Molecular Spectra and Conformational Structure
of 2,3-Dichlorobutane and 3,4-Dichlorohexane

Stokr J., Doskocilova D., Sykora S., Hörhold H.H., Schneider B.

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Abstract

Infrared and NMR spectra of the stereoisomers of 2,3-dichloro- and 2,3-dibromobutane, and of 3,4-dichloro- and 3,4-dibromohexane have been measured in a broad temperature range. Conformational structure with respect to rotation around the 2,3-bond in the butanes, and the 3,4-bond in the hexanes has been determined in the solid and liquid state, and compared with the results of semiempirical conformer energy calculations.

Keywords: PVC models, NMR, IR, Stereo conformations, Molecular dynamics, Dichlorobutane, Dichlorohexane

MOLECULAR SPECTRA
AND CONFORMATIONAL STRUCTURE
OF STEREOISOMERS OF 2,3-DICHLOROBUTANE
AND 3,4-DICHLOROHEXANE

J.Štokr[a], D.Doskočilová[a], S.Sýkora[a], H.H.Hörhold[b] and B.Schneider[a]

[a] *Institute of Macromolecular Chemistry,*
Czechoslovak Academy of Sciences, Prague 6
[b] *Department of Chemistry,*
F. Schiller University, Jena, GDR

Infrared and NMR spectra of the stereoisomers of 2,3-dichloro- and 2,3-dibromobutane, and of 3,4-dichloro- and 3,4-dibromohexane have been measured in a broad temperature range. Conformational structure with respect to rotation around the 2,3-bond in the butanes, and the 3,4-bond in the hexanes has been determined in the solid and liquid state, and compared with the results of semiempirical conformer energy calculations.

The stereoisomers of 2,3-dichlorobutane and 3,4-dichlorohexane are the simplest model compounds containing secondary chlorine atoms on neighbouring carbons. Therefore they are important models of chlorinated polyethylene and chlorinated PVC. Of these compounds, the conformational structure of the stereoisomers of 2,3-dichlorobutane (and also 2,3-dibromobutane) has been studied by NMR spectra measured at room temperature[1-3]. Concerning vibrational spectra, only the infrared spectra of a mixture of stereoisomers of 2,3-dichlorobutane[4], the Raman spectra of isolated stereoisomers of 2,3-dichlorobutane[5], and both infrared and Raman spectra of isolated stereoisomers of 3,4-dichlorohexane (and 3,4-dibromohexane)[6,7] have been measured; none of these spectra have been used for structure analysis. The NMR spectra of the stereoisomers of 3,4-dichlorohexane have not been studied previously. We have measured both infrared and NMR spectra of pure stereoisomers of 2,3-dichlorobutane, 3,4-dichloro- and 3,4-dibromohexane in a broad temperature range in order to determine their conformational structure in the solid and liquid state. The conformer energies of the chloro-derivatives have also been determined theoretically by a semiempirical calculation.

EXPERIMENTAL

The stereoisomers of 2,3-dichlorobutane have been prepared in the chemical laboratories of this Institute. They were separated by preparative gas chromatography on a column filled with Cellite containing 15% of a 1 : 1 mixture of Benton 34 and Apiezon L at 70°C. The resulting steric purity was better than 98% in both isomers. The stereoisomers of 3,4-dichloro- and 3,4-dibromo-hexane have been prepared at the Institut für Organische Chemie und Biochemie, F. Schiller Universität, Jena, and the details of their preparation are described elsewhere[6,7].

Infrared spectra have been measured on the Zeiss UR 10 spectrometer with KBr, NaCl and LiF prisms, provided with a special low-temperature cell. NMR spectra have been measured on the JEOL JNM-3-60 spectrometer operating at 60 Mc, with a resolution of 10^{-8} and equipped with a variable temperature head.

RESULTS

Calculation of Conformer Energies

In the semiepirical calculation, interatomic nonbonded interactions approximated by the Buckingham potential, dipolar interactions of polar bonds and the three-fold barrier of C—C bonds have been considered. Assuming tetrahedral configuration on carbon atoms, all dihedral angles for each conformer have been adjusted to the nearest minimum of potential energy. Details of the method and the values of various intramolecular interactions are described elsewhere[8]. The results of these calculations are given in Tables I and II.

TABLE I

Conformer Energies of 2,3-Dichlorobutane

	meso-Form		*dl*-Form	
	conformer	relative energy	conformer	relative energy
I	T	0	*III* T	1·19
	G^+		*V* G^+	0
II		1·81		
	G^-		*IV* G^-	0·95

Infrared Spectra of 2,3-Dichlorobutane

Each of these molecules has three rotational isomers; in the *meso*-form (Fig. 1, isomers *I* and *II*), two of these are equienergetic mirror-image conformers. In the *dl*-form (Fig. 1, isomers *III* − *V*), all conformers are of C_2 symmetry, in the *meso*-form

conformer *I* has a centre of symmetry, whereas conformer *II* has only C_1 symmetry.

In these molecules, determination of conformational structure from infrared spectra is based on an analysis of the C—Cl stretching vibrations. Various types of C—Cl-stretching vibrations are described by means of symbols S_{XY}, where X and Y designate atoms situated in *trans* position with respect to the chlorine atom.

meso-2,3-*Dichlorobutane*. Of the two possible rotational isomers of this molecule, conformer *I* (Fig. 1) should exhibit in the region of C—Cl stretching vibrations one S_{CIH} band in the infrared and another S_{CIH} band in the Raman spectrum. An S_{CIH} type chlorine atom is expected to absorb around 650 cm^{-1} in the infrared spectrum[9]. Conformer *II* (Fig. 1) has two types of chlorine atoms, one of S_{CH} and another of $S_{HH'}$ type. The frequency of the S_{CH} type stretching vibration is expected to occur around 690 cm^{-1}, of the $S_{HH'}$ around 650 cm^{-1} (*cf.*[9,10]).

The infrared spectrum of liquid *meso*-2,3-dichlorobutane (Fig. 2*b*) exhibits two bands at 650 and 690 cm^{-1}. In the spectra of solutions in CS_2, the intensity of the band at 650 cm^{-1} increases (Fig. 2*c*). Conformers with *trans* chlorine atoms have a much smaller dipole moment, and because of this an intensity increase in CS_2
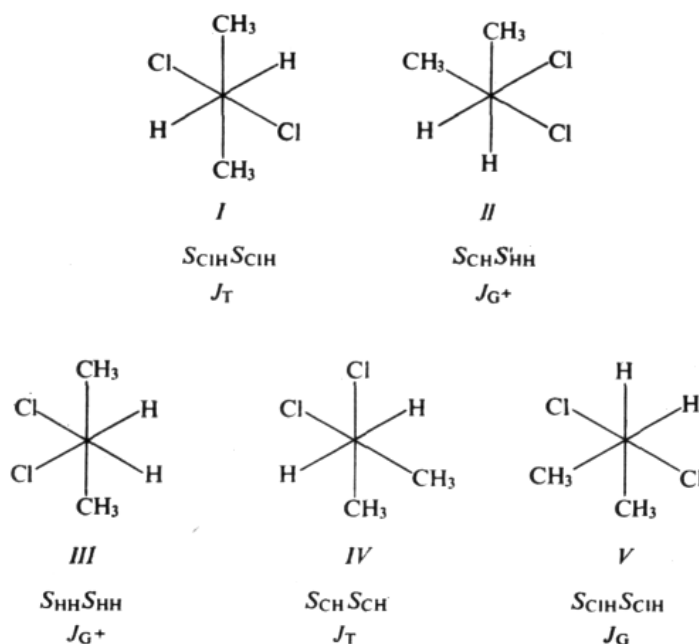

FIG. 1

Conformational Structure of 2,3-Dichlorobutane
meso-Isomer(*I, II*), *dl*-isomer(*III—V*).

solution indicates that the band at 650 cm^{-1} corresponds to a conformer with a *trans* position of chlorine atoms.

The infrared spectrum of solid *meso*-2,3-dichloro-butane (Fig. 2a) exhibits only one band at 650 cm^{-1}, showing that conformer *I* (Fig. 1) in which the two Cl atoms are mutually in *trans* position, is present in the crystal, similarly as in crystalline 1,2-dichloroethane[11]. Infrared spectra of liquid samples (Fig. 2b) exhibit a strong band at 690 cm^{-1} corresponding to conformer *II*. Similar bands are exhibited in Raman spectra of liquid samples[5]. The intensity of the band at 702 cm^{-1} is much higher than the intensity of the band at 652 cm^{-1}. From this it can be concluded that the symmetrical S_{ClH} type C—Cl vibration of conformer *I* appears at 702 cm^{-1}, overlapping the S_{CH} type band of conformer *II*. Similarly the antisymmetrical vibration of the S_{ClH} type chlorine atom of conformer *I* overlaps the $S_{HH'}$ type C—Cl stretching band of conformer *II*. Because of this overlapping of infrared bands at 650 cm^{-1}, temperature changes of the intensity ratio of the bands at 650 and 700 cm^{-1} cannot be used for a determination of the energy difference between conformers *I* and *II*. Assuming equal extinction coefficients of the $S_{HH'}$ type and S_{CH} type C—Cl

TABLE II

Conformer Energies of 3,4-Dichlorohexane

meso-Form			dl-Form		
conformer		relative energy	conformer		relative energy
TTT	$S_{HCl}S_{ClH}$	0	TTT	$S_{HH}S_{HH}$	1·42
TTG$^+$	$S_{HCl}S'_{ClH}$	0·26	TTG$^+$	$S_{HH}S_{HC}$	1·59
TTG$^-$	$S_{HCl}S_{ClC}$	2·52	TTG$^-$	$S_{HH}S'_{HH}$	6·54
TG$^+$T	$S_{HH}S_{CH}$	1·72	TG$^+$T	$S_{HCl}S_{ClH}$	0
TG$^+$G$^+$	$S_{HH}S_{CH'}$	8·49	TG$^+$G$^+$	$S_{HCl}S_{ClC}$	3·60
TG$^+$G$^-$	$S_{HH}S_{CC}$	3·88	TG$^+$G$^-$	$S_{HCl}S'_{ClH}$	6·19
TG$^-$G$^+$	$S_{HC}S'_{HH}$	2·14	TG$^-$T	$S_{HC}S_{CH}$	2·03
TG$^-$G$^-$	$S_{HC}S_{HC}$	1·86	TG$^-$G$^+$	$S_{HC}S_{CC}$	3·88
G$^+$TG$^+$	$S_{CCl}S'_{ClH}$	2·79	TG$^-$G$^-$	$S_{HC}S'_{CH}$	1·98
G$^+$TG$^-$	$S_{CCl}S_{ClC}$	>5	G$^+$TG$^+$	$S_{CH}S_{HC}$	1·72
G$^+$G$^+$G$^+$	$S'_{CH}S'_{CH}$	9·27	G$^+$TG$^-$	$S_{CH}S'_{HH}$	6·90
G$^+$G$^+$G$^-$	$S_{CH}S_{CC}$	4·15	G$^+$G$^+$G$^+$	$S_{CCl}S_{ClC}$	6·91
G$^+$G$^-$G$^+$	$S_{CC}S'_{HH}$	11·33	G$^+$G$^+$G$^-$	$S_{CCl}S'_{ClH}$	11·58
G$^-$TG$^+$	$S'_{HCl}S'_{ClH}$	0·86	G$^+$G$^-$G$^+$	$S_{CC}S_{CC}$	7·10
G$^-$G$^+$G$^+$	$S'_{HH}S'_{CH}$	17·71	G$^+$G$^-$G$^-$	$S_{CC}S'_{CH}$	4·60
			G$^-$TG$^-$	$S'_{HH}S'_{HH}$	7·78
			G$^-$G$^+$G$^-$	$S'_{HCl}S'_{ClH}$	15·74
			G$^-$G$^-$G$^-$	$S'_{HC}S'_{CH}$	2·10

stretching vibrations in conformer *II*, the population of the two conformers can be roughly estimated. Under this assumption, the population of conformer *I* which is stable in the crystal, is seen to increase with increasing temperature in the liquid state.

dl-2,3-*Dichlorobutane*. Of the three possible rotational isomers of this molecule (Fig. 1), conformer *III* should exhibit two S_{HH} type C—Cl stretching bands, a symmetrical and an antisymmetrical one, both of which are expected to absorb around $600-640 \text{ cm}^{-1}$ ($cf.$[9,10]). Conformer *IV* should exhibit in this region two S_{CH} type bands, with frequencies around 680 cm^{-1}. Conformer *V* should exhibit two S_{CIH} type bands, one active in the infrared and the other in the Raman spectrum, in consequence of the strong interaction of the C—Cl stretching vibrations. They can be expected to occur[9] around 650 and 700 cm^{-1}.

The infrared spectrum of liquid *dl*-2,3-dichlorobutane exhibits two bands of medium intensity at 595 and 705 cm^{-1}, both of them of doublet character, and a strong band at 655 cm^{-1} (Fig. 2e). The intensity of this band increases in CS_2 solution (Fig. 2f). Similarly as in the *meso* isomer, we assign this band to the conformer with *trans* chlorine atoms. The bands at 600 cm^{-1} evidently correspond to the conformer with S_{HH} type chlorine atoms (conformer *III* in Fig. 1) and the bands at 700 cm^{-1} to the conformer with S_{CH} type chlorine atoms (conformer *IV*, Fig. 1). In the solid state, the infrared band at 655 cm^{-1} disappears (Fig. 2d), and there remain the bands at 600 and 700 cm^{-1}. The intensity ratio of these bands depends
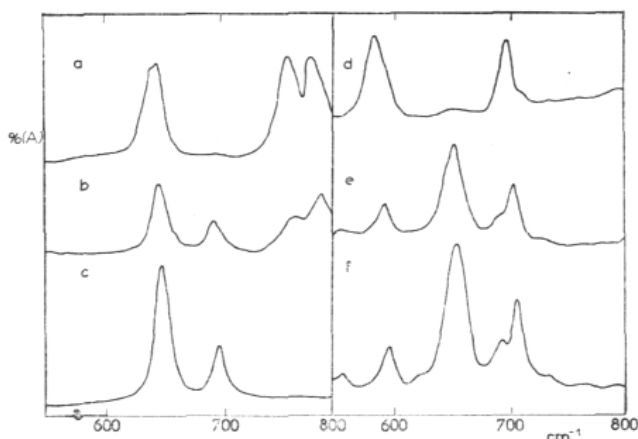

FIG. 2

Infrared Spectra of 2,3-Dichlorobutane

a meso-Isomer, solid; *b meso*-isomer, liquid; *c meso*-isomer, solution in CS_2; *d dl*-isomer, solid; *e dl*-isomer, liquid; *f dl*-isomer, solution in CS_2.

on the cooling procedure (Fig. 3). Therefore we assume that both conformers with gauche chlorine atoms are present in the solid state. This assignment does not contradict the appearance of Raman spectra[5] exhibiting a medium intensity band at 599 cm^{-1}, a very weak band at 653 cm^{-1} and a very strong band at 695 cm^{-1}. From the temperature dependence of infrared spectra, the energy difference between the three rotational isomers could be estimated: $E_{III} = E_{IV}$; $E_V - E_{III} = 0,450$ kcal/mol. Considering the influence of the dipole moment, these values are in fair agreement with the results of theoretical calculations (Table I).

NMR *Spectra* of 2,3-*Dichlorobutane*

NMR spectra of the neat samples of the pure stereoisomers of *meso*- and *dl*-2,3-di-chlorobutane have been measured in the temperature range -40 to $+70°C$. Similarly as the room temperature spectra previously published[1,2], they were analyzed explicitly in terms of an $A_3XX'A_3'$ system. The couplings $J_{AX'}$ and $J_{AA'}$ were assumed as equal to zero. The resulting spectral parameters are summarized in Table III. We see that the coupling constant J_{AX} exhibits hardly any temperature variation, whereas $J_{XX'}$ which is sensitive to conformer population, increases slightly with increasing temperature in both isomers.

In the *meso* isomer, the following relations hold between $J_{XX'}$ and the conformer mol fractions (Fig. 1, conformers *I*, *II*):

$$J_{XX'} = x_I J_T + 2 x_{II} J_G$$

and with

$$x_I + 2x_{II} = 1 \,, \tag{1}$$

$$x_I = (J_{XX'} - J_G)/(J_T - J_G) \,.$$

Similarly in the *dl*-isomer (Fig. 1),

$$J_{XX'} = x_{IV} J_T + (x_{III} + x_V) J_G \,,$$

and with

$$x_{III} + x_{IV} + x_V = 1 \,, \tag{2}$$

$$x_{IV} = (J_{XX'} - J_G)/(J_T - J_G) \,.$$

For a quantitative evaluation of conformer populations from the coupling data, a knowledge of the coupling parameters J_T and J_G is required. Unfortunately, these cannot be estimated with sufficient accuracy at the time being. Bothner-By has used[1] the values $J_T = 11$, $J_G = 1$ in his analysis of 2,3-dichlorobutane, but somewhat higher values of these parameters cannot be excluded. For this reason, only a rough

estimate of the conformational structure of the stereoisomers of 2,3-dichlorobutane can be obtained from NMR data. Our further considerations will be based on the assumed values $J_T - J_G = 10$, and $J_G = 1 - 2$.

With this assumption, neat *meso*-2,3-dichlorobutane would at room temperature exhibit the following conformer population: $x_I = 0.4 - 0.5$; $x_{II} = 0.3 - 0.25$. From Table III and equation (1), x_I is seen to increase slightly with increasing temperature. A similar increase of the population of conformer I with temperature can be also observed in infrared spectra.

With respect to the very small value of $J_{XX'}$ in the *dl*-isomer, the conformers $III + V$ are expected to predominate strongly over form IV. The estimated room temperature value of x_{IV} is $0.1 - 0.2$. The value of x_{IV} increases with increasing temperature.

Conformer populations determined from NMR spectra agree fairly well with theoretical conformer energies (Table I) and with the analysis of infrared spectra if approximately equal extinction coefficients are assumed for all types of chlorine atoms. The increase of the population of conformer III of the *meso*-isomer (Fig. 1) with increasing temperature can be explained by the large difference in dipole moments between the two isomers[12].

TABLE III

NMR Spectral Parameters of Neat 2,3-Dichlorobutane (c/s at 60 Mc/s)

t, °C	δ_{AX}	J_{AX}	$J_{XX'}$
	meso-isomer		
−25	155·5	6·3	5·85
−10	153·15	6·4	5·90
+20	150·25	6·4	6·15
+40	149·15	6·4	6·20
+70	147·8	6·3	6·25
	dl-isomer		
−43	162·2	6·45	2·85
−10	161·2	6·45	3·10
+20	160·1	6·45	3·25
+40	159·1	6·60	3·30
+62	159·0	6·60	3·40

Infrared Spectra of Stereoisomers of 3,4-*Dichloro- and* 3,4-*Dibromohexane*

By rotation around the 3,4-bond, conformational structures analogous to those of 2,3-dichlorobutane are formed in these molecules. However, these molecules contain further two rotational axes — the 2,3- and 4,5-bonds. In consequence of this, nine conformers can be derived from each of the rotational isomers of 2,3-dichlorobutane. Of the 27 possible conformers in each stereoisomer, 15 are nonequivalent in the *meso*-form, and 18 are nonequivalent in the *dl*-form.
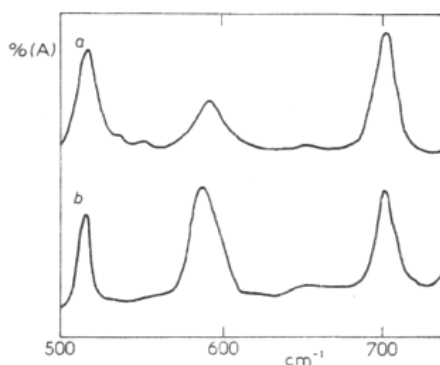

FIG. 3
Examples of Different Types of Infrared Spectra of Solid *dl*-2,3-Dichlorobutane
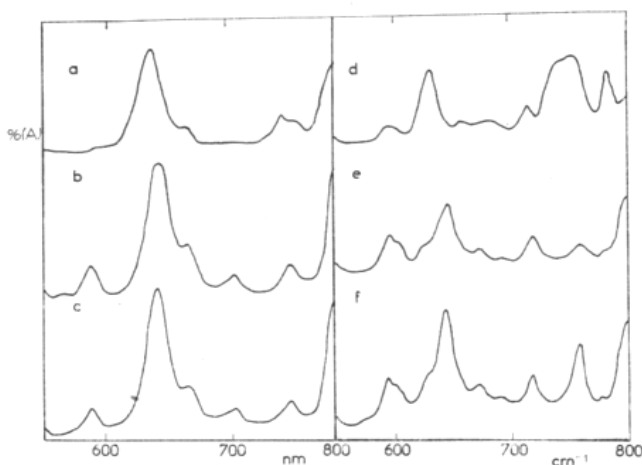

FIG. 4

Infrared Spectra of 3,4-Dichlorohexane
   a meso-Isomer, solid; *b meso*-isomer, liquid; *c meso*-isomer, solution in CS_2; *d dl*-isomer, solid; *e dl*-isomer, liquid; *f dl*-isomer, solution in CS_2.

meso-3,4-*Dichlorohexane*. Infrared spectra of liquid *meso*-3,4-dichlorohexane exhibit in the range of C—Cl stretching vibrations lines at 590, 648, 673 and 712 cm^{-1}, of which the band at 650 cm^{-1} is the strongest (Fig. 4b). In CS$_2$ solution, the relative intensity of this band increases (Fig. 4c). This fact, as well as the intensities of Raman lines indicate that this band corresponds to conformers with *trans* chlorine atoms. According to theoretical calculations (Table II) there exist three favoured conformers with *trans* chlorine atoms (TTT, TTG$^+$, G$^-$TG$^+$) which cannot be differentiated in the spectra. The band at 590 cm^{-1} (S_{HH} type Cl atom) probably corresponds to the conformer TG$^+$T with gauche chlorine atoms. This conformer has one S_{HH} type Cl atom and one S_{CH} type Cl atom. The S_{CH} type Cl atom probably absorbs at 673 cm^{-1}. According to theoretical calculations, there should exist another favoured conformer with gauche chlorine atoms, TG$^-$G$^-$, with two S_{CH} type Cl atoms. We assume that this conformer also absorbs at 673 cm^{-1}. The band at 712 cm^{-1} which is very weak in the infrared spectrum and which corresponds to a medium intensity band in the Raman spectrum can probably be assigned to one of the two conformers with *trans* chlorine atoms and no center of symmetry (TTG$^+$; G$^-$TG$^+$).

In the infrared spectrum of solid samples the bands at 590 cm^{-1} and 712 cm^{-1} disappear, the band at 673 cm^{-1} becomes very weak and the intensity of the band at 650 cm^{-1} increases (Fig. 4c). From this it follows that in the solid state, *meso*-3,4-dichlorohexane similarly as 2,3-dichlorobutane, assumes a conformation with *trans* chlorine atoms, probably TTT.

dl-3,4-*Dichlorohexane*. The infrared spectrum of liquid *dl*-3,4-dichlorohexane exhibits in the range of C—Cl stretching vibrations bands at 595, 602, 635, 645, 673, 692 and 720 cm^{-1} (Fig. 4e). Of these, the band at 645 cm^{-1} is the strongest, and its intensity increases in CS$_2$ solution (Fig. 4f). From this it is evident that this band corresponds to the conformer with *trans* chlorine atoms. According to theoretical calculations, only one such form, TG$^+$T, with S_{ClH} type Cl atoms, is energetically favoured. This band disappears in infrared spectra of solid samples (Fig. 4d). All other bands in infrared spectra of liquid and solid samples correspond to conformers with gauche chlorine atoms. According to theoretical calculations, four conformers with gauche chlorine atoms (TTT, TTG$^+$, G$^+$TG$^+$, TG$^-$G$^-$) have ΔE values below 2 kcal/mol. Temperature changes of the intensities of these bands indicate that the doublet at 600 cm^{-1} and the band at 720 cm^{-1} have an equal temperature trend. From this it can be assumed that both these bands correspond to the conformer TTG$^+$, with one S_{HH} and one S_{CH} Cl atom. The very weak bands at 673 and 692 cm^{-1} correspond to S_{CH} type Cl atoms, and by comparison with the theoretical calculations could be assigned to the conformers G$^+$TG$^+$ and TG$^-$G$^-$. Infrared spectra of solid samples exhibit only one strong band (Fig. 4d) at 632 cm^{-1} which is weak in the infrared spectrum of the liquid sample. This line is assumed to correspond to the S_{HH} type vibration of conformer TTT.

NMR *Spectra of the Stereoisomers of* 3,4-*Dichlorohexane and* 3,4-*Dibromohexane*

NMR spectra of neat samples of the pure stereoisomers of *meso-* and *dl*-3,4-dichloro- and 3,4-dibromohexanes have been measured at -20, $+20$ and $+70°C$. Room temperature spectra of 10% w/v solutions in CS_2 have also been measured. All these spectra exhibit a methyl proton triplet at high field, a very complicated methylene proton band about 50 c/s downfield from the methyl, and the methine proton multiplet at lowest field (about 180 c/s from the methyl) (Fig. 5). The complete spectra can be described in terms of $K_3ABXX'A'B'K_3'$ systems. The pattern of the X band contains information concerning conformational structure around the 3,4-bond, the pattern of the AB band conformational structure around the 2,3- and 4,5-bonds. The latter seems too complicated for unequivocal analysis from present experimental data. On the other hand, the X-band can be analyzed relatively easily, if long range couplings are neglected. Because of the free rotation of the methyl groups, the J_{AK} and J_{BK} coupling constants may be assumed to be equal. From the point of view of the analysis of the X band, the methylene–methyl interaction may be regarded as sufficiently weak ($J_{AK}/\delta_{AK} \approx J_{BK}/\delta_{BK} \approx 0.14$). Under these conditions, the X band can be analyzed in terms of an $ABXX'A'B'$ system by an extended effective frequency method, taking into account the strong AB coupling. The method of analysis is described in greater detail in the Appendix. The resulting spectral parameters are summarized in Table IV and the $J_{XX'}$ values are compared with those of 2,3-dichlorobutane in Fig. 6.

From the values of $J_{XX'}$, conformational structure around the 3,4 bond can be estimated, using equations (*1*) and (*2*), in a manner completely analogous to 2,3-dichlorobutane. In this approach, conformation around the 2,3- and 4,5-bonds is disregarded, and the mol fraction values $x_I - x_V$ are used to designate in each

TABLE IV

J_{XX} (c/s) Coupling Constants Obtained by Analysis of Methine Proton Band in NMR Spectra of 3,4-Dichloro- and 3,4-Dibromohexanes

State	t, °C	*meso*-Cl	*meso*-Br	*dl*-Cl	*dl*-Br
	-20	7·6	9·35	2·2	2·4
Neat	$+20$	7·8	9·15	2·4	2·6
	$+70$	7·95	8·65	2·9	2·95
10% w/v (CS_2)	$+20$	8·65	9·5	2·7	2·7

case the sum of the nine conformers with the respective conformation around the 3,4-bond corresponding to one of the forms of Fig. 1. The coupling parameters J_T, J_G are subject to the same uncertainty, but they can reasonably be assumed to be the same in the series butane–hexane. From Table IV and equation (1), in *meso*-3,4-dichlorohexane the room-temperature value of x_I is estimated to lie between $0.57 - 0.67$ and in *meso*-3,4-dibromohexane between $0.70 - 0.80$. In the former, x_I increases slightly with increasing temperature, but the temperature trend is reversed in the latter.
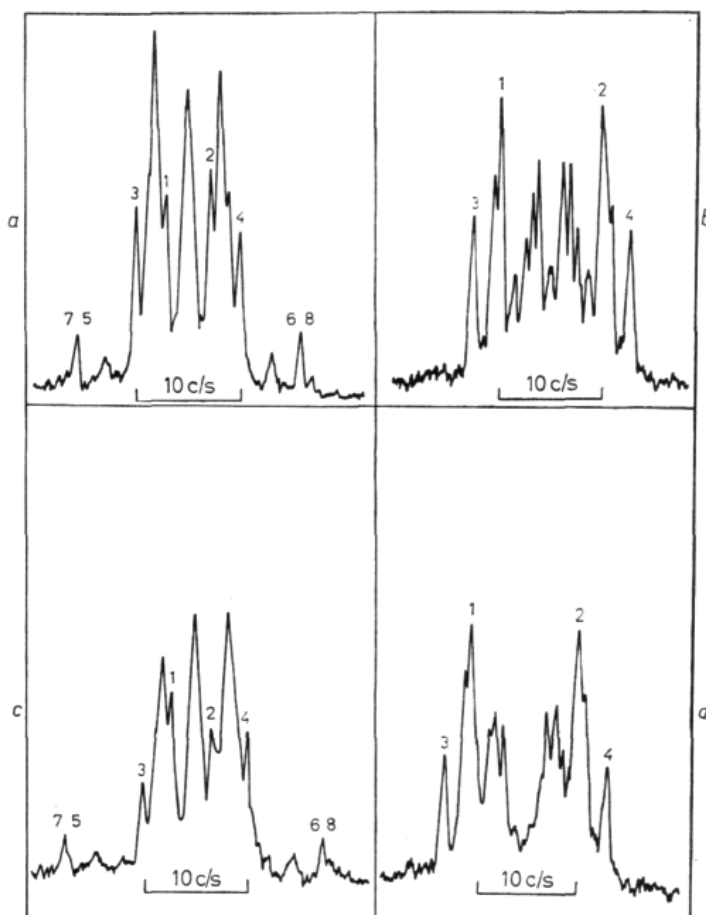

Fig. 5

NMR Spectra of Methine Protons in 3,4-Dihalogenohexanes (10% w/v in CS_2, 20°C)

a meso-3,4-Dichlorohexane; *b dl*-3,4-dichlorohexane; *c meso*-3,4-dibromohexane; *d dl*-3,4-dibromohexane.

The fact that, with respect to the rotation around the 3,4-bond, 2,3-dichlorobutane and 3,4-dichlorohexane have a similar conformational structure (Table V), is in agreement with the analysis of infrared spectra and with the results of theoretical calculations. The higher population of conformers with *trans* chlorine atoms in *meso*-3,4-dichlorohexane can be explained by the smaller influence of the dipole moment in a larger molecule.

From Table IV and equation (2), in *dl*-3,4-dichlorohexane, x_{IV} is estimated to lie between $0.04-0.14$, and in *dl*-3,4-dibromohexane between $0.06-0.16$. In both these compounds, x_{IV} increases with increasing temperature. According to theoretical calculations, x_{IV} corresponds to only one conformer with $\Delta E < 2$ kcal/mol (TG^-G^-). In infrared spectra, this conformer could be assigned either to the band at 673 cm^{-1} or at 692 cm^{-1}. The intensities of both these bands agree with the values of x_{IV} determined from NMR spectra (Table V).

TABLE V
Conformer Population from NMR Data in 2,3-Dihalogenobutanes and 3,4-Dihalogenohexanes

Compound	State	t, °C	*meso*	*dl*
			x_I	x_{IV}
2,3-Dichlorobutane	neat	-25	$0.38-0.48$	$0.10-0.20$
		$+20$	$0.41-0.51$	$0.12-0.22$
		$+70$	$0.42-0.52$	$0.14-0.24$
	10% w/v in CS$_2$	$+20$	$0.54-0.64^a$	$0.14-0.24^a$
2,3-Dibromobutane	neat	$+20$	$0.59-0.69^a$	$0.10-0.20^a$
	10% w/v in CS$_2$	$+20$	$0.68-0.78^a$	$0.11-0.21^a$
3,4-Dichlorohexane	neat	-20	$0.56-0.66$	$0.02-0.12$
		$+20$	$0.58-0.68$	$0.04-0.14$
		$+70$	$0.59-0.69$	$0.09-0.19$
	10% w/v in CS$_2$	$+20$	$0.66-0.76$	$0.07-0.17$
3,4-Dibromo-hexane	neat	-20	$0.73-0.83$	$0.04-0.14$
		$+20$	$0.71-0.81$	$0.06-0.16$
		$+70$	$0.66-0.76$	$0.09-0.19$
	10% w/v in CS$_2$	$+20$	$0.75-0.85$	$0.07-0.17$

[a] Data of Bothner-By[1].

CONCLUSIONS

Analysis of infrared and Raman spectra of the stereoisomers of 2,3-dichlorobutane and 3,4-dichlorohexane has shown that in the solid state the *meso*-isomers always exist in a form with *trans* chlorine atoms, whereas the *dl*-isomers exist in a form with gauche chlorine atoms. In the liquid state in all these compounds the conformers with *trans* chlorine atoms are the most favoured. Results of the analysis of infrared and NMR spectra together with their temperature dependence have shown that theoretically calculated conformer energies can be used as a basis for a plausible interpretation of infrared spectra, and do not contradict the parameters resulting from analysis of NMR spectra.
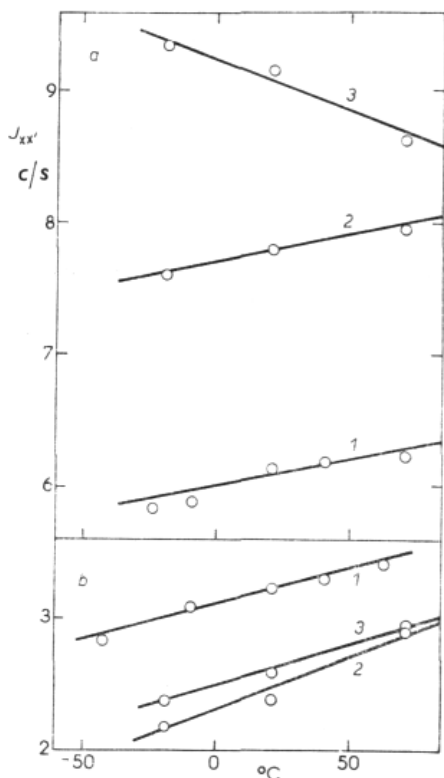

FIG. 6

Temperature Dependence of the $J_{XX'}$ Vicinal Coupling Constants in 2,3-Dichlorobutane, 3,4-Dichloro and 3,4-Dibromohexane

a meso-Isomers; *b dl*-isomers; *1* 2,3-dichlorobutane; *2* 3,4-dichlorohexane; *3* 3,4-dibromohexane.
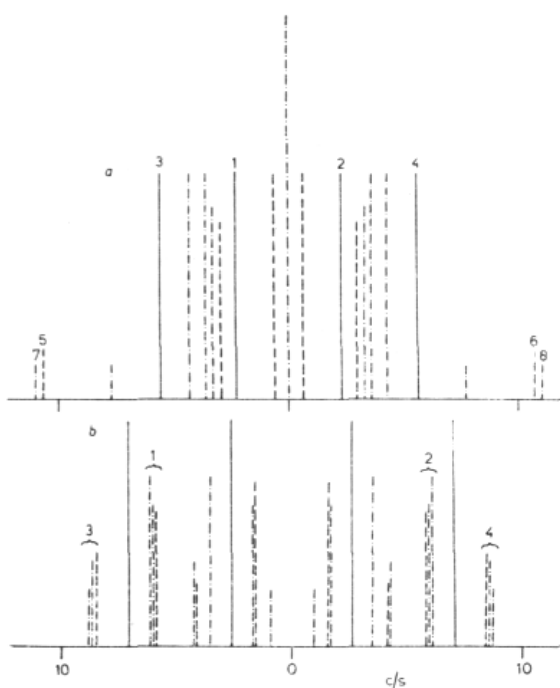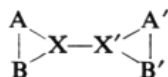
FIG. 7

ABXX′A′B′ Spectral Patterns Typical of *meso*- and *dl*-3,4-Dihalogenohexanes

a J_{XX} 7·7; *d* 5·6; εb 2·3; *b* J_{XX} 2·6; *d* 7·1; εb 2·6; ———— singlets; ----- quartets centered on 0; –•–•–•– quartets centered on $\pm\frac{1}{2}(d \pm \varepsilon b)$.

Analysis of NMR spectra of the stereoisomers of 3,4-dibromohexane has shown that in the liquid state these compounds have a conformational structure analogous to that of the corresponding chloro derivatives.

APPENDIX

The wave function of the system

$$
\begin{array}{c}
\text{A} \\
| \\
\text{B}
\end{array}
\!\!>\!\!\text{X}\!-\!\text{X}'\!\!<\!\!
\begin{array}{c}
\text{A}' \\
| \\
\text{B}'
\end{array}
$$

can be expressed in the form

$$\psi \approx \varphi(\text{AB})\,\varphi(\text{XX}')\,\varphi(\text{A}'\text{B}') \qquad (A1)$$

The function $\varphi(\text{XX}')$ can in first approximation be described as an eigenfunction of the effective Hamiltonian $H^{\ddagger}_{\text{XX}'}$ of the fragment XX'. The parameters of $H^{\ddagger}_{\text{XX}'}$ are given by the relations

$$
\begin{aligned}
J^{\ddagger}_{\text{XX}'} &= J_{\text{XX}'} \\
\nu^{\ddagger}_{\text{X}} &= \nu_{\text{X}} + \varrho_{\text{A}} J_{\text{AX}} + \varrho_{\text{B}} J_{\text{BX}} \\
\nu^{\ddagger}_{\text{X}'} &= \nu_{\text{X}'} + \varrho_{\text{A}'} J_{\text{A}'\text{X}'} + \varrho_{\text{B}'} J_{\text{B}'\text{X}'}
\end{aligned}
\qquad (A2)
$$

where ν designates the Larmor precession frequency and ϱ the spin density of the respective nucleus. The values of ϱ_{A}, ϱ_{B} for various states of the AB system are given in Table VI. The Hamiltonian $H^{\ddagger}_{\text{XX}'}$ is defined by the state of the (AB), (A'B') fragments. In general, of course, the state of the XX' part also affects the state of the (AB) and (A'B') groups, and consequently also the value of the effective shift $\delta^{\ddagger}_{\text{AB}}$ entering into the calculation of ε.

The XX' transitions of the system ABXX'A'B' can be described in terms of 10 quartets summarized in Table VII, from which suitable explicit expressions for the analysis of the X band can easily be constructed. Typical spectral patterns arising from a combination of these 10 quartets are illustrated in Fig. 7.

TABLE VI

Spin Densities in an AB System
$\varepsilon = [1 + (J/\delta)^2]^{-1/2}$.

State	$\varphi(\text{AB})$	$\varrho(\text{A})$	$\varrho(\text{B})$
$+1$	$\alpha\alpha$	$1/2$	$1/2$
0_+	$\alpha\beta \cos\theta + \beta\alpha \sin\theta$	$\varepsilon/2$	$-\varepsilon/2$
0_-	$-\alpha\beta \sin\theta + \beta\alpha \cos\theta$	$-\varepsilon/2$	$\varepsilon/2$
-1	$\beta\beta$	$-1/2$	$-1/2$

TABLE VII

Structure of X-Band in ABXX'A'B' Systems

$d = \frac{1}{2}(J_{AX} + J_{BX});\ b = \frac{1}{2}(J_{AX} - J_{BX});\ \varepsilon = [1 + (J_{AB}/\delta^{\mp}_{AB})^2]^{-1/2}.$

| State of nuclei | | Centre of quartet | Effective shift |
AB	A'B'	$(\nu_x = 0)$	$\delta^{\mp}_{XX}$
$+1$	$+1$	$+d$	0
-1	-1	$-d$	0
0_+	0_+	$+\varepsilon b$	0
0_-	0_-	$-\varepsilon b$	0
$+1$	-1	0	$2d$
-1	$+1$		
$+1$	0_-	$+\frac{1}{2}(d - \varepsilon b)$	
0_-	$+1$		
-1	0_+	$-\frac{1}{2}(d - \varepsilon b)$	$d + \varepsilon b$
0_+	-1		
$+1$	0_+	$+\frac{1}{2}(d + \varepsilon b)$	
0_+	$+1$		
-1	0_-	$-\frac{1}{2}(d + \varepsilon b)$	$d - \varepsilon b$
0_-	-1		
0_+	0_-	0	$2\varepsilon b$
0_-	0_+		

From the experimental spectra of the *meso*-3,4-dihalogenohexanes, the values of $2d$ and $2\varepsilon b$ can be directly read off from the $\pm d$ (Fig. 7a, lines *3, 4*) and $\pm \varepsilon b$ (lines *1, 2*) singlets. Knowing $2d$, we can determine J_{xx} from the outer two lines of the quartet with $\delta^{\mp}_{XX'} = 2d$ (lines *5, 6*). Their position cannot be read off quite accurately, because they are overlapped by the lines *7, 8*. The experimental frequency, corresponding to the mean of lines *7, 5* and *6, 8* is therefore used for an approximate calculation of J_{xx}. This approximate value of J_{xx}, together with d and εb, is then used to estimate the shift between $\nu_7 - \nu_5$, and $\nu_6 - \nu_8$, and to obtain the corrected spacing $\nu_5 - \nu_6$. From this and $2d$, the final value of J_{xx} is calculated. Due to the large number of un-resolved overlapping lines in the spectrum, and to the uncertainty in the values of J_T and J_G used in further applications of the spectral parameters obtained, a more elaborate analysis of the system did not seem warranted.

In the spectra of the *dl*-isomers (Fig. 7b), the experimental lines *1, 2, 3, 4* correspond fairly accurately to the quartet with $\delta^{\mp}_{XX'} = 2d$, and J_{XX} can be directly read off from the spacing $\nu_3 - \nu_1$ or $\nu_1 - \nu_4$.

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