Conformational Structure of Stereoisomers of 2,4-Dichloropentane

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Abstract:

By analysis of vibrational and NMR spectra and by theoretical conformer-energy calculations 2,4-dichloropentane was shown to contain, in addition to the previously established forms TT and GG of the d,l isomer and TG of the meso isomer, small amounts of other conformers.

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Synopsis

By analysis of vibrational and NMR spectra and by theoretical con-
former-energy calculations 2,4-dichloropentane was shown to contain,
in addition to the previously established forms TT and GG of the d,l
isomer and TG of the meso isomer, small amounts of other conformers.

Stereoisomers of 2,4-dichloropentane are important models of syndio-
tactic and isotactic poly(vinyl chloride), and for this reason they have
been the subject of several communications (1–9). From infrared spec-
tra the TT conformer has been found in the d,l isomer, and the TG con-
former (Fig. 1) in the meso isomer (1). Analysis of NMR spectra has
shown the d,l isomer to contain also the GG form and the meso isomer
to contain the two mirror-image forms TG and GT in mobile equilibrium
(3,5). These three conformational forms were also the only ones admit-
ted by theoretical conformer-energy calculations (5–7). However, they
alone were not sufficient for explaining all the parameters obtained by
analysis of NMR spectra (5,10), for the assignment of all lines in the in-
frared and Raman spectra, and for the interpretation of some lines in the
infrared spectra of PVC (11). For this reason we have revised the de-
tails of the analysis of vibrational and NMR spectra of these compounds;
at the same time, the possibility of the formation of further conformers
has been investigated theoretically. In this paper the first preliminary
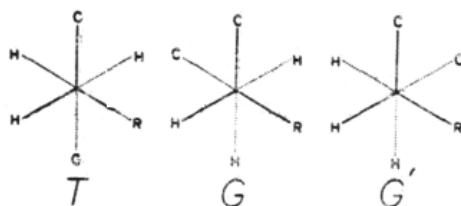results of this work are presented.

Fig. 1. Designation of conformational structures.

EXPERIMENTAL

For preparation of the sample a mixture of stereoisomeric forms of d,l-2,4-dichloropentane was prepared by a method previously described (2). The separation of the stereoisomers was performed by repeated fractionation on an efficient column (9). In this way stereoisomeric forms of highest purity were obtained (meso 100.00%, d,l 99.99%, determined by gas chromatography).

Infrared spectra were recorded on the Zeiss UR 10 spectrometer with a KBr and NaCl prism in a variable-temperature cell (12) suitable for measurement in the range −170 to +100°C. Crystallization and quenching of samples were performed directly in the cell. Maximum absorbances were measured by the baseline method.

Raman spectra were recorded on the DFS 12 spectrometer with a Toronto type mercury tube for excitation. Depolarization factors were determined by the method of two polaroids. Low-temperature spectra were measured in cells with a vacuum jacket.

NMR spectra of "neat" d,l- and meso-2,4-dichloropentane were measured in the temperature range −35 to +125°C. on a JNM-3-60 spectrometer operating at 60 Mc. with a resolution of 10^{-8}. Spectra were calibrated by the side-band method. Line frequency values (referred to the center of the methyl proton doublet) were averaged from a large number of independent runs, giving a mean deviation of ±0.1 cps.

Theoretical

From vibrational spectra the conformational structure was determined by means of C–Cl stretching vibrations. Bands observed in the vibrational spectra were assigned to various conformers with the use of the frequency ranges established for different types of Cl atoms in papers by Shipman et al. (13) and by Caraculacu et al. (14). As in secondary chlorides, with several chlorine atoms separated by only one methylene group, these frequency ranges may in some cases be unreliable (10); the frequencies of C–Cl stretching vibrations have also been calculated by means of a simple model, with methyl, methylene, and methine groups substituted by point masses situated at carbon atom positions. The force constants used were K_{C-C}, $F_{C-C*C-C}$, and $F_{C-C*C-C-C}$, taken from the paper by Schachtschneider and Snyder (15), and K_{C-Cl}, H_{C-C-C}, and H_{C-C-Cl}, calculated from the frequencies of the simple molecules methyl chloride, propane, and trans-1,2-dichloroethane; these constants were empirically adjusted so as to agree with experimental values for T and TT conformations of 2-chlorobutane and 3-chloropentane. This force field describes satisfactorily the C–Cl stretching frequencies of all conformational forms in simple alkyl chlorides. A more detailed analysis of the force field will be given in a subsequent communication (16).

TABLE I

Conformers and Vicinal Coupling Constants of d,l-2,4-Dichloropentane

$$
\begin{array}{c}
H^X H^{A'} Cl \\
| \quad | \quad | \\
CH_3-C-C\!\!-\!\!-C-CH_3 \\
| \quad | \quad | \\
Cl \; H^A \; H^{X'}
\end{array}
$$

Conformer		$2J$	$2J'$
x_1	TT	$2J_T$	$2J_G$
x_2	GG	$2J_G$	$2J_T$
$2x_3$	TG	$J_T + J_G$	$J_T + J_G$
$2x_4$	GG'	$2J_G$	$J_T + J_G$
$2x_5$	TG'	$J_T + J_G$	$2J_G$
x_6	G'G'	$2J_G$	$2J_G$

TABLE II

Conformers and Vicinal Coupling Constants of
meso-2,4-Dichloropentane

$$
\begin{array}{c}
H^X H^A H^X \\
| \quad | \quad | \\
CH_3-C-C-C-CH_3 \\
| \quad | \quad | \\
Cl \; H^B Cl
\end{array}
$$

Conformer		$2J_{AX}$	$2J_{BX}$
$2x_1$	TG	$J_T + J_G$	$J_T + J_G$
$2x_2$	TG'	$2J_G$	$J_T + J_G$
x_3	TT	$2J_G$	$2J_T$
x_4	GG	$2J_T$	$2J_G$
$2x_5$	GG'	$J_T + J_G$	$2J_G$
x_6	G'G'	$2J_G$	$2J_G$

For the determination of conformational structure from NMR spectra, values of vicinal coupling constants were applied. In a number of preceding communications concerning 2,4-disubstituted pentanes the relations between the experimentally determined values of methylene—methine coupling constants and conformer population have been discussed in detail [summarized by Bovey (17)], the presence of preferred, sterically unhindered conformers only being considered. In the present communication the effect of all conformers was considered. The contribution of these additional forms to the resulting values of the vicinal coupling constants d,l- and meso-2,4-dichloropentane is summarized in Tables I and II. If deviations from staggered bonds occur, all the values of J_T and, especially, of J_G cannot in general be expected to be equal. In all cases, however, the values of J_G should be much smaller than those of J_T.

With the aid of Tables I and II the sum and difference of vicinal coupling constants may be expressed as a function of conformer mole fractions. For d,l-2,4-dichloropentane

$$2d = J + J' = \Sigma J(x_1 + x_2 + x_3) + \Sigma J'(2x_4 + 2x_5) + 2J_G x_6 \tag{1}$$

$$2b' = J - J' = \Delta J(x_1 - x_2 - x_4 + x_5) \tag{2}$$

and for meso-2,4-dichloropentane

$$2d = J_{AX} + J_{BX} = \Sigma J(2x_1 + x_3 + x_4) + \Sigma J'(2x_2 - 2x_5) + 2J_G x_6 \tag{3}$$

$$2b = J_{AX} - J_{BX} = \Delta J(-x_2 - x_3 + x_4 + x_5) \tag{4}$$

where $\Sigma J = J_T + J_G$, $\Sigma J' = \frac{1}{2}(J_T + 3J_G)$, and $\Delta J = J_T - J_G$.

Theoretical conformer-energy calculations in the present work were based on three types of nonbonded interaction:

(1) Dispersion and exchange interactions approximated by the Buckingham (18) exp {−6} potential. The parameters of this interaction were obtained by the Scott-Scheraga (19) procedure.

(2) Dipolar interactions of C−Cl bonds.

(3) Threefold barrier of the C−C bond (19).

Contrary to older calculations, dihedral angles corresponding to pure staggered forms were not held fixed, and the angles were adjusted to the nearest energy minimum, as in Abe's calculation of linear hydrocarbons (20) and in the Scott-Scheraga calculation of polyethylene (21). The results of this calculation indicate that the conformers previously considered are not the only forms that can exist in 2,4-dichloropentane. The details of the calculation will be published elsewhere (22).
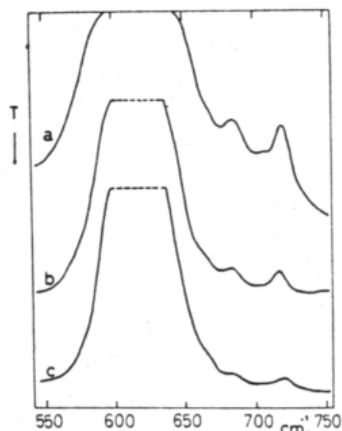
Fig. 2. Infrared spectrum of d,1-2,4-dichloropentane: (a) 33°C., cell thickness 100 μ; (b) 0°C., 50 μ; (c) −44°C., 50 μ.
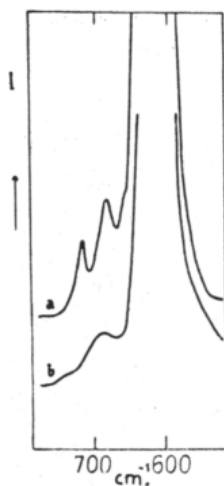

Fig. 3. Raman spectrum of d,1-2,4-dichloropentane: (a) liquid, 30°C.; (b) crystalline, −70°C.

Results

Vibrational Spectra. Infrared spectra of d,1-2,4-dichloropentane measured at room temperature (Fig. 2) exhibit, in addition to the previously described bands at 610 and 630 cm.$^{-1}$ (the former with a larger half-band width), two weak bands at 685 and 718 cm.$^{-1}$. The intensity of these bands is about 50 times less than that of the main bands, and they can be meausred well at a cell thickness of 50 and 100 μ. In some spectra an additional line can be detected at 706 cm.$^{-1}$ (Fig. 2a). The Raman spectrum (Fig. 3) exhibits similar lines at 610, 628, 682, and
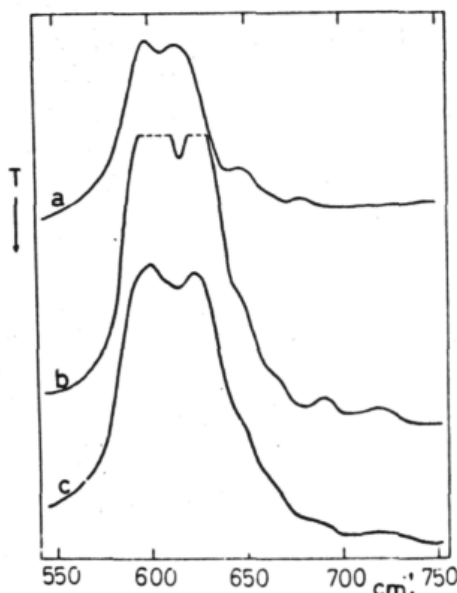
Fig. 4. Infrared spectrum of d,l-2,4-dichloropentane: (a) crystalline, −50°C., (b) sample quenched to −130°C., (c) quenched sample heated to −50°C.

716 cm.$^{-1}$, the first of these unpolarized, the second and fourth polarized ($\rho = 0.2$), and the band at 682 cm.$^{-1}$ having a depolarization factor $\rho = 0.6$. In infrared spectra the intensity of the lines at 718 and 685 cm.$^{-1}$ decreases smoothly with decreasing temperature, and at temperatures below −30°C. a shoulder appears at 665 cm.$^{-1}$. By careful cooling to below −40°C. the sample can be made to crystallize. The infrared spectrum of crystalline d,l-2,4-dichloropentane exhibits (Fig. 4a) two strong bands at 600 and 615 cm.$^{-1}$ (the former with a smaller half-band width), a shoulder at 650 cm.$^{-1}$, and a very weak band at 682 cm.$^{-1}$. The band at 718 cm.$^{-1}$ disappears completely. In Raman spectra (Fig. 3b) these bands correspond to lines at 600 and 622 and a very weak one at 682 cm.$^{-1}$. By rapid quenching of the sample from room temperature to −130°C. crystallization can be prevented. Infrared spectra of quenched samples (Fig. 4b) exhibit two strong bands at 600 and 625 cm.$^{-1}$, the former broader and asymmetric. Besides these the spectra exhibit shoulders at 645 and 663 cm.$^{-1}$ and weak bands at 690 and 720 cm.$^{-1}$. By heating the quenched sample to −50°C. all lines except those at 600 and 625 and the shoulder at 645 cm.$^{-1}$ disappear (Fig. 4c).

The spectrum of meso-2,4-dichloropentane measured at room temperature exhibits two strong bands at 618 and 686 cm.$^{-1}$ and a weaker band at 645 cm.$^{-1}$, with an absorbance about 15 times smaller than that of the band at 686 cm.$^{-1}$ (Fig. 5). With decreasing temperature the relative intensity of the band at 645 cm.$^{-1}$ decreases. In crystalline samples this band disappears completely. The absorbance ratio of the 618
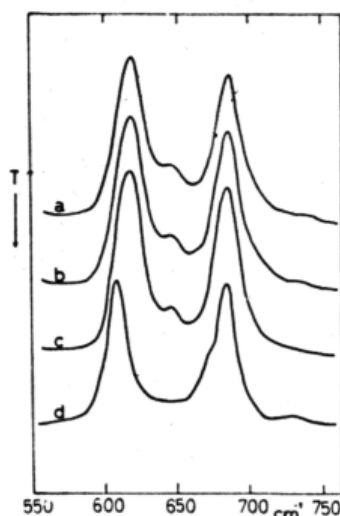
Fig. 5. Infrared spectrum of meso-2,4-dichloropentane: (a) liquid, 30°C., contact film; (b) liquid, 0°C., contact film; (c) liquid, −46°C., contact film; (d) crystalline, −65°C., cell thickness 50 μ.

and 686 cm.$^{-1}$ bands is practically temperature-independent and does not change, even by crystallization. In addition to these bands a very weak band at 730 cm.$^{-1}$ is observed in the spectra at all temperatures, even in crystalline samples.

The Raman spectrum of the liquid sample exhibits only two strong lines at 619 and 684 cm.$^{-1}$, with an equal depolarization ratio of $\rho = 0.3$.

NMR Spectra. Values of methylene−methine coupling constants of d,l- and meso-2,4-dichloropentane were obtained by analysis of the methylene proton band. This band was analyzed in terms of AA′ and AB transitions of an AA′XX′ and ABX$_2$ system, respectively, with the application of second-order correction terms (10). The resulting parameters are summarized in Tables III and IV, and in Figure 6.

In d,l-2,4-dichloropentane the value of d is seen to decrease very slightly, and the value of b′ rather strongly, with increasing temperature meso-2,4-Dichloropentane exhibits a temperature-independent negative value of b and a value of d measurably decreasing with temperature.

Discussion

d,l-2,4-Dichloropentane. In addition to the lines of the preferred TT conformer the infrared spectrum of this isomer exhibits temperature-dependent lines at 685 and 718 cm.$^{-1}$, indicating temperature changes of conformer population. The frequency of the 718 cm.$^{-1}$ band agrees with that predicted for the GG conformation (23). Moreover, the calculation by means of the above-described simple force field predicts a frequency

TABLE III

NMR Spectral Parameters of d,l-2,4-Dichloropentane

Temp., °C.	Chemical shift,[a] cps		$J_{AA'}$	d	$|b'|$[b]
	ν_{CH_2}	ν_{CH}			
−36	25.6	167.9	−14.8	6.6_2	4.5_3
−10	25.6	166.8	−15.0	6.6_5	4.4_3
+20	26.0	165.2	−14.6	6.4_8	4.2_4
+45	26.0	166.2	−14.8	6.5_1	4.0_6
+69	26.4	165.5	−14.6	6.4_8	3.9_4
+98	27.2	164.7	−14.8	6.3_8	3.5_4
+125	28.0	164.0	−	6.4_8	3.4_3

[a] From center of CH_3 doublet.

[b] Calculated for $J_{AA'} = -14.8$; $d = \frac{1}{2}(J_{AX} + J_{AX'})$; $b' = \frac{1}{2}(J_{AX} - J_{AX'})$.

TABLE IV

NMR Spectral Parameters of meso-2,4-Dichloropentane

Temp., °C.	Chemical shift,[a] cps		J_{AB}	δ_{AB}	d	b
	ν_{CH_2}	ν_{CH}				
−33	37.3	157.8	−14.2	13.4	7.2_7	-0.4_1
−5	37.8	158.7	−14.3	13.6	7.0_1	-0.4_0
+20	37.1	158.6	−14.4	14.2	7.0_5	-0.4_4
+45	36.9	157.0	−14.4	14.4	6.9_8	-0.4_0
+70	37.3	157.9	−14.3	14.3	6.8_1	-0.2_5
+95	37.1	156.8	−14.5	14.7	6.8_9	-0.4_4
+123	37.5	156.9	−14.5	14.8	6.6_5	-0.4_0

[a] From center of CH_3 doublet; $d = \frac{1}{2}(J_{AX} + J_{BX})$; $b = \frac{1}{2}(J_{AX} - J_{BX})$.

of 727 cm.$^{-1}$ for the GG form. The value of ΔH estimated from the temperature change of absorbance of this band is in fair agreement with the
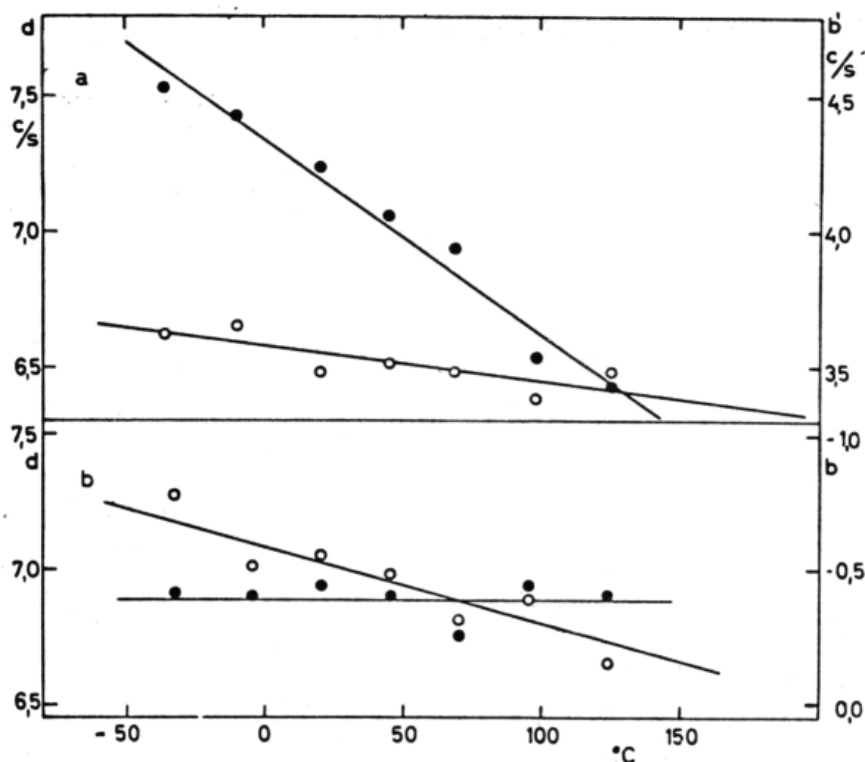
Fig. 6. Temperature dependence of the sum and difference of vicinal coupling constants in NMR spectra of methylene–methine 2,4-dichloropentane. (a) The d,l isomer; (○) $d = \frac{1}{2}(J + J')$; (●) $b' = \frac{1}{2}(J - J')$. (b) The meso isomer: (○) $d = \frac{1}{2}(J_{AX} + J_{BX})$; (●) $b = \frac{1}{2}(J_{AX} - J_{BX})$.

value obtained from NMR data. The band at 685 cm.$^{-1}$ can be assigned either to the TG or to the GG′ conformation. Calculated values of C–Cl stretching frequencies give preference to the TG assignment (16). This is in agreement with the theoretical conformer-energy calculations, according to which the energy of the TG form is only slightly higher than that of the GG form. The band at 706 cm.$^{-1}$ found in some spectra might correspond to the GG′ conformer. Its very small intensity could be in agreement with the calculated energy of this conformer, which is about 4 kcal./mole. For all other forms the theoretical calculation yielded higher energies. At present we are not able to explain the appearance of shoulders in the spectra of the crystalline sample. Depolarization factors in Raman spectra confirm the assignment of the line at 727 cm.$^{-1}$ and do not contradict the assignment of the line at 685 cm.$^{-1}$.

In NMR spectra of the d,l isomer the very slight decrease of the sum of vicinal coupling constants with temperature could be caused by the presence of a small amount of conformers GG′, TG′, and G′G′. In the

absence of these conformers the observed slight temperature change of d might also be caused by differences of J_G in the conformers TT, GG, and TG. The observed slight decrease of d does not contradict the interpretation of infrared spectra. The temperature change of the difference of coupling constants $J - J'$ has in the past been used for the calculation of energy differences between the forms TT and GG (5,10). Such calculations, giving a good rough estimate of the corresponding ΔH (≈ 2.5 kcal./mole from the present data) are, nevertheless, strictly valid only in the absence of additional conformational forms and will probably have to be somewhat revised.

meso-2,4-Dichloropentane. Infrared spectra of meso-2,4-dichloropentane exhibit, in addition to the bands of the preferred conformer TG, a line at 645 cm.$^{-1}$ with temperature-dependent intensity. This band lies in the range of the $S_{HH'}$ type of CCl stretching vibrations. An $S_{HH'}$ type of chlorine atom occurs in conformers TG', GG', and G'G'. Frequency calculations (16) have shown that this region could also contain a band of the form TT. According to theoretical energy calculations, TG' appears to be the most favored of the forms in question (ΔH in the vicinity of 2 kcal./mole). However, the form TT, with an estimated ΔH in the vicinity of 2.5 kcal./mole, cannot be excluded. Energy calculations also admit the presence of very small amounts of forms GG and GG'. Of these the GG form would absorb near 730 cm.$^{-1}$; a very weak band does appear in this region, but its intensity does not change with temperature. The GG' conformation is expected to exhibit a band at a frequency identical with that of the TG' or, possibly, also that of the TG conformer (16), and this conformer might therefore escape detection.

In NMR spectra of meso-2,4-dichloropentane the sum of the vicinal coupling constants exhibits a stronger temperature dependence than in the d,l isomer. The observed decrease of the parameter d might be caused by the presence of conformer TG' or GG' and is in agreement with the assignment of infrared spectra. As in other models of isotactic vinyl polymers (24,25), meso-2,4-dichloropentane exhibits a nonzero negative value of the difference between vicinal coupling constants, $J_{AX} - J_{BX}$. Considering only the presence of conformer TG $\leftrightarrow$ GT, attempts have been made to explain this value by the effect of orientation of electronegative substituents (10) or by deviations of dihedral angles (10,24,25) from the ideal staggered forms. Equation (3) indicates that the nonzero negative value of parameter b might be caused by the presence of conformers TG' or TT. The temperature independence of parameter b, established by the present work, could be explained by the simultaneous presence of smaller amounts of forms GG and GG'. This does not contradict the results of theoretical energy calculations and agrees with the present interpretation of infrared spectra.

Through analysis of infrared and NMR spectra and theoretical conformer-energy calculations the meso isomer of 2,4-dichloropentane was shown

to contain, in addition to the preferred form, small amounts of the form TG'; the presence of small amounts of forms GG', TT, and GG cannot be excluded. In the d,l isomer, small amounts of the form TG were found, in addition to the previously considered forms TT and GG; the presence of very small amounts of form GG' cannot be excluded. Detection of measurable amounts of these additional forms indicates that deviations from the pure, staggered arrangement of bonds in 2,4-dichloropentane have to be considered.

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