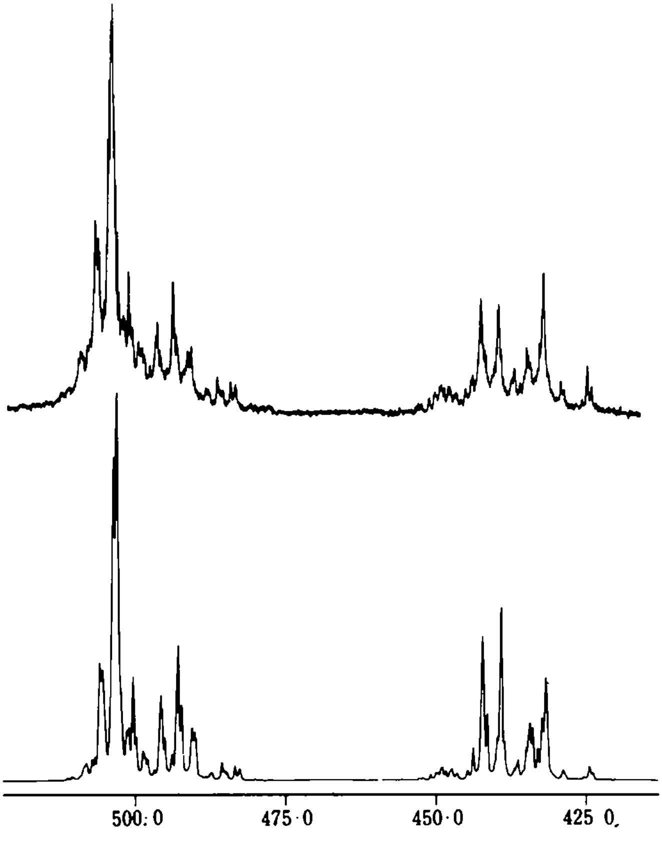

FIG 1. The observed (top) and the calculated (bottom) PMR spectra of α-BHC in deuterated acetone.

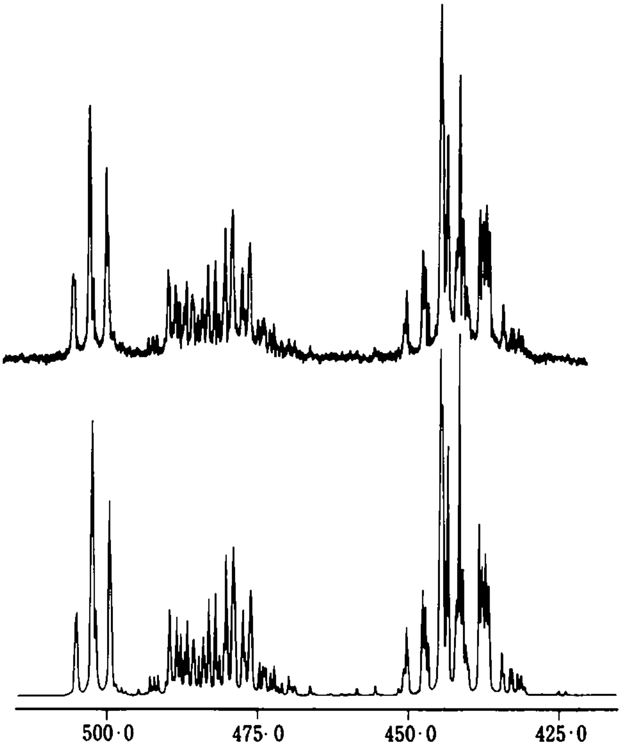

FIG 2. The observed (top) and the calculated (bottom) PMR spectra of δ-BHC in deuterated acetone.

isomers. The results of the spectral analysis are summarized in Table 1, in which the spin coupling constants of β-BHC previously obtained from the ^{13}C-satellite spectrum[4] are also included. The labels of the protons in each isomer are defined as shown in Fig. 5.

The averaged chemical shift of the four types of protons in the γ-isomer at low temperature is 5·072 ppm from internal TMS, while the single line chemical shift at room temperature is 4·931 ppm. Thus the chemical shift is temperature dependent, and moves to lower field as the temperature decreases. The same trend is also found in the β-isomer. In order to compare the chemical shifts of the γ-isomer with those of the others, a correction is made by adding −0·141 ppm to each proton chemical shift obtained at low temperature. The estimated values are also given in Table 1.

The chemical shifts obtained for the BHC isomers in acetone are characterized in Fig. 6, in which a or e in the parenthesis indicates the orientation of C—Cl bond (not C—H bond) at the nearest neighbours of the proton under study. The numbers in parenthesis show how many data are included in each group.

For the α-, β- and δ-isomers the chemical shifts were also determined in $CDCl_3$ to make further discussion, and are shown in Table 2. The ^{13}C chemical shifts of the five isomers in acetone are shown in Fig. 7.

In Table 3 the spin coupling constants are given according to the type of coupled protons. The symbol in the parenthesis indicates the position at which the proton is attached. For example, the symbols outside the parenthesis in three bond coupling

TABLE 1. THE CHEMICAL SHIFTS AND THE COUPLING CONSTANTS IN BHC ISOMERS

		α-Isomer	β-Isomer[a]	γ-Isomer[b]	δ-Isomer	ε-Isomer
Chemical Shifts (ppm from TMS)[d]	δ_1	5·041	4·476	5·417 (5·276)[c]	5·019	5·024
	δ_2	$= \delta_1$		5·079 (4·938)	4·821	4·898
	δ_3	4·965		5·136 (4·995)	4·409	$= \delta_2$
	δ_4	4·372		4·584 (4·443)	4·419	$= \delta_1$
	δ_5	$= \delta_3$		$= \delta_3$	$= \delta_3$	$= \delta_2$
	δ_6	$= \delta_4$		$= \delta_2$	$= \delta_2$	$= \delta_2$
Three-Bond Coupling (Hz)	J_{12}	3·38 ± 0·03	10·58 ± 0·04	2·11 ± 0·05	2·83 ± 0·01	3·01 ± 0·05
	J_{23}	3·28 ± 0·02		3·47 ± 0·05	10·85 ± 0·02	11·27 ± 0·04
	J_{34}	10·90 ± 0·02		10·81 ± 0·09	10.20 ± 0·02	$= J_{12}$
	J_{45}	10·24 ± 0·02		$= J_{34}$	$= J_{34}$	$= J_{12}$
Four-Bond Coupling (Hz)	J_{13}	−0·49 ± 0·02	−0·20 ± 0·04	−0·52 ± 0·07	−0·41 ± 0·01	−0·45 ± 0·05
	J_{15}	−0·38 ± 0·03		$= J_{13}$	$= J_{13}$	$= J_{13}$
	J_{24}	$= J_{15}$		−0·51 ± 0·09	−0·21 ± 0·02	$= J_{13}$
	J_{26}	$= J_{13}$		1·21 ± 0·07	0·10 ± 0·02	0·14 ± 0·04
	J_{35}	−0·23 ± 0·02		−0·36 ± 0·09	−0·21 ± 0·03	$= J_{26}$
Five-Bond Coupling (Hz)	J_{14}	0·26 ± 0·03	−0·20 ± 0·06	0·24 ± 0·06	0·20 ± 0·02	0·43 ± 0·04
	J_{25}	$= J_{14}$		0·26 ± 0·06	−0·08 ± 0·02	−0·07 ± 0·04
	J_{36}	−0·05 ± 0·03		$= J_{25}$	$= J_{25}$	$= J_{25}$

[a] Ref. 4.

[b] Obtained at −50°. The weighted average of the chemical shifts is 5·072 ppm, while the chemical shift at room temperature (a little broad line) is 4·931 ppm.

[c] Estimated values at room temperature, obtained by adding −0·141 ppm to the values at low temperature.

[d] In acetone solution (about 4 mol %).

constants indicate the protons attached at the outside positions of the coupled protons. Thus, a(ee)a means that two equatorial protons are coupled and their adjacent protons are both axial. Similarly the symbol (aea) in four bond coupling constants means that two axial protons are coupled and an equatorial proton is attached in between. In five bond coupling constants, two coupled protons are simply indicated in the parenthesis.

DISCUSSION

Spin coupling constants

Generally speaking, the coupling constants are affected by the electronegativity of neighbouring atoms or groups, and by the dihedral angle ϕ between the coupled protons. It has already been suggested that in six-membered rings in the chair conformation, $^3J_{ee}$ and $^3J_{ae}$ ($\phi = 60°$) are particularly sensitive to small change in ϕ, whereas $^3J_{aa}$ ($\phi = 180°$) is relatively insensitive to small change in ϕ, and thus any marked changes in $^3J_{aa}$, consequent upon substitution, may reasonably be attributed to the substituent electronegativity.[5]

In the $^3J_{aa}$ in BHC isomers, a very typical trend is observed. They are all smaller than the corresponding value in cyclohexane, 13·12 Hz,[6] which reflects the substituent effect of the electronegative chlorine atoms. Furthermore, $^3J_{aa}$ is largest when the

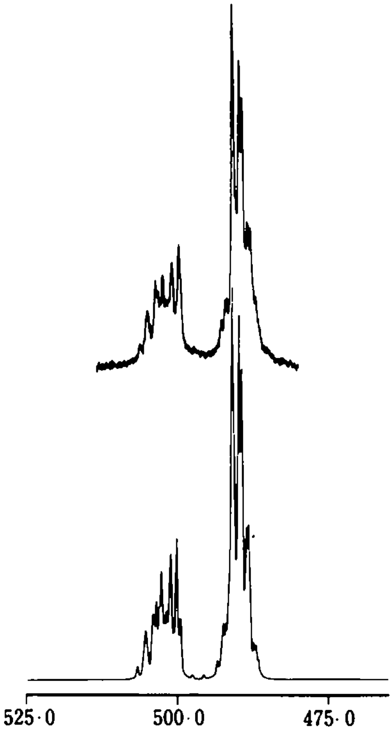

FIG 3. The observed (top) and the calculated (bottom) PMR spectra of ε-BHC in deuterated acetone.

both outside adjacent positions are occupied by equatorial protons or axial chlorine atoms. It decreases as successive adjacent positions are occupied by equatorial chlorine atoms; *i.e.*, ${}^3J_{aa}$ decreases in the order of ${}^3J_{e(aa)e}$, ${}^3J_{e(aa)a}$ and ${}^3J_{a(aa)a}$.

As mentioned above, since the ${}^3J_{aa}$ has been indicated to be relatively insensitive to small change in ϕ, the trend of ${}^3J_{aa}$ in BHC isomers seems to be attributed to the effect of orientation of the electronegative substituents rather than ring distortion.

TABLE 2. SOLVENT EFFECTS ON THE PROTON CHEMICAL SHIFTS (PPM FROM TMS)

Compound		Acetone	Chloroform	Difference
α-BHC	δ_1	5·04	4·66	0·38
	δ_3	4·96	4·76	0·20
	δ_4	4·37	4·23	0·14
β-BHC[a]		4·48	3·95	0·53
δ-BHC	δ_1	5·02	4·66	0·36
	δ_2	4·82	4·15	0·67
	δ_3	4·41	4·35	0·06
	δ_4	4·42	3·94	0·48

[a] Saturated solution.

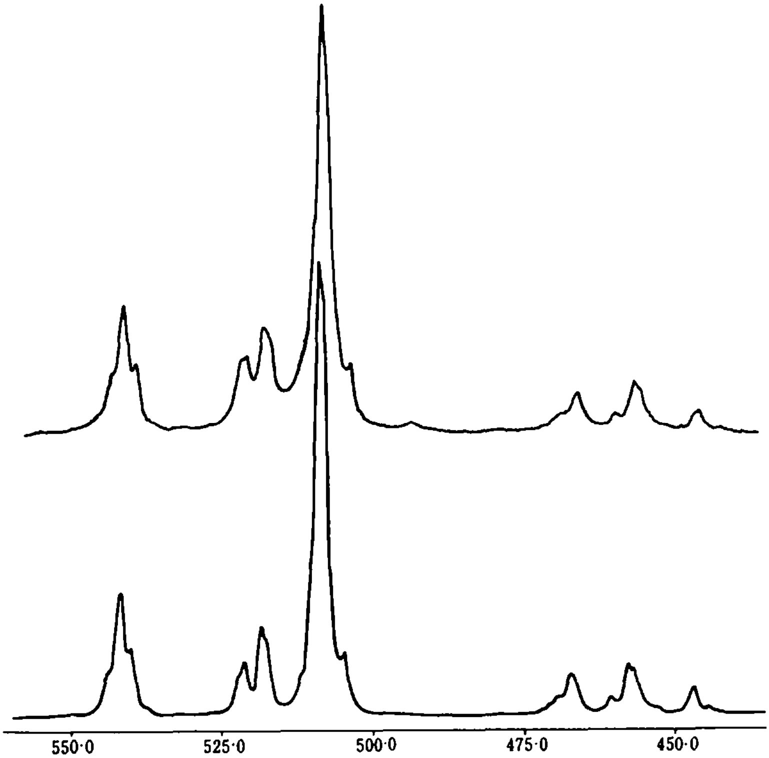

FIG 4. The observed (top) and the calculated (bottom) PMR spectra of γ-BHC in deuterated acetone at about −50°.

The importance of the orientation of the substituent with respect to the fragment H–C–C–H has been suggested by some workers,[5, 7, 8] in which an electronegative substituent exerts its maximum effect on $^3J_{ae}$ or $^3J_{ee}$ when it is in a planar *trans* arrangement with one of the coupled protons. That is, such an arrangement *decreases* the coupling constants to the greatest extent. On the other hand, an indication was made by Cohen and Schaefer[9] that the presence of an electronegative substituent at a

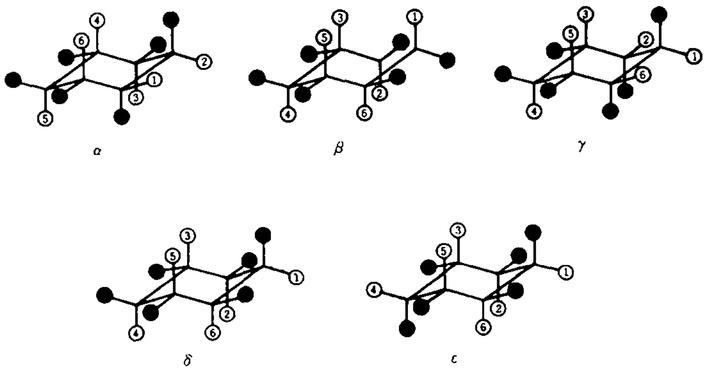
α β γ δ ε

FIG 5. The five BHC isomers.

Table 3. Spin coupling constants recompiled by the type of coupled protons

^3J	a(aa)a	10·24(α) 10·58(β) 10·20(δ)	e(aa)a	10·90(α) 10·81(γ) 10·85(δ)	e(aa)e	11·27(ε)
	a(ea)a	2·83(δ) 3·01(ε)	e(ea)a	3·28(α) 3·47(γ)		
	a(ee)a	3·38(α)	e(ee)a	2·11(γ)		
^4J	(aaa)	−0·23(α) −0·20(β) −0·36(γ) −0·21(δ) −0·21	(aea)	0·10(δ) 0·14(ε)		
	(eaa)	−0·38(α) −0·51(γ) −0·41(δ) −0·45(ε)	(eea)	−0·49(α) −0·53(γ)	(eee)	1·21(γ)
^5J	(aa)	−0·05(α) −0·20(β) −0·08(δ) −0·07(ε)	(ea)	0·26(α) 0·26(γ) 0·24(γ) 0·20(δ)	(ee)	0·43(ε)

position one carbon atom removed from the coupling path, *i.e.*, in the system XC–CH$_A$–CH$_B$–, causes an *increase* in J_{AB}. Although the latter effect is not shown explicitly to have an orientation dependence such as in the former, it may be reasonable to assume similar orientation dependence for the effect of the electronegative substituent at a position one carbon atom removed from the coupling path. But in this instance, the trend should be reversed. Thus an electronegative substituent at the outside adjacent position *increases* the $^3J_{aa}$ if it is in a planar *trans* arrangement with a coupled proton. This postulate explains well the above trend that is found in $^3J_{aa}$ in BHC isomers. $^3J_{e(aa)e}$ is the largest because both coupling protons are in a planar *trans* arrangement with outside adjacent chlorine atoms. The same interpretation may be adopted for the intermediate and the smallest values of $^3J_{e(aa)a}$ and $^3J_{a(aa)a}$, respectively.

The axial-equatorial coupling constants, $^3J_{ae}$, are also smaller than the corresponding value in cyclohexane, 3·65 Hz,[6] and also in this case $^3J_{a(ea)a}$ is smaller than $^3J_{e(ea)a}$, while the $^3J_{ee}$ in cyclohexane (2·96 Hz) is between the two values obtained in the BHC isomers. The smaller value of $^3J_{ae}$ than for that of cyclohexane results from the fact that the axial proton is in a planar *trans* arrangement with an axial chlorine atom, but the smaller value of $^3J_{a(ea)a}$ than $^3J_{e(ea)a}$ is difficult to explain by the orientation dependence of the outside adjacent chlorine atoms, because there is no arrangement of the coupled protons *trans* planar to a chlorine atom. Considering that $^3J_{ae}$ is sensitive to small changes in dihedral angle ϕ, an alternative mechanism due to ring deformation which affects the dihedral angles between the coupled protons will be operable. Indeed, a relatively small value of $^3J_{e(ea)a}$ and a relatively large value of $^3J_{e(ee)a}$ in the γ-isomer may be a consequence of ring deformation due to the chlorine atoms with the diaxial relationship (at the positions 2 and 6 in Fig. 5). The repulsive effect of the two chlorine atoms in the diaxial positions will increase the dihedral angle between the two equatorial protons in the γ-isomer from 60° leading to a decrease of $^3J_{ee}$. At the same time the dihedral angle between the equatorial and the axial protons becomes smaller, which in turn causes $^3J_{ae}$ to increase.

Small changes of $^3J_{ea}$ from $^3J_{e(ea)a}$ to $^3J_{a(ea)a}$ in the other isomers may also presumably reflect the small changes in the dihedral angle. A possible explanation involves the chlorine–chlorine repulsion in the highly substituted six-membered ring. Because of the large size and the electrostatic force of chlorine atoms the dihedral angle between the two chlorines in a *gauche* arrangement will be slightly larger than 60°. This leads to a slight increase in the dihedral angle between the two protons in a gauche arrangement, which in turn makes the coupling constant between them smaller. This effect will be twice as significant in an a(ea)a arrangement than in an e(ea)a, because in the former case the chlorine arrangement is *gauche–gauche–gauche*, while in the latter it is *trans- gauche–gauche*. Thus the coupling constant will be smaller in $^3J_{a(ea)a}$ than $^3J_{e(ea)a}$.

The larger value of $^3J_{ee}$ in the α-isomer than the corresponding cyclohexane value may be explained in a similar manner. There is no *trans* planar arrangement of the coupled protons with any chlorine atom, and the substituent exerts its effect to the least extent. On the other hand ring deformation may occur due to the chlorine repulsion as described above, which makes the dihedral angle between the two equatorial protons smaller than 60°, and the large coupling constant will result.

In the four bond coupling constants, ^4J, a trend is also found for the coupled proton configuration, although the values are small. Including the sign the values decrease in the order $^4J_{ee}$, $^4J_{aa}$ and $^4J_{ae}$. Conformation and substituent dependences of ^4J have been studied on a theoretical basis by Barfield.[10] A semi-empirical INDO calculation showed that the value of ^4J varies from about $-1{\cdot}0$ to $+1{\cdot}5$ Hz in the propanic fragment depending upon the two dihedral angles ϕ and ϕ' (for the definitions see reference), and all the electronegative substituent effects result in the positive shift in ^4J. Experimental values obtained in the present work seem to support Barfield's conclusion.

The large value of $^4J_{ee}$, which corresponds to the all-*trans* or "W" arrangement of the coupled protons ($\phi = \phi' = 180°$) has been found experimentally in various compounds.[11] In the present case also, $^4J_{ee}$ is the largest and has a positive value. On the other hand, $^4J_{ea}$ ($\phi = 180°$, $\phi' = 60°$) should be larger than $^4J_{aa}$ ($\phi = \phi' = 60°$) according to Barfield's calculation, whereas the obtained values in the BHC isomers show a reverse trend. This reverse trend, however, may reasonably be interpreted by the substituent effect. Barfield showed that the greatest substituent effect occurs in $^4J_{ee}$ or $^4J_{aa}$ when the substituent is placed at the C_2 carbon in the fragment $-C_1-C_2-C_3-$, and the coupled protons are both *trans* or both gauche to the substituent. The substituent at C_1 or C_3 has a small effect. As a result, whereas $^4J_{ea}$ is little affected by the chlorine substitution, $^4J_{aa}$, where the coupled protons are arranged both *trans* or both *gauche* to the chlorine atom, is affected to a large extent, and will exceed the value of $^4J_{ae}$. Among $^4J_{aa}$, the values in $^4J_{(aea)}$ are considerably larger than those in $^4J_{(aaa)}$ and have a positive sign. This means that the substituent effect at C_2 is larger when the chlorine atom is *trans* to both coupled protons than when it is *gauche*.

This may be reasonable by analogy with ^3J, in which the substituent effect is largest when the coupled proton and the substituent have a *trans* planar configuration.

In the five bond coupling constants, the value is also largest for the equatorial–equatorial coupling constant, and then equatorial–axial and axial–axial couplings follow, the last one taking a negative sign. But in the present stage, the explanation of ^5J seems to be difficult.

In conclusion it can be said that for the small change of the coupling constants in the BHC isomers the conformational dependences of the electronegative substituents certainly play an important role as well as the changes in the dihedral angle due to the ring deformation.

Proton chemical shifts

It has been generally accepted that the main factor which determines proton chemical shifts of BHC isomers is the magnetic anisotropy effect due to the C—Cl bonds. The results shown in Fig. 6 suggests that the proton chemical shifts are mainly determined by the orientation of the neighbouring C—Cl bonds, and effects from more remote C—Cl bonds are not so important. These results, however, seems somewhat different from the discussions hitherto made. A widely accepted concept is that some of the remote C—Cl bonds are as important as neighbouring ones. A possible explanation for this is that the anisotropy effects from remote positions may be cancelled out by each other. However, a trial calculation of position factors based on McConnell's formula [12] $(1\text{-}3cos^2\theta)/3R^3$ for all C—Cl bonds could not draw any unambiguous conclusion for the results in Fig. 6.

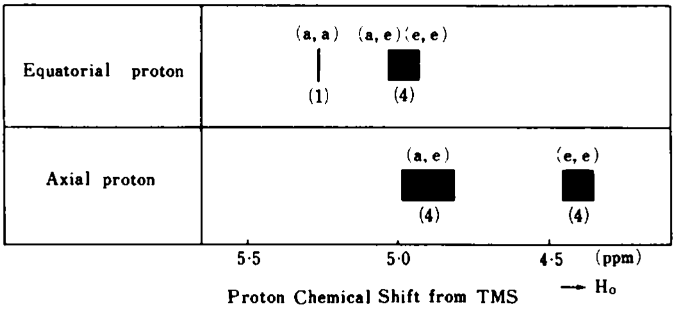

FIG 6. The proton chemical shifts of five isomers of BHC summarized according to the proton configuration and to the position of adjacent chlorine atoms. For example (a.e.) means that the two chlorine atoms at the adjacent positions take the axial and the equatorial configurations. The number in the parenthesis is the number of the protons classified.

The solvent effects on the proton chemical shifts must be taken into account at this point. Acetone was used as a solvent, since it has relatively high solubility for the BHC isomers (about 10% w/w) and it can also be used for low temperature measurement. But when a comparison is made for the chemical shifts of the δ-BHC between those obtained in acetone in the present work and those in benzene reported by Harris and Sheppard,[2] one finds a remarkable difference.

We have tried to obtain the proton chemical shifts of α-, β- and δ-BHC in the less polar solvent, $CDCl_3$. The concentrations of the BHC isomers in $CDCl_3$ are nearly the same as those in acetone. The chemical shifts from internal TMS are shown in Table 2. For comparison the chemical shifts of the δ-isomer were also observed in CCl_4 and in cyclohexane. The spectral patterns in both solvents are nearly the same as in $CDCl_3$.

All chemical shifts move to higher field when the solvent changes from acetone to $CDCl_3$, but there exists remarkable differences in the change of each proton chemical shift. For example, in δ-BHC the chemical shift of H_2 moves by 0·67 ppm, while that of H_3 moves only by 0·06 ppm. Apparently there is some specific interaction between the solvent and the solute molecules, depending upon the proton positions in the BHC isomers. When a comparison is made including the similar data for the α-isomer, it is found that the axial protons adjacent to the axial chlorine atoms are least affected by the change of solvent. It may be seen from the molecular geometry, that the proton at this position is highly shielded by chlorine atoms towards approach by solvent molecules. This trend also has been shown in the chemical shifts of the δ-isomer in benzene, where the chemical shifts move as a whole to higher field, but that of H_3 varies least. Generally dioxane was used as solvent in early days,[1, 3] but the solvent effect of dioxane seems to be too pronounced to make an adequate discussion on the bond anisotropy from the data obtained in that solvent.

In the following the chemical shifts obtained in $CDCl_3$ are used to make some elucidation about the magnetic anisotropy effects of the C—Cl bonds. At first the chemical shifts of H_3 and H_4 of α-BHC are examined. These protons are both axial. It is assumed that the main difference in the chemical shifts originate from the magnetic anisotropy effect of the C—Cl bonds, and the different orientations of the C—Cl bonds play the most important role in the chemical shift difference. The position factors were calculated for all the C—Cl bonds which will bring different contributions to H_3 and H_4 chemical shifts. If the value of $\Delta\chi$ of the C—Cl bond is assumed as -6 to -8×10^{-6} cm^3/mol,[3, 12–14] then the difference in the chemical shifts between H_3 and H_4 is calculated to be 0·22 to 0·29 ppm, and the chemical shift of H_3 should be at higher field. On the contrary the experimental values show that the resonance position of H_3 is at lower field. If one desires to take into account some other effects to interprete the experimental difference of the chemical shifts, one must add other factors which bring the shift to the order of 0·75 ppm to cancel it out. This seems to be unplausible.

On the other hand, the chemical shift difference between H_3 and H_4 of δ-BHC can be interpreted by the C—Cl bond anisotropy effect. In the same way, the shielding from the C—Cl bonds was calculated. From the calculation the chemical shift of H_4 is shown to be at lower field than that of H_3 by about 0·31 to 0·41 ppm, the same trend as the experimental result of 0·31 ppm in the difference as well as the resonance position. The above two examples indicate that in some cases the anisotropy effect of the C—Cl bond satisfactorily explains experimental values, but all the chemical shifts can not be interpreted well in the same way. More refined calculations, *e.g.* refinement of point dipole approximation[15] or the additional calculations of a C—H bond anisotropy effect, would lead to some improvement, but it would be difficult to explain all the chemical shifts of each proton only by the magnetic anisotropy effect due to C—Cl, C—C, and C—H bonds. Probably the anisotropy effects of the C—Cl bonds plays one of the most important roles on proton chemical shifts in the BHC isomers, but some other factors must contribute to them, *e.g.*, the effects due to the electric field or Van der Waal's force as well as some specific interaction between the molecules.

The anisotropic susceptibilities of C—Cl, C—C and C—H bonds of the γ- and δ-BHC have been determined from a study of single crystals.[13] Although the self-consistency of the anisotropy values is poor, rather reasonable values were obtained. Attempts to obtain the bond anisotropy from the high resolution NMR data have been made by many workers, but the chemical shift is often complicated by many factors other than the anisotropy effect. The approach from the single crystal study, though difficult, seems to be important as well as the high resolution NMR.

^{13}C *chemical shifts*

Since cyclohexane gives the ^{13}C chemical shift at 27·6 ppm from internal TMS under the same experimental conditions, ^{13}C shifts of the BHC isomers move to lower field by about 35 ppm on the average. The variation range of the shifts is about 8 ppm (Fig. 7).

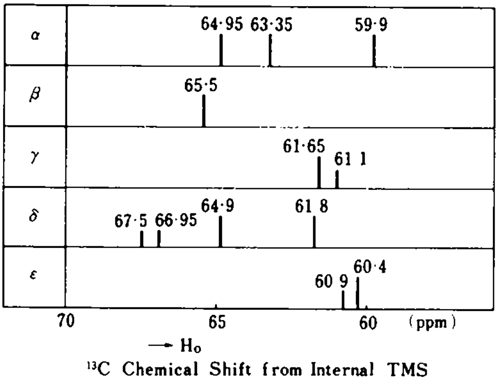

FIG 7. ^{13}C chemical shifts of BHC isomers. The height of the vertical line represents the relative intensity of the peak.

An assignment of the spectral lines was attempted by the relative intensities. For example, in ε-isomer the weaker line can be assigned to the carbon atom to which an axial chlorine atom is attached. In δ-BHC either of the weaker two lines can be assigned to the carbon atom attached by an axial chlorine atom. While these two carbon atoms in δ- and ε-isomers are in a similar environmental situation, *i.e.*, both adjacent and next adjacent positions are all occupied by equatorial chlorine atoms, the shift difference between these weaker lines is 6–6·5 ppm, which is rather large compared with the whole variation range. Thus it will be difficult to make further assignment for the other spectral lines from the data obtained here by comparison of the structure. A part of this difficulty may come from the different solvent effects on the different carbon atoms.

Since γ-BHC undergoes ring inversion at room temperature, ^{13}C chemical shifts are averaged to give two lines with an intensity ratio of 1 : 2.

EXPERIMENTAL

α-, γ- and δ-BHC were obtained from Tokyo Kasei Kogyo Co., Tokyo, and purified by a zone-melting technique. A purified ε-isomer was kindly offered by Dr. N. Kurihara of the Department of Agricultural Chemistry, Kyoto University. The NMR spectra were measured as a 4 mol % solution of the BHC isomer in deuterated acetone (for the β-isomer a saturated solution was used), degassed and sealed in a 5 mm sample tube. The ^{13}C spectra were obtained from about a 1·5 mol % solution in acetone in an 8 mm thin-wall sample tube, (TMS as internal reference).

PMR were obtained by a Varian HA-100 spectrometer at 100 MHz. ^{13}C spectra were obtained on the same apparatus at 25·15 MHz with decoupling protons by V3512/1 Heterodecoupler at RF/AF sweep mode, and about 50 to 100 times accumulations were made by the Spectrum Data System, SS-100. The proton resonance spectra of these isomers were analysed by LAOCOON MBYH program* using a FACOM 270/30 computer.

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