NMR Study of Molecules in Anisotropic Systems. II.† 1a,2a,3e,4e,5e,6e- and 1e,2e,3e,4e,5e,6e-Hexachlorocyclohexanes Dissolved in Nematic Liquid Crystals

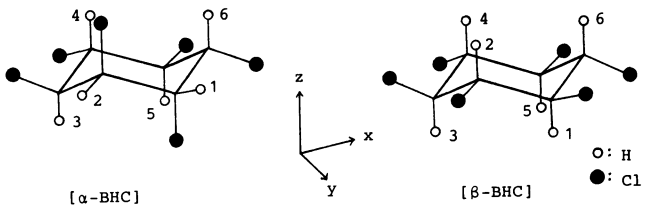
Hideaki FUJIWARA,* Naoto SHIMIZU, Tatsuya TAKAGI, and Yoshio SASAKI
Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-oka, Suita, Osaka 565
(Received April 20, 1985)

NMR spectra of the titled compounds (α- and β-BHC) have been measured in nematic solvents and analyzed. Vibrational corrections were important for the full interpretation of the observed direct couplings. The order parameters showed that the BHC molecules orient most preferably with their six-membered rings parallel to the optic axis of the nematic solvents. Molecular structure of α-BHC derived from the direct couplings corresponds well with those determined by the X-ray method on a crystal and calculated by the MNDO MO method. For β-BHC, however, discrepancies are found with the crystallographic structure, suggesting molecular deformations in the crystal state. Principal axes have been determined for the order matrix and compared with those for the moment of inertia. The difference between the two principal axis systems in α-BHC is interpreted as due to a steric repulsive effect between the two axial chlorine atoms and the solvent molecules.

NMR spectroscopy of molecules dissolved in anisotropic systems, such as liquid crystals, provides unique informations of direct spin–spin couplings and anisotropies in chemical shifts.[1,2] The direct couplings can give accurate structures of molecules in mobile state, *e.g.*, the r_α structures of benzene determined from NMR spectroscopy in ZLI1167 and from electron diffraction in gas phase agree well with each other.[3] The accurate determination also makes it possible to examine experimentally environmental effects on molecular structure, *i.e.*, the effect of solvent[4] as well as that of the phase under investigation[5] which may be gas, liquid (liquid crystal), or solid. A nematic solvent ZLI1167 is reported[4] as an ideal solvent for benzene derivatives which gives rise to negligible distortion on the molecular structure, whereas it has a weak basic character as revealed with some organotin compounds.[6] Anisotropic environment may also induce a specific molecular deformation of anisotropic nature, which is considered responsible to the observation of dipolar or quadrupolar coupling constants even for molecules with high symmetry such as T_d or O_h.[7] All these properties of the solvents originate from solute-solvent molecular interactions and are of wide interests in view of the similar situations met by molecules dissolved in membrane systems with biological importance.

In the present study, benzene hexachloride (BHC) molecules are taken up which have a flexible framework compared to the rigid benzene ring, and their molecular structures and preferred orientations determined by the NMR spectroscopy. The results are discussed by comparing the principal axes of the moment of inertia and those of the order matrix and by comparing molecular structures derived from several physicochemical methods. The isomers treated here are 1a,2a,3e,4e,5e,6e- and 1e,2e,3e,4e,5e,6e-hexachlorocyclohexane, *i.e.*, α- and β-BHC, respectively.

†See Ref 16 for I.



Experimental

α- and β-BHC (City Chemical Co., USA) were recrystallized several times from ethanol. Nematic solvents ZLI1167 and ZLI1132 (Merck) were used without any special purification. NMR spectra were recorded on a Hitachi R-900M FT spectrometer operating at 90 MHz and at 34.1 °C. Concentrations of the samples were 1 wt% for α-BHC in ZLI1167, and less than 1 wt% (saturated) for β-BHC in ZLI1167 and in ZLI1132. A data point of 16 k was used in all measurements and the spectral width and the number of fid's accumulated were 2700 Hz and 3500 for α-BHC, 3150 Hz and 4400 for β-BHC in ZLI1167, and 4950 Hz and 4500 for β-BHC in ZLI1132. Typical line widths were 6 Hz for α-BHC, and 8 Hz (in ZLI1167) and 15 Hz (in ZLI1132) for β-BHC. The sample tube was not rotated when ZLI1132 was used as a solvent.

Spectral analysis was carried out by a computer program LAOCN3 modified to apply to the oriented system.[8] The observed direct couplings were corrected for harmonic vibrations by the program VIBR[9] and processed to the program SHAPE[10] to derive the order and the structural parameters. Principal axes of the moment of inertia were calculated by the program XYZ.[11] All these calculations were achieved with an ACOS System 1000 computer at the Computation Center in Osaka University. Diagonalization of the order matrix was done by a Basic program on a NEC personal computer.

Results and Discussion

Spectral Analysis Leading to the Order and the Structural Parameters. α-BHC belongs to the C_2 point group and gives AA'BB'CC' spin spectra in oriented state, including three chemical shifts and nine

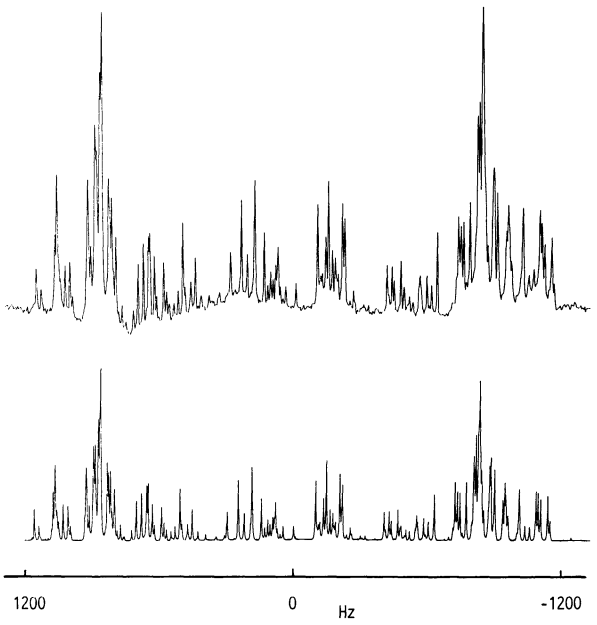


Fig. 1. ^{1}H NMR spectra of α-BHC observed (upper) and simulated (lower) in ZLI1167.

TABLE 1. NMR SPECTRAL PARAMETERS OF α-BHC IN NEMATIC SOLUTION OF ZLI1167[a]

Direct couplings:[b]		Indirect couplings:[18]
D_{12}=	553.95±0.05 (567.61)	J_{12}= 3.28
D_{13}=	69.37±0.04 (70.02)	J_{13}=−0.49
D_{14}=	29.37±0.04 (29.01)	J_{14}= 0.26
D_{15}=	−5.20±0.05 (−5.22)	J_{15}=−0.38
D_{16}=	−86.46±0.04 (−90.05)	J_{16}= 3.28
D_{34}=	−238.41±0.03 (−242.15)	J_{34}= 10.90
D_{35}=	380.74±0.02 (371.60)	J_{35}=−0.23
D_{36}=	11.10±0.03 (9.74)	J_{36}=−0.05
D_{45}=	−188.24±0.04 (−190.53)	J_{45}= 10.24
Chemical shifts:[c]		
$\nu_1-\nu_3$=	1.33±0.06	
$\nu_1-\nu_4$=	62.82±0.06	

a) In units of Hz at 90 MHz. b) Probable errors are given and in parenthese listed are D_{ij}'s corrected for harmonic vibrations. c) Positive frequency toward low field side.

TABLE 2. STRUCTURAL AND ORDER PARAMETERS OF α-BHC IN NEMATIC PHASE ZLI1167 AT 34.1 °C

	Without vibration corrections	With vibration corrections
Distance ratios:		
r_{12}/r_{45}=	0.803±0.003	0.818±0.004
r_{13}/r_{45}=	1.212±0.008	1.226±0.008
r_{14}/r_{45}=	1.334±0.004	1.382±0.006
r_{15}/r_{45}=	1.208±0.007	1.258±0.005
r_{16}/r_{45}=	0.785±0.006	0.795±0.007
r_{34}/r_{45}=	0.988±0.003	1.001±0.003
r_{35}/r_{45}=	0.848±0.005	0.869±0.005
r_{36}/r_{45}=	1.297±0.009	1.293±0.009
Order parameters:[a]		
S_{xx}=	−0.0720±0.0017	−0.0791±0.0014
S_{zz}=	0.0834±0.0014	0.0902±0.0009
S_{xz}=	0.0028±0.0008	0.0010±0.0009

a) r_{45}=3.092Å assumed.

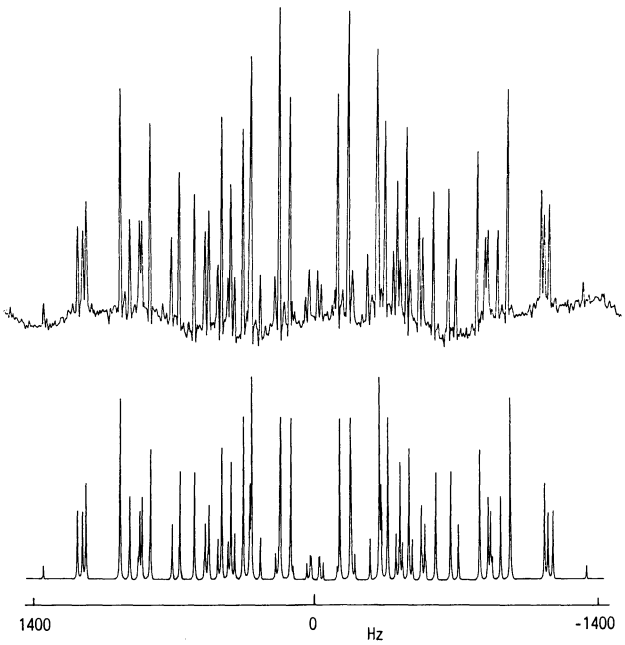


Fig. 2. ^{1}H NMR spectra of β-BHC observed (upper) and simulated (lower) in ZLI1167.

direct couplings as independent variables besides the indirect couplings which are usually substituted by those determined in isotropic media. The spectral pattern observed in ZLI1167 (Fig. 1) is characteristic and the spectral analysis is not laboring. Iteration was made on 96 lines in a final step and rms error between the observed and the simulated frequencies was 0.3 Hz. The results are summarized in Table 1. Order and structural parameters were calculated from the direct couplings (D_{ij}) by the use of SHAPE and they are listed in Table 2, where rms error between the observed and the recalculated D_{ij} values is zero since nine unknown parameters (three order parameters and six structural parameters) are determined from nine experimental data.

β-BHC has the C_{3v} symmetry and gives AA'A''-A'''A''''A''''' spectra in nematic solvents, including one chemical shift and three direct couplings as independent variables. The spectra observed in ZLI1167 (Fig. 2) and ZLI1132 resemble each other and are analyzed easily (Table 3). Iterations were made on 62 lines (in ZLI1167) and 43 lines (in ZLI1132), and rms errors were 0.3 Hz (in ZLI1167) and 0.5 Hz (in ZLI1132). Calculations of the order and the structural parameters from experimental D_{ij} values are summarized in Table 4. Since only one order parameter and one structural parameters are variable independently against three data of D_{ij}, the system is overdetermined. Least squares fits, however, resulted in only partial agreement between the experimental and the recalculated D_{ij}'s, and the rms errors remained large in both nematic solvents used here, *i.e.*, 0.99 Hz in ZLI1167

Table 3. NMR Spectral parameters of β-BHC in nematic solutions of ZLI1167 and ZLI1132[a)]

	in ZLI1167	in ZLI1132
Direct couplings:[b)]		
D_{12}	−188.23±0.01 (−191.18)	313.28±0.03 (318.18)
D_{13}	236.99±0.01 (230.98)	−395.83±0.03 (−385.80)
D_{14}	−17.66±0.02 (−17.44)	29.95±0.05 (29.59)
Indirect couplings:[18)]		
J_{12}	10.58	
J_{13}	−0.20	
J_{14}	−0.20	

a) In units of Hz at 90 MHz. b) Probable errors are given and in parentheses listed are D_{ij}'s after vibration correction.

Table 4. Structural and order parameters of β-BHC in nematic solutions of ZLI1167 and ZLI1132

	Without vibration corrections	With vibration corrections
	In ZLI1167	
r ratios:		
r_{13}/r_{12}	0.857±0.001	0.8755±0.0003
r_{14}/r_{35}	1.317±0.001	1.3291±0.0002
Order parameter:[a)]		
S_{zz}	0.0714±0.0007	0.07584±0.00004
rms error/Hz	0.99	0.01
	In ZLI1132	
Distance ratios:		
r_{13}/r_{12}	0.855±0.001	0.8737±0.0002
r_{14}/r_{12}	1.317±0.001	1.3279±0.0002
Order parameter:[a)]		
S_{zz}	−0.1223±0.0006	−0.12668±0.00001
rms error/Hz	1.56	0.03

a) r_{12}=3.092Å assumed.

and 1.56 Hz in ZLI1132 (Table 4).

Corrections for Harmonic Vibrations. It was unexpected that the D_{ij} values observed for the simplest β-BHC were not reproduced well in the above calculation. Model calculations were attempted assuming anisotropic molecular deformations, *e.g.*, C_{2h} symmetry, under the uniaxial orienting system, but they all resulted in unrealistic (very large) deformations. This is the case for both of the nematic solvents used, one of which (ZLI1132) orients parallel to and another (ZLI1167) perpendicular to the external magnetic field. Therefore, corrections for vibrations are considered necessary before invoking to a special molecular deformation. Although such corrections are very small and frequently negligible for the H–H direct couplings, they are known to become important in some cases for a full analysis of the direct couplings, *e.g.*, in cyclopropane[12)] D_{15} is reduced by 1.2 Hz after such correction. Valence force constants which are necessary for the vibrations are not available for BHC itself. Therefore, necessary date are cited from a general valence force field for secondary chlorides[13)] after a dimensional modification to mdyn/Å.[††14)] Calculations of the vibrational corrections are included also in Tables 3 and 4. Rms errors between the experimental and the recalculated D_{ij} values are reduced in great deal and are virtually zero for both of the nematic solvents, supporting successful corrections (Table 4). Vibrational corrections are also applied to α-BHC (Table 1), for which structural parameters change slightly after the correction but not the rms error since the number of unknown parameters equals to that of the experimental data (Table 2).

††dyn=10^{-5}N.

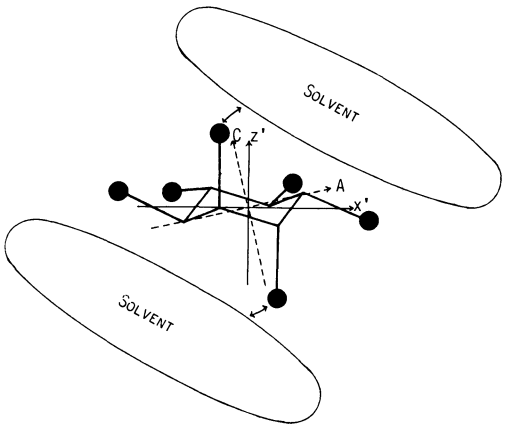


Fig. 3. Principal axis systems for the order matrix (solid line) and for the moment of inertia (dashed line) in α-BHC.
Only Cl atoms are depicted (●).

Orientational Probability from the Order Matrix. As seen from the sign of the order parameters, BHC molecules are most easily oriented like that the *z* axis directs perpendicular to the external magnetic field in ZLI1167 but parallel to it in ZLI1132. When orientation is expressed relative to the optic axis of the nematic solvent, all order parameters need be multiplied by -2 in ZLI1167 which itself orients perpendicular to the external field. Therefore, most probable orientation of the BHC molecules is that their *z* axis is perpendicular to the optic axis in both nematic solvents.

For α-BHC, an off-diagonal element S_{xz} remains non-zero. This S_{xz} is, however, able to be reduced to zero by an appropriate redefinition (rotation) of the cartesian coordinates, *i.e.*, by a diagonalization of the order matrix.[15)] In case of α-BHC such an appropriate rotation is the one that makes $S_{x'z'}=\sum_{pq}\mathrm{COS}\theta_p\mathrm{COS}\theta_q S_{pq}(p,q=x, y, z)$ equal zero where θ means the angle between the new (x',y',z') and the old (x,y,z) axes. The new axes are found to be close to the old ones, resulting $S_{x'x'}=-0.08582$ and $S_{z'z'}=0.09799$ for the principal values. Principal axes are also defined with the moment of inertia. They are depicted in Fig. 3 by dashed lines (*A* and *C* axes), *B* axis coinciding with *y* axis which is the molecular C_2 axis. In case of β-BHC, principal axes of the order matrix agree with those of the moment of inertia because of its C_{3v} symmetry. For δ-BHC, where only one chlorine atom is located at an axial position and others are at equatorials, these two

Table 5. Molecular structure of α-BHC determined from several physico-chemical methods

Ratio	NMR	MNDO[a]	X-ray[b]	Cyclohexane[c]
r_{12}/r_{45}=	0.818	0.825	0.82	0.815
r_{13}/r_{45}=	1.226	1.237	1.25	1.234
r_{14}/r_{45}=	1.383	1.364	1.28	1.344
r_{15}/r_{45}=	1.258	1.232	1.24	1.234
r_{16}/r_{45}=	0.795	0.821	0.75	0.815
r_{34}/r_{45}=	1.001	0.997	1.00	1.000
r_{35}/r_{45}=	0.870	0.843	0.82	0.839
r_{36}/r_{45}=	1.284	1.303	1.31	1.305

a) optimized value of r_{45}=3.094Å. b) from ref. 20, r_{45}=2.983Å. c) calculated from data by gas electron-diffraction study[19], r_{45}=3.092Å.

Table 6. Molecular structures of β-BHC determined from several physico-chemical methods

Ratio	NMR ZLI1167	NMR ZLI132	MNDO[a]	X-ray[b]	Cyclohexane[c]
r_{13}/r_{12}=	0.876	0.874	0.945	0.74	0.839
r_{14}/r_{12}=	1.329	1.328	1.376	1.24	1.306

a) r_{12}=3.038Å. b) From Ref. 21, r_{12}=3.238Å. c) From Ref. 19, r_{12}=3.092Å.

axis systems have been found virtually coincident in a multiple quantum NMR study.[16] In case of α-BHC, two axial chlorine atoms make the *C* axis depart from the *z* axis. But the *z'* axis was not found to deviate considerably from the *z* axis. This is probably because there exists a steric stress effect between the axial chlorine atoms and the solvent molecules, which prevents the *C* axis from being directed perpendicular to the solvent molecules (Fig. 3). A difference of 11° was observed between the two axis systems as shown in Fig. 3.

Solution Structure of the BHC Molecules. Molecular structures are calculated from the observed direct couplings. The direct couplings have been corrected for harmonic vibrations, and hence r_α structure is derived. The results are compared with those determined from other physicochemical methods in Tables 5 and 6, where distance ratios are listed which are derived accurately in the NMR method. In these Tables, NMR means solution structure oriented in nematic phase, X-ray means crystallographic structure, and MNDO means the optimized structure according to the MNDO MO calculation[17] which is listed in place of the unavailable gas-phase structure. These structures corresponds well to each other, supporting reliability of the NMR method adopted here. It is rather difficult to find any dependency of the structure on the phase of investigation in case of α-BHC, but for β-BHC proton distances are seen to be relatively elongated along the *z* axis in crystal state. Such deformation is expected to come from molecular interactions characteristic in crystal states which will be well reflected to the framework of protons located at an outermost sphere of the molecule.

The author (HF) is grateful to Professors P. Diehl and H. Boesiger for sending lists of VIBR and SHAPE.

References

1) J. W. Emsley and J. C. Lindon, "NMR Spectroscopy Using Liquid Crystal Solvents," Pergamon Press, Oxford (1975).
2) C. L. Khetrapal, A. C. Kunwar, A. S. Tracey, and P. Diehl, in "NMR Basic Principles and Progress," ed by P. Diehl, E. Fluck, and R. Kosfeld, Springer, Heidelberg (1975), Vol. 9.
3) P. Diehl and W. Niederberger, *J. Magn. Reson.*, **9**, 495 (1973).
4) P. Diehl, H. Boesiger, and H. Zimmermann, *J. Magn. Reson.*, **33**, 113 (1979).
5) See for example: H. Fujiwara, A. Kawamura, T. Takagi, and Y. Sasaki, *J. Am. Chem. Soc.*, **105**, 125 (1983).
6) H. Fujiwara and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, **1981**, 35.
7) Ref. 1) chap. 4 and E. E. Burnell and C. A. de Lange, *J. Chem. Phys.*, **76**, 3474 (1982).
8) H. Fujiwara, K. Takahashi, and Y. Sasaki, *J. Magn. Reson.*, **41**, 171 (1980).
9) P. Diehl and W. Niederberger, *J. Magn. Reson.*, **9**, 495 (1973).
10) P. Diehl, P. M. Henrichs, and W. Niederberger, *Mol. Phys.*, **20**, 139 (1971).
11) QCPE program No. 178, Indiana University.
12) N. J. D. Lucas, *Mol. Phys.*, **22**, 233 (1971).
13) W. H. Moore and S. Krimm, *Spectrochim. Acta*, **29A**, 2025 (1973).
14) A torsional constant for C-C-C-C is approximated by that for cyclohexane: C. D. Chalk, B. G. Hutley, J. McKenna, L. B. Sims, and I. H. Williams, *J. Am. Chem. Soc.*, **103**, 260 (1981), and a bend-bend constant for Cl-C-C-Cl is set to 0.150 which gives smaller rms error in β-BHC.
15) J. M. Anderson, *J. Magn. Reson.*, **4**, 231 (1971).
16) H. Fujiwara, N. Shimizu, T. Takagi, Y. Sasaki, and K. Takahashi, *J. Magn. Reson.*, in press.
17) a) M. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977); b) M. S. Dewar and H. S. Rzepa, *J. Compt. Chem.*, **4**, 158 (1983).
18) K. Hayamizu, O. Yamamoto, K. Kushida, and S. Satoh, *Tetrahedron*, **28**, 779 (1972).
19) H. J. Geise, H. R. Buys, and F. C. Mijlhoff, *J. Mol. Struct.*, **9**, 447 (1971).
20) G. Smith, C. H. L. Kennard, and A. H. White, *Cryst. Struct. Commun.*, **5**, 683 (1976).
21) G. Smith, C. H. L. Kennard, and A. H. White, *J. Chem. Soc., Perkin Trans.*, **1976**, 614.