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THE CONFORMATION OF NON-AROMATIC RING COMPOUNDS, Part XLIX (1)

RELATIONSHIP BETWEEN THE CONFORMATIONAL EQUILIBRIA IN HALOGENATED OPEN-CHAIN AND SIX-MEMBERED CARBOCYCLIC COMPOUNDS

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Recently, the conformational equilibria in some vicinal dihalogenoalkanes (see Fig.1) have been studied (2,3) by means of dipole moments in benzene and in carbon tetrachloride solution at 25°C. From the experimental equilibrium constants the gauche interaction energies between the various substituents (Br, Cl and CH_3) in the two solvents were calculated, assuming the H/H, Br/H, Cl/H and CH_3/H interactions to be zero. The CH_3/CH_3, CH_3/Br and CH_3/Cl gauche interactions appeared to be solvent-independent; the halogen/halogen interactions are smaller in benzene than in carbon tetrachloride by 0.4 kcal/mole. Table 2 lists the gauche interactions in the open-chain compounds which were calculated in refs. 2 and 3.

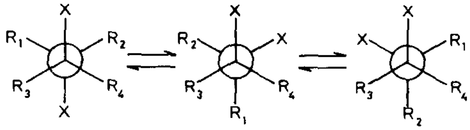
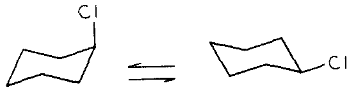
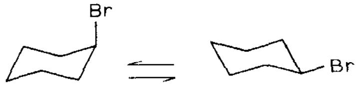
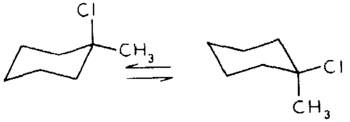
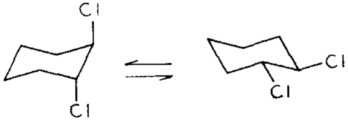
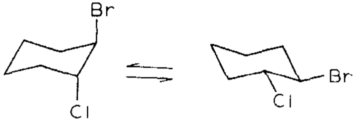
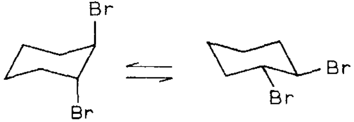


FIG.1. The conformers of vicinal dihaloalkanes with X = Br or Cl; R_1, R_2, R_3 and R_4 = H or CH_3

In this paper a similar set of interaction energies is derived from the experimental $-\Delta G^o$ values of a series of halogeno(methyl)cyclohexanes. In a monosubstituted cyclohexane the axial substituent R is considered to have two gauche interactions of the type R/CH_3, whereas no such interactions are present in the equatorial isomer (cf. refs. 4 and 5). The diaxial form of a trans-1,2-disubstituted cyclohexane has two R_1/CH_3 and two R_2/CH_3 interactions, whereas the diequatorial form has one R_1/R_2 interaction. In Table 1, the free energy differences $-\Delta G^o$ for 9 1-halo-, 1-halo-1-methyl- and trans-1,2-dihalocyclohexanes are presented in terms of the gauche interactions. With the aid of the experimen-

TABLE 1. *Gauche* Interactions and Free Energy Differences in various Halocyclohexanes

Compound	Solvent[a]	$-\Delta G^o$ in terms of *gauche* interactions	$-\Delta G^o$ experimental kcal/mole	Ref.
	*	$2\ Cl/CH_3$	$+ 0.4^b$	6
	*	$2\ Br/CH_3$	$+ 0.5$	6
	*	$2\ Cl/CH_3 - 2\ CH_3/CH_3$	$- 1.1^c$	7
	B T	$4\ Cl/CH_3 - 1\ (Cl/Cl)_B$ $4\ Cl/CH_3 - 1\ (Cl/Cl)_T$	$+ 0.1^d$ $- 0.3^d$	8 8
	B T	$2\ Br/CH_3 + 2\ Cl/CH_3 - 1\ (Br/Cl)_B$ $2\ Br/CH_3 + 2\ Cl/CH_3 - 1\ (Br/Cl)_T$	$- 0.2^d$ $- 0.6^d$	8 8
	B T	$4\ Br/CH_3 - 1\ (Br/Br)_B$ $4\ Br/CH_3 - 1\ (Br/Br)_T$	$- 0.4^d$ $- 0.8^d$	8 8

a. B = benzene, T = carbon tetrachloride, * = solvent-independent (cf. refs. 5 and 9).

b. This value has also been found for 1-chloro-4,4-dimethylcyclohexane in ref. 10.

c. " " " " " " " 1-chloro-1,4,4-trimethylcyclohexane in ref. 7.

d. These values have been determined from dipole moment measurements, using $\mu_{AA} = 1.1$ D and $\mu_{EE} = 3.4$ D. The values differ slightly from those presented in refs. 11 and 12, where μ_{EE} was taken equal to 3.3 D.

tal $-\Delta G^o$ values, we have 9 equations and 9 parameters to be evaluated. The results are given in Table 2.

TABLE 2

Halogen/halogen, Halogen/methyl and Methyl/methyl *gauche* Interaction Energies (kcal/mole) in Open-chain and in Six-membered Ring Compounds

Interaction	Solvent[a]	Open-chain compounds (2,3)	Cyclohexane compounds
CH_3/CH_3	*	0.8	0.7_5
Br/CH_3	*	0.2_5	0.2_5
Cl/CH_3	*	0.1	0.2
Br/Br	B	1.4	1.4
	T	1.8	1.8
Br/Cl	B	1.0_5	1.1
	T	1.4_5	1.5
Cl/Cl	B	0.7_5	0.7
	T	1.1_5	1.1

a. B = benzene, T = carbon tetrachloride, * = solvent-independent.

From Table 2 it is seen that an excellent agreement exists between the *gauche* interaction energies in the open-chain and in the six-membered cyclic compounds. A similar agreement has been found between the *gauche* interaction in butane and the interactions in the various dimethylcyclohexanes (13).

As the Cl/CH_3 interaction in chloropropane has been reported to be attractive rather than repulsive (14), a breakdown of the relationship between the conformational equilibria in chloropropane and chlorocyclohexane has been suggested (5,15). However, a recent determination (16) of the equilibrium composition in chloropropane indicates that the anti form is more stable than the gauche isomer by $0.1_4 \pm 0.1$ kcal/mole, which is in excellent agreement with the Cl/CH_3 *gauche* interaction energy derived by us (3), see Table 2.

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