SIMPLE METHOD OF CALCULATING ENERGY DIFFERENCES BETWEEN CONFORMATIONAL STRUCTURES IN COMPOUNDS OF THE TYPE $(R_1R_2R_3)C \cdot CH_2 \cdot C(R_4R_5R_6)$ WITH R = H, CI OR ALKYL

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ABSTRACT

Analysis of experimental ΔH values in compounds of the type $(R_1R_2R_3)$ $C \cdot CH_2 \cdot C(R_4R_5R_6)$ with R = H, Cl or alkyl has shown that ΔH in these compounds is primarily determined by interactions of atoms in 1,3 positions lying on parallel bonds, and that the contributions of the specific atoms or groups are constant and additive. The values of these additive contributions have been determined and used for the calculation of energy differences between conformers of many molecules. Very good agreement with experimental data has been obtained.

INTRODUCTION

The sensitivity of C-Cl stretching vibrations to conformational structure is well known and has been utilized in a number of papers on the structure of halogensubstituted paraffins¹⁻³. In many molecules, conformers stable in the solid state, as well as energy differences between various conformers present in the liquid state have been determined. Great attention has been paid to substances with chlorine atoms in 1,3-positions which serve as model compounds of some polymers, especially of PVC^{4-6} . The results all seemed to indicate that simple rules could be found, according to which the number of conformers present in the liquid state and their mutual stability could be determined^{6,7}. In order to complement these rules, we have determined the conformational structures and the corresponding conformer energy differences for 4-chloro-2,2-dimethylpentane and 2-chloro-2methylbutane.

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EXPERIMENTAL

4-Chloro-2,2-dimethylpentane was prepared by reaction of 2,2-dimethylpentan-4-ol with thionyl chloride in the presence of pyridine. After isolation and purification by gas chromatography (Perkin-Elmer F-34, 2 m column filled with 20% squalane/Chromosorb W, t = 40 °C), a product of 99.5% purity was obtained. B.p. = 94 °C/250 mm Hg, $n_D^{20} = 1.4182$ (ref. 8: b.p. = 93 °C/250 mm Hg, $n_D^{20} = 1.4182$). 2,2-Dimethylpentan-4-ol was obtained by catalytic hydrogenation of a methanolic solution of 2,2-dimethylpentan-4-one prepared by the method of Man et al.⁹ on RaNi W-4 at 90 °C and 60 atm. B.p. = 136 °C/735 mm Hg (ref. 10: b.p. = 137-137.5 °C/736 mm Hg).

2-Chloro-2-methylbutane was prepared by shaking 2-methyl-butan-2-ol with conc. HCl¹¹. By column rectification a product with b.p. = 84–84.5 °C/735 mm Hg, $n_D^{20} = 1.4053$ (ref. 12: b.p. = 85.6 °C/760 mm Hg, $n_D^{20} = 1.4055$) was obtained.

Infrared spectra (400–3500 cm⁻¹) were measured on a Zeiss UR-10 spectrometer and Raman spectra with a DFS-12 spectrometer (He–Ne laser (40 mW) excitation source). The temperature dependence of vibrational spectra was measured in the range -130° to $+30^{\circ}$ C in special variable temperature cells^{13,14}.

STRUCTURE OF 2-CHLORO-2-METHYLBUTANE AND 4-CHLORO-2,2-DIMETHYLPENTANE

If only staggered conformers are considered, then 2-chloro-2-methylbutane can form two, and 4-chloro-2,2-dimethylpentane three different conformers (Figs. 1 and 2). These conformers differ by symmetry and type of chlorine atom. For all the various conformers, the types of chlorine atoms are given in Figs. 1 and 2, using the conventional designation*.



Fig. 1. Rotational isomers of 2-chloro-2-methylbutane.

^{*} The letters T, S and P designate tertiary, secondary or primary chlorine atom and the indexes H and C designate atoms situated in *trans* position with respect to chlorine. Each index refers to rotation about one bond. Unprimed symbols refer to planar structures and primed symbols to non-planar forms.



Fig. 2. Rotational isomers of 4-chloro-2,2-dimethylpentane.

2-CHLORO-2-METHYLBUTANE

In the v(C-CI) range, 2-chloro-2-methylbutane exhibits two bands at 558 and 617 cm⁻¹ and, in agreement with Shipman et al.², these are assigned to conformers I and II (Fig. 1). In the solid state, the band at 617 cm⁻¹ disappears and only the band at 558 cm⁻¹ remains. From this it is evident that only conformer I is present in the solid state. From the temperature dependence of the intensities of these bands, $\Delta H = 0.7 \pm 0.1$ kcal/mole has been calculated.

4-CHLORO-2,2-DIMETHYLPENTANE

In the v(C-Cl) range, liquid 4-chloro-2,2-dimethylpentane exhibits two bands at 629 and 669 cm⁻¹. Fig. 2 shows that this compound can exist in three forms. Conformers I and III have chlorine atoms of type S_{HH} and S'_{HH}, with v(C-Cl)expected below 650 cm⁻¹, and conformer II has an S'_{CH} type chlorine atom with v(C-Cl) expected above 650 cm⁻¹. The band at 669 cm⁻¹, which disappears upon crystallization, corresponds evidently to conformer II. As the conformers with parallel C-CH₃ bonds in 1,3 position are energetically unfavoured⁶, only conformer I is assumed to be present in solid 4-chloro-2,2-dimethylpentane. For the same reason, the band at 629 cm⁻¹ appearing in the vibrational spectra of this compound in the liquid state, is assumed to correspond predominantly to conformer I, although the presence of a small amount of conformer III cannot be excluded. If conformer III is neglected, the energy difference between conformers I and II can be calculated from the temperature dependence of the intensities of the bands at 629 cm⁻¹, giving 0.6 ± 0.1 kcal/mole.

DISCUSSION

If only staggered conformers are considered, then the energy differences between rotational isomers of 1,3-substituted paraffins are determined predominantly by the interactions of atoms or groups on parallel bonds in positions 1 and 3. As an example, all the interactions of conformer 3 (Table 1) of 3-chloropentane are shown in Fig. 3.



Fig. 3. 1,3 Parallel interactions in 3-chloropentane (TG conformer).

In chloro-substituted paraffins, the following 1,3-interactions can appear: H-H; C-H; Cl-H; C-C; C-Cl; Cl-Cl. An inspection of the experimental ΔH values of chloro-substituted paraffins (Table 1) shows the approximate energy contributions of these interactions to be additive. The values of these contributions are given in Table 2. Using these values, the calculated ΔH values shown in Table 1 were obtained. From Table 2, ΔH of all these compounds can be calculated with an accuracy comparable with the accuracy of the experimental results.

A small difference between the experimental and calculated ΔH appeared in 2-chlorobutane^{17,18}. The experimental ΔH of this compound has been obtained from three C-Cl stretching bands, two of which overlap strongly. By a careful separation of these bands, ΔH values (Table 1) consistent with the calculated values can be obtained.

In 1,3-dichloropropane, the energy differences between various conformers have so far not been determined experimentally. Saeki and Takeo²³ found that conformers 1, 2 and 3 are present in the liquid state, conformer 1 being the most stable. The latter is also present in the solid state. These qualitative results agree with the energy differences calculated from Table 2.

 ΔH values of all rotational isomers of *meso*- and *d,l*-2,4-dichloropentane have also been calculated and the calculated values agree well with experimental results obtained by analysis of vibrational and NMR spectra²⁴. For the three stereoisomers of 2,4,6-trichloroheptane, ΔH values have only been calculated for the experimentally observed forms²⁵. Once again, the calculated and experimental energy differences agree well.

Of the 1,3-halogen-substituted paraffins for which ΔH values could be found in the literature, only 3-chloro-3-ethylpentane has not been included in Table 1. The interpretation of the spectrum²⁶ on which the ΔH values of this compound were based, assumed the band at 538 cm⁻¹ to be a v(C-Cl) vibration. In our study of the conformational structure of 4-chloro-2,2,4-trimethylpentane²⁰, the band at

TABLE 1

CONFORMER ENERGIES AND 1,3 PARALLEL INTERACTIONS OF HALOGENO-PARAFFINS

Compound	No.	Conformer	1,3 Parallel interactions	$\Delta H(n-1)^*$ exp. (kcal/mole)	$\Delta H(n-1)$ calc. (kcal/mole)
1-Chloro- propane ^{15,16} **	1 2	C-C-C-X C-C-C X	(X-H) -	0.0 -0.3 -	0.0 -0.3
2-Chloro- butane ^{17,18}	1	с-с-с-с і	(X-H)	0.0	0.0
	2	c-c-c i i x c	(X-H); 2(C-H)	0.3	0.4
	3	c-c-c x	2(C-H)	0.6	0.7
2-Chloro-2- methylbutane	1	c c-c-c-c x	(X–H); 2(C–H)	0.0	0.0
	2	С с-с-с-х с	4(C-H)	0.7	0.7
4-Chloro-2,2- dimethylbutane ¹⁹	1	C x-c-c-c-c C	4(C-H)	0.0	0.0
	2	с с-с-с-с х с	3(C-H); (C-X)	1.0	1.3
4-Chloro-2,2- dimethylpentane	1	C C-C-C-C-C X C	3(C-H); (C-X)	0.0	0.0
	2	сс x-с-с-с-с с	4(C-H); (C-C)	0.6	0.5
5	3	X C C - C - C - C C C C	3(C-H); (C-X); (C-C)		1.8

Compound	No.	<i>Conformer</i>	1,3 Parallel interactions	∆H(n−1)* exp. (kcal/mole)	⁴ ∆H(n−1) calc.) (kcal/mole)
4-Chloro-2,2,4- trimethylpentane	1 20	X C c-c-c-c-c C C	3(C-H); (C-X); (C-C)	0.0	0.0
	2	C C x-C-C-C-C I I C C	4(C-H); 2(C-C)	0.3	0.5
Butane ²¹	1	с-с-с-с		0.0	0.0
	2	с-с-с і с	2(C-H)	0.8	0.4
3-Chloropentane ²²	1	C-C-C-C-C !	2(X-H)	0.0	0.0
	2	C-C-C-C x c	2(C-H); 2(X-H)	0.65	0.4
	3	c-c-c-c x	(X–H); 2(C–H)	0.8	0.7
	4	C C-C-C X C	(X-H); 4(C-H)	0.9	1.1
	5	C-C-C C X C	2(C-H); (C-C); 2(X-H) —	2.2
	6	C C C-C-C X	2(C-H); (C-C)	-	2.8
1,3-Dichloro- propane ²³	1	x c-c-c i x	2(X-H)		0.0
	2	C-C-C-X X	(X-H)	see text	0.3
	3	X-C-C-C-X			0.6
	4	C-C-C X X	(X-X)		>3.1

454

Compound	No.	Conformer	1,3 Parallel interactions	ΔH(n-1) exp. (kcal/mole	* ∆H(n−1) calc. calc.) (kcal/mole)
<i>d,l-2,4-</i> Dichloro- pentane ²⁴	1	x c-c-c-c-c x	2(X-H)	0.0	0.0
	2	C x-C-C-C-X C	4(C-H)	~2.5	1.4
	3	$\begin{array}{c} \mathbf{C} \mathbf{X} \\ \mathbf{X} - \mathbf{C} - \mathbf{C} - \mathbf{C} - \mathbf{C} \\ \mathbf{C} \mathbf{C} \end{array}$	(C-H); (C-X)	-	2.3
	4	x-c-c-c x	(X–H); 2(C–H); (C–C)) —	2,5
	5	x c 	2(C-H); 2(C-X)		4.0
	6	X X c-c-c-c c	2(C-H); (X-X)		>3.5
meso-2,4-Dichloro- pentane ²⁴	1	с с-с-с-х х	(H–X); 2(C–H)	0.0	0.0
	2	c x 	(X-H); (C-H); (C-X)	2.5	1.3
	3	C -C-C-X 	3(C-H); (C-X)	_	2.0
	4	X C X-C-C-C-X	2(C-H); (C-C)	_	2.1
	5	ċċ c-c-c-c-c ↓ ↓	(X-X)		>2.4
	6	C C -C-C -C-C X X	2(C-H); (C-C); (X-X))	>4.6

Compound	No.	Conformer	1,3 Parallel interactions	∆H(n−1)* exp. (kcal/mole)	$\Delta H(n-1)$ calc. (kcal/mole)
2,4-Dichloro-2,4- dimethylpentane	1 20	X C c-c-c-c-c c X	2(C-H); 2(C-X)	0.0	0.0
	2	X C C-C-C-C-X I I C C	3(C-H); (C-X); (C-C)	0.5	0.5
	3	C C X-C-C-C-X C C	4(C-H); 2(C-C)	_	1.0
	4	C C C-C-C-C-C X X	2(C-H); (C-C); (X-X)		>1.3
<i>syndio-2</i> ,4,6-Tri- chloroheptane ²⁵	1	x c-c-c-c-c-c-c-c x x	4(X-H)	0.0	0.0
	2	x c-c-c-c-c x c-x	2(X-H); 4(C-H)	1.5	1.4
iso-2,4,6-Tri- chloroheptane ²⁵	1	x c-c c i-c-c-c-x x	2(X–H); 4(C–H)	0.0	0.0
	2	с с x-с-с-с-с-с-х х	2(X–H); 4(C–H)	0.5	0.0
<i>hetero</i> -2,4,6-Tri- chloroheptane ²⁵	1	x c-c-c-c-c-c-x l l x c	3(X-H); 2(C-H)	0.0	0.0

Compound	No.	Conformer	1,3 Parallel interactions	$\Delta H(n-1)^{4}$ exp. (kcal/mole)	$\Delta H(n-1)$ calc. (kcal/mole)
	2	x c-c-c-c-c x c-c x c-c x x	3(X-H); 2(C-H)	0.2	0.0
	3	x c-c-c-c-x x-c c c	(X–H); 6(C–H)		1.4

* ΔH values as determined from measurements in the liquid state.

** For liquid 1-chloropropane, two ΔH values have been reported: 0.05 kcal/mole¹⁵ and -0.3 kcal/mole¹⁶.

TABLE 2

ENERGY CONTRIBUTIONS OF 1,3 PARALLEL INTERACTIONS

1,3 Parallel interactions	∆H (kcal/mole)		
Н-Н	0.0		
CI-H	-0.3		
C-H	0.2		
C-Cl	1.5		
C-C	1.8		
ClCl	>2.5		

 540 cm^{-1} was found not to be a v(C-Cl) vibration and, for this reason, the experimental conformer energies of 3-chloro-3-ethylpentane are considered to be incorrect and are therefore not cited in Table 1.

In 2,4-dichloro-2,4-dimethylpentane and in *hetero*-2,4,6-trichloroheptane, the ΔH values calculated by means of Table 2 for the conformers No. 3 are around 1 kcal/mole. These two conformers have not been detected experimentally. This can be explained by the fact that both these conformers contain chlorine atoms of the same type as the energetically more favoured forms, and for this reason they could not be detected by analysis of ν (C-Cl) bands in vibrational spectra.

For some of the compounds included in Table 1, semi-empirical conformer energy calculations have been performed²⁷. ΔH values calculated by this method

showed poorer agreement with experimental values than those calculated by means of the additive contributions of Table 2.

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