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A NOVEL ATTRACTIVE 1-3 INTERACTION IN TRANS-1,4-DICHLOROCYCLOHEXANE.

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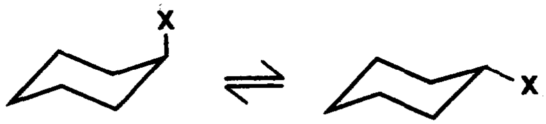
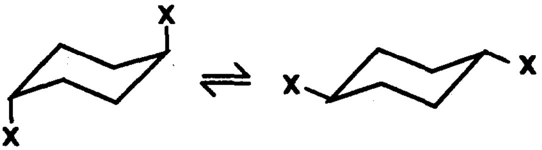
The anomalous stabilization of the diaxial form of trans-1,4-dihalocyclohexane (II X=Cl,Br) and similar systems, compared to the monosubstituted compounds I, has been widely questioned in the past few years[1-4], but no definite explanation has been reported.

(I)



(II)



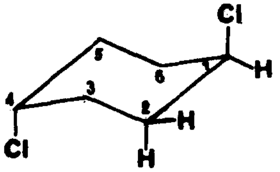
We have determined the free energy difference (ΔG^{o}aa → ee) between the two chair conformations of trans-1,4-dichloro cyclohexane by peak area NMR measurements in a number of solvents at -65°C (table 1) which also gives the solvent dielectric constants at this temperature and the difference in the solvation energies of the conformers, calculated by a known theory of solvation[5,6,10]. The agreement allows the prediction of the vapour phase free energy of +0.8 kcals/mole (table 1), i.e. an extra stabilisation of the di-axial form over that predicted from eq^{tn} I (X=Cl) (ΔG(ax-eq) = 0.52 kcals/mole[7]) of 1.8 kcals/mole. Due to the solvent dependence of equilibrium II this value is twice the value obtained by direct comparison of measurements in solution[7].

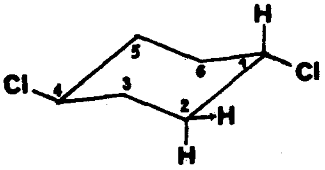
Table 1. Observed and Calculated ΔGaa-ee values for trans-1,4-dichlorocyclohexane.

		ΔG^oaa-ee	(kcals/mole)
Solvent	ϵ (-65°C)	obs.	calc.
vapour	1.0	-	0.80
$CFCl_3$	2.5	0.14	0.23
CF_2Br_2	3.0	0.08	0.14
CS_2	3.5	0.08	0.07
$CHCl{:}CCl_2$	4.0	0.02	0.02
$CDCl_3$	6.6	-0.03	-0.15
cis$CHCl{:}CHCl$	14.0	-0.15	-0.32
acetone-d_6	30.0	-0.43	-0.47
DMF-d_7	50.0	-0.60	-0.58

This extra stabilisation of the di-axial form has been ascribed to charge..charge interactions between the C-X bonds (X=Cl,Br[1], OCO.CF_3[2]) but the equivalent dipole-dipole[3,4] explanation was shown not to explain similar results on 4-halocyclohexanones. We show that neither explanation can account for the observed stabilisation and present a new explanation.

The charge distribution (CNDO/2)[8] for II(X=Cl) is as follows:





	ax-ax	eq-eq
$C_{1,4}$	.089	.089
$C_{2,3,5,6}$	.022	.021
H_1	.010 (eq)	.017 (ax)
H_{2e}	.002	.005
H_{2a}	.013	.009
Cl	-.171	-.175

With this distribution the electrostatic interactions between the C-Cl bonds are calculated as 0.13 and 0.26 kcals/mole for the ax-ax and eq-eq forms, an extra stabilisation of the di-axial form of only 0.13 kcals/mole. The interaction between the C-Cl dipoles calculated by the dipole-dipole formula[9], using C-Cl dipoles of 1.5D and a dielectric constant of unity, gives energies of 0.20 and 0.58 kcals/mole for the ax-ax and eq-eq forms, a stabilisation of 0.38 kcals/mole, much too small to account for the observed effect.

In the diaxial conformer of II (X=Cl), the hydrogen atoms on $C_{2,5}$, in a planar trans arrangement with the axial chlorine, are more positive than usual. These hydrogens are in close proximity to the axial C_4 chlorine atom, resulting in an attractive interaction. In the diequatorial conformation the axial C_2 hydrogen is less charged and, more importantly, it is much further away from the C_4 chlorine. Therefore it does not contribute any extra stabilisation. The calculated H..Cl polar interaction in the diaxial form is 0.26 kcals/mole. As there are four such interactions in the diaxial conformer, the nett attractive interaction is 1.0 kcals/mole, in reasonable agreement with the observed stabilisation energy. We conclude therefore that the attractive 1,3 interactions between the negatively charged halogens and the positive hydrogen atoms are the major factor in the extra stabilisation of the diaxial form of II.

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