Rotational Isomerism. Part XV.[1] The Solvent Dependence of the Conformational Equilibria in *trans*-1,2- and *trans*-1,4-Dihalogenocyclohexanes

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The free energy difference between the two chair conformations of *trans*-1,2-dichloro- and -1,2-dibromo-cyclohexane (II) and *trans*-1,4-dichloro- and -1,4-dibromo-cyclohexane (III) has been determined by peak area n.m.r. measurements in a number of solvents at low temperature. Both equilibria show a strong solvent dependence [despite the absence of a dipole moment for either of the interconverting species in (III)] and this is given a quantitative explanation in terms of a known theory of solvation. From this the vapour phase free energy differences [$\Delta G(aa \longrightarrow ee)$] have been estimated as 0·9 and 1·5 kcal mol^{-1} (II; X = Cl and Br) and 0·8 and 0·9 kcal mol^{-1} (III; X = Cl and Br), *i.e.* in all cases the diaxial conformer is preferred in the vapour phase. In the *trans*-1,2-dihalogenocyclohexanes this is interpreted on the basis of steric (repulsive) X · · · X interactions in the diequatorial conformer. The extra stability of the diaxial conformer of (III), over that of the corresponding cyclohexyl halides is shown by calculations of both dipole–dipole and charge–charge interactions between the C–X bonds not to arise from this mechanism. Attractive 1,3-polar interactions between the positively charged axial hydrogen atoms and the axial halogens are shown to account for the stabilisation of the axial conformers in the 1,4-compounds.

IN preceding papers of this series an electrostatic theory of solvation has been described[2,3] and applied to a variety of rotational and conformational equilibria, including that of the mono- and di-halogenocyclohexanes.[1] In this latter investigation the negligible solvent

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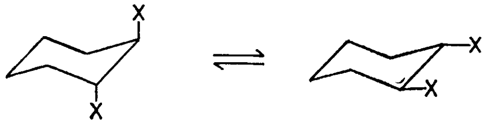
[1] Part XIV, R. J. Abraham and T. M. Siverns, *J.C.S. Perkin II*, 1972, 1587.

[2] R. J. Abraham and M. A. Cooper, *J. Chem. Soc.* (*B*), 1967, 202.

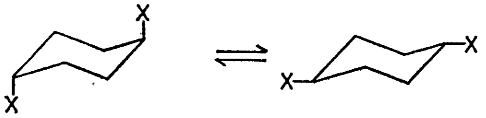
[3] R. J. Abraham, *J. Phys. Chem.*, 1969, **73**, 1192.

dependence of equilibrium (I; X = Cl or Br) and the large solvent dependence of equilibrium (II; X = Cl or Br) were explained quantitatively. It was also predicted that equilibrium (III; X = Cl or Br) should have a noticeable solvent dependence despite the absence of a dipole moment of either conformer.

(I)



(II)



(III)

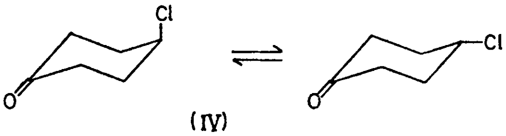
The extensive and unambiguous experimental data for (I) [4,5] show clearly the absence of any significant solvent effect, and there is nothing to be gained by any further experimental studies.

Equilibrium (II) has also been extensively investigated by variable temperature i.r.,[6] single temperature i.r.,[7] and n.m.r. spectroscopy (averaged couplings) [8] and dipole moments.[1] These demonstrate clearly the large solvent effect on (II) but are not very consistent. For example in CCl_4 solution ΔE ($E_{ee} - E_{aa}$) for (II; X = Cl) is given as 0·58,[6] 0·37 (i.r.),[7] —0·2 (n.m.r.),[8] and 0·0 kcal mol^{-1} (d.m.).[1] For equilibrium (III) extensive data on a range of solvents have not been reported.

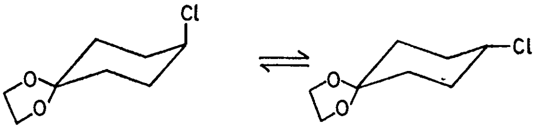
The only physical technique for investigating such equilibria in solution which is not subject to systematic errors due to approximations made in treating the experimental data is the direct integration of the signals of the individual conformers observed by low temperature n.m.r. spectroscopy. We therefore decided to investigate the solvent dependence of (II and III; X = Cl and Br) by this method. This was attempted for (II; X = Cl and Br) by Reeves and Stomme [9] in an early study and for (III; X = Cl and Br) by Wood and Woo but for only two solvents.[10] Our results should thus provide a stringent test of the solvent theory and also by extrapolation give the vapour phase values for (II) and (III).

The equilibrium (III) is of some interest at the moment. A number of investigations have shown that for polar substituents X, the diaxial form is strongly preferred over what would be predicted from the corresponding equilibrium (I). Wood and Woo have observed this in solution for X = Cl, Br,[10] and OCO·CF_3 [11] and have ascribed the non-additivity to charge attractions between the negatively charged atom X on C-1 and the positively charged C-4 atom. These atoms are closer together in the diaxial form than in the diequatorial isomer.

Stolow [12] found a similar anomaly in the equilibria (IV) and (V) in which the axial conformer was stabilised by 0·85 kcal mol^{-1} in (IV) and 0·66 kcal mol^{-1} in (V) over the chlorocyclohexane (I). Stolow notes that as the dipole moment of the ethylene acetal group is in the *opposite* direction to that of the carbonyl group then dipole–dipole interactions between the C-1 and C-4 substituents should stabilise the axial conformer in (IV) but destabilise it in (V), contrary to experiment. He concludes that dipolar interactions are not the reason for the stability of the axial forms of (IV) and (V).



(IV)



(V)

We shall show that the electrostatic interaction does not explain the observed data and suggest an alternative explanation.

THEORY

The theory follows that of ref. 1, with one minor addition. As the experimental data given are the most precise and unambiguous data yet obtained for the solvent dependence of any conformational equilibrium it was felt that the complete solvent theory should be used, including the recently derived generalised polar term. This is derived elsewhere,[13] but the solvation energy of any molecule in state A, *i.e.* the difference between the energy in the vapour ($E^{v}{}_{A}$) and in any solvent ($E_{A}{}^{s}$) of dielectric constant ε, is given by equation (1) where $x = (\varepsilon - 1)/(2\varepsilon + 1)$, $l = 2(n_D{}^2 - 1)/(n_D{}^2 + 2)$, $b = 4{\cdot}35\ (T/300)^{\frac{1}{2}}\ (a^{\frac{3}{2}}/r^3)\ (k_A + h_A\, a^2/r^2)^{\frac{1}{2}}$, and $f = \{(\varepsilon - 2)(\varepsilon + 1)/\varepsilon\}^{\frac{1}{2}}$. n_D Is the solute

$$E^{s}{}_{A} = E^{v}{}_{A} - k_A/(1 - lx) - 3h_A x/(5 - x) - bf\{1 - \exp(-bf/16RT)\} \quad (1)$$

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[4] E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, 1968, **90**, 689.

[5] J. A. Hirsch, *Topics Stereochem.*, 1967, **1**, 199.

[6] O. D. Ul'yanova, M. K. Astrovskii, and Y. A. Prentin, *Russ. J. Phys. Chem.*, 1970, **44**, 562.

[7] P. Klaeboe, J. J. Lothe, and K. Lunde, *Acta Chem. Scand.*, 1957, **11**, 1677.

[8] R. U. Lemieux and J. W. Loan, *Canad. J. Chem.*, 1964, **42**, 893.

[9] L. W. Reeves and K. O. Stromme, *Trans. Faraday Soc.*, 1961, **57**, 390.

[10] G. Wood and E. P. Woo, *Canad. J. Chem.*, 1967, **45**, 2477.

[11] G. Wood, E. P. Woo, and H. M. Miskow, *Canad. J. Chem.*, 1969, **47**, 429.

[12] R. D. Stolow in 'Conformational Analysis,' ed. G. Chiurdoglu, Academic Press, London, 1971.

[13] R. J. Abraham in 'Structure of Molecules and Internal Rotation,' ed. W. J. Orville-Thomas, Wiley, London, 1973.

refractive index, T the temperature, k_A and h_A are $\mu^2{}_A/a^3$ and $q^2{}_A/a^5$, μ_A and q_A being the solute dipole and quadrupole moments and a the solute molecular radius. r Is the solute–solvent distance and was taken as 1·8 Å. The theory and parameters used in equation (1) are now identical to those of ref. 1 and not reproduced here. It should just be mentioned that the extra term in equation (1) gives only minor contributions for all normal solvents, though it does now produce the theoretically correct result that as $\varepsilon \longrightarrow \infty$, $E^S{}_A \longrightarrow \infty$.[3] For example for the most polar solvent used, dimethylformamide (DMF), with ε *ca.* 50 at −55 °C the contribution of this term to the energy difference between the conformers in (II; X = Cl) is only 0·3 kcal mol^{-1} in a total solvation energy of 2·0 kcal mol^{-1}. Thus for all but very accurate work this can be neglected.

EXPERIMENTAL

All compounds were prepared by known methods,[14] and purified by column chromatography in order to avoid overlapping of impurity signals in the observed region.

The spectra were obtained on Varian A56/60 and HA100 spectrometers for 8% v/v solutions for *trans*-1,2-dichloro- and 1,2-dibromo-cyclohexanes and owing to their low solubility at low temperatures for concentrations corresponding to the saturated solution (*ca.* 4% v/v) in each solvent for the *trans*-1,4-dichloro- and-1,4-dibromo-compounds using tetramethylsilane as internal standard.

The spectra were determined at −65 °C except for those for DMF solutions (−55 °C) owing to the viscosity of this solvent. 3—8 Spectra for each solvent were taken at the same temperature and the difference of the population was obtained directly from peak area measurements. Due to the different band width of the peaks corresponding to the axial and equatorial hydrogen atoms, care was taken to avoid different saturation coefficients.[15] The spectra were 'transferred' on thick paper, cut, and weighted. An average of three weights was taken for each spectrum. The experimental error obtained for the ΔG^0 values in each solvent by this technique is given with the values in Tables 1 and 2. The solvent dielectric constants at −65 °C given in Table 2 have been obtained from the known temperature coefficients of the dielectric constants.[16,17] In Table 1 the solvent dielectric constants have been corrected in the case of the non-polar solvents for the contribution of the polar solute[3] (*trans*-1,2-dichlorocyclohexane, ε = 9·43 at 20 °C). This was not considered necessary for the other solvents.

RESULTS AND DISCUSSION

The free energy differences for the equilibria (II and III; X = Cl and Br) are given in Tables 1 and 2 for a variety of solvents. The observed values are given directly from the standard equation $\Delta G = -RT \ln K$ and are therefore clearly free energies at −65 °C. The solvent theory merely calculates solvation energies (ΔE) values. When differences in free energy of a conformational equilibrium among various solvents are considered then the zero-point energy, contribution of higher vibrational states and Pdv terms would be expected to cancel out, *i.e.* $\delta\Delta G = \delta\Delta E$ to a very good approximation. However, these effects may be present in any given solvent, *i.e.* ΔS is not necessarily zero and thus $\Delta G \neq \Delta E$. The extrapolated ΔE^{v} values obtained by the theory (see later) should most rigorously be considered as ΔG^{v} values (see ref. 18 for a full discussion).

TABLE 1

Observed and calculated ΔG (ΔE) values for *trans*-1,2-dihalogenocyclohexanes (II; X = Cl or Br)

		$\Delta G(\Delta E = E_{ee} - E_{aa})$/kcal mol^{-1}			
		X = Cl		X = Br	
Solvent [a]	ε [b]	Obs.	Calc.	Obs.	Calc.
Vapour	1·0		0·93		1·50
n-Pentane	2·2 [c]	0·23(0·05)	0·31	0·98(0·05)	0·97
n-Hexane	2·2 [c]			0·97(0·03)	0·97
$CFCl_3$	3·0 [c]	0·10(0·04)	0·08	0·84(0·01)	0·77
Toluene	3·0			0·32(0·01)	
CS_2	3·5	−0·02(0·02)	0·00	0·75(0·04)	0·68
$CHCl : CCl_2$	4·0	−0·15(0·02)	−0·10	0·64(0·04)	0·61
$CDCl_3$	6·6	−0·46(0·03)	−0·37	0·27(0·04)	0·36
CH_2Cl_2	13·7	−0·68(0·04)	−0·66	0·05(0·03)	0·10
[$^2H_6$]Acetone	30·0	−0·85(0·03)	−0·91	−0·04(0·02)	−0·13
[$^2H_7$]DMF	50·0 [d]	−0·94(0·04)	−1·10	−0·28(0·04)	−0·29

[a] 8% (v/v) Solutions. [b] Solvent dielectric at −65 °C except where indicated. [c] Corrected for solute. [d] −55 °C (See text).

TABLE 2

Observed and calculated ΔG (ΔE) values for *trans*-1,4-dihalogenocyclohexanes (III; X = Cl or Br)

		$\Delta G(\Delta E = E_{ee} - E_{aa})$/kcal mol^{-1}			
		X = Cl		X = Br	
Solvent [a]	ε [b]	Obs.	Calc.	Obs.	Calc.
Vapour	1·0		0·80		0·88
$CFCl_3$	2·5	0·14(0·02)	0·23	0·30(0·02)	0·33
CF_2Br_2	3·0	0·08(0·05)	0·14	0·22(0·02)	0·24
CS_2	3·5	0·08(0·04)	0·07		
$CHCl : CCl_2$	4·0	0·02(0·02)	0·02	0·00(0·02)	0·12
$CDCl_3$	6·6	−0·03(0·02)	−0·15	0·03(0·02)	−0·04
CH_2Cl_2	13·7			−0·18(0·06)	−0·21
cis-CHCl : CHCl	14·0	−0·15(0·03)	−0·32	−0·12(0·02)	−0·22
[$^2H_6$]Acetone	30·0	−0·43(0·02)	−0·47	−0·36(0·02)	−0·36
[$^2H_7$]DMF	50·0 [c]	−0·60(0·03)	−0·58	−0·49(0·02)	−0·47

[a] Saturated solutions at −65 °C, *ca.* 4% (v/v). [b] Solvent dielectric at −65 °C. [c] At −55 °C.

The observed ΔG values are in good agreement with those of previous investigations. Wood and Woo[10] obtained for (III; X = Cl) in $CDCl_3$–CH_2Cl_2 (2 : 3) ΔG −0·16 kcal mol^{-1}. They also obtained values for toluene solution of −0·16 (X = Cl) and −0·21 kcal mol^{-1} (X = Br) and these again demonstrate, like the corresponding result in Table 1 the very anomalous behaviour of this solvent in these equilibria.[1] Reeves and Stromme[9] obtained values of ΔG for (II) in CS_2 solution of −0·21 (X = Cl) and +0·31 kcal mol^{-1} (X = Br). The discrepancy with our results (Table 2) is undoubtedly due to the higher solute concentrations used in their work (28 mol %). Their value of ΔG for (II; X = Br) when extrapolated to infinite dilution in

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[14] W. Kwestroo, F. A. Meijer, and E. Havinga, *Rec. Trav. chim.*, 1954, **73**, 717.

[15] F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, 1969, **91**, 344.

[16] A. A. Maryott and E. R. Smith, 'Tables of Dielectric Constants of Pure Liquids,' N.B.S. circular 514, Washington, 1951.

[17] Landolt-Börnstein, Physical Chemisty Tables.

[18] J. Reisse in 'Conformational Analysis,' ed. G. Chiurdoglu, Academic Press, London, 1971.

acetone is —0·1 kcal mol^{-1}, in complete agreement with our results.

The results in Tables 1 and 2 can also be compared with those obtained by different techniques, though now the differences in temperature and the measured parameters must be considered. (For example the variable temperature i.r. method gives ΔH, not ΔG, *etc.*). The only other extensive investigation was that of Klaboe *et al.*[7] using single temperature i.r. methods. They obtained ΔH (ΔE) values for equilibrium (II) for several solvents ranging from 0·41 (C_6H_{12}) to —0·53 kcal mol^{-1} (nitromethane) for X = Cl and 0·85 to —0·32 kcal mol^{-1} for X = Br. The values for the bromo-compound are in very good agreement with ours, but those for the chloro-compound differ appreciably. These authors stress that their method gives rigorously only $\delta\Delta E$ values and these are in substantial agreement with our results in both cases.

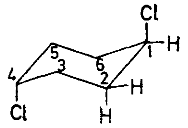
Tables 1 and 2 also give the calculated ΔE values for these solutions. Equation (1) when combined with the analogous equation for conformer B merely evaluates the quantity $\Delta E^{v} - \Delta E^{s}$ for any solvent S; it does not predict ΔE^{v}. The values of ΔE^{v} given in the Tables are obtained as those values which give the best agreement of the solution data in the Tables. Thus the significance of the agreement between the observed and calculated values lies in the comparison between the solvents.* The agreement is indeed excellent. For equilibrium (II) apart from toluene which is not considered in these systems (see earlier), the largest difference is 0·16 kcal mol^{-1} (DMF) and the average difference between the observed and calculated values 0·06 (X = Cl) and 0·05 kcal mol^{-1} (X = Br). This is over a range of solvent dielectric constant from 2·5 to 50·0 and a change in free energy of *ca.* 1·2 kcal mol^{-1}. The extrapolated value of ΔE^{v} also compares reasonably with that obtained by variable temperature i.r. studies for X = Cl of 0·6 [19] and 0·7 [6] $kcal^{-1}$ mol^{-1} though for the reasons mentioned earlier there could be significant differences in the values of the two measured quantities. The vapour phase value for the dibromo-compound has not previously been determined.

The agreement between the observed and calculated values for equilibrium (III) (Table 2) is also excellent, with a maximum deviation of 0·17 kcal mol^{-1} and average deviations of 0·07 (X = Cl) and 0·05 kcal mol^{-1} (X = Br). Again in these compounds the vapour-phase values have not been previously determined apart from an early electron diffraction measurement (<0·2 kcal mol^{-1}) [20] and it is these we now wish to consider.

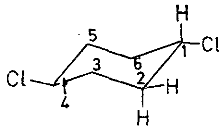
Free Energy Differences in trans-1,4-*Dihalogenocyclohexanes.*—Our results not only substantiate the anomalous behaviour of equilibrium (III) compared to (I) mentioned previously but also considerably enhance the extra stabilisation of the diaxial conformer for X = Cl and Br. Thus from their solution values of ΔG Wood and Woo [10] calculated the additional stabilisation of the diaxial form of (III) from that predicted from (I) of 0·8 (X = Cl) and 0·7 kcal mol^{-1} (X = Br), using the ΔG values for (I) of —0·52 and —0·48 kcal mol^{-1} (X = Cl and Br) reported by Jensen.[15]

Using the extrapolated vapour-phase values of Table 2 gives additional stabilisation energies of the diaxial conformer of 1·84 kcal mol^{-1} for both compounds. The difference arises from the lack of a solvent dependence of (I) and the pronounced solvent dependence of (III). Thus even comparisons between different equilibria in solution may be significantly different from the true (vapour-phase) values. Note that the extra stabilisation of the diaxial conformer in (III; X = OCO·CF_3) of 0·9 kcal mol^{-1} in [$^2H_6$]acetone solution [11] and of (IV) and (V) (0·85 and 0·66 kcal mol^{-1}) in CCl_4 and $CFCl_3$ solutions [12] would certainly be increased if solvation effects were removed.

It is of interest to consider the possible mechanisms contributing to the extra stabilisation of the axial–axial conformers of (III). A pertinent question is whether quantum mechanics can throw any light on the problem. In order to test this we have calculated the energies of cyclohexyl chloride and *trans*-1,4-dichlorocyclohexane using the CNDO/2 programme.[21] In this the geometry used was the standard (but not tetrahedral) geometry given in ref. 1.



ax - ax



eq - eq

TABLE 3

CNDO/2 Charge densities in *trans*-1,4-dichlorocyclohexane

	ax–ax	*eq–eq*
C-1, C-4	0·089	0·089
C-2, C-3, C-5, C-6	0·022	0·021
1-H	0·010 (*eq*)	0·017 (*ax*)
2*eq*-H	0·002	0·005
2*ax*-H	0·013	0·009
Cl	—0·171	—0·175

The programme gives $E_{eq} - E_{ax}$ for cyclohexyl chloride of +1·0 kcal mol^{-1} and $E_{ee} - E_{aa}$ for *trans*-1,4-dichlorocyclohexane of +2·71 kcal mol^{-1}. The value for equilibrium (I) is in the wrong sense (axial more stable), but it is of some interest that the *difference* between the two ΔE values is virtually identical to the observed value (calc. 1·7, obs. 1·8 kcal mol^{-1}). The quantum mechanical calculations do not by themselves provide any insight into which interactions are responsible for the extra stabilisation of the diaxial conformer,

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* Conceptually it is simpler to consider that ΔE^{v} is obtained directly from one observed ΔE^{s} value (*e.g.* n-hexane) and then see if all the other solvents fit.

[19] K. Kozima and K. Sakashita, *Bull. Chem. Soc. Japan*, 1958, **31**, 796.

[20] V. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, 1959, **13**, 1737.

[21] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

as of course the calculation includes ' classical ' electrostatic interactions as well as quantum mechanical forces.

However, it is a relatively simple matter to calculate the electrostatic interactions between the polar C–Cl groups. It is important to realise that the charge–charge interaction advocated by Wood and Woo[11] and the dipole–dipole interaction rejected by Stolow[12] are different ways of saying the same thing. The electrostatic interaction between the polar $\overset{+}{\mathrm{C}}$–$\overset{-}{\mathrm{X}}$ bonds can be calculated either by summing the charge attractions and repulsions or the charges may be approximated by a bond dipole moment and the dipole–dipole energy calculated using the well known formula.[22] Provided that the C–X bond length is much less than the interdipole distance the methods are identical.* We will now calculate the interaction on both methods.

For the charge–charge interactions the excessive electron densities on the C and Cl atoms need to be obtained and these are taken directly from the CNDO output and shown in Table **3**. The calculated dipole moment from CNDO/2 for cyclohexyl chloride is 2·29 (*eq*) and 2·05 D(*ax*) which compare very well with the observed dipole moment (2·2 D)[23] and give some support to the validity of the charge distribution obtained.

With the charge in electrons and the distance in Å the electrostatic interaction between two charges in a molecule is given by equation (2) with W in kcal mol^{-1}.

$$W_{ij} = 332{\cdot}00\, e_i e_j / r_{ij} \qquad (2)$$

With the C–Cl charges shown, and computed distances we obtain energies of interaction for the C ··· C, C ··· Cl, and Cl ··· Cl interactions of 0·895, −1·321(×2), and 1·874 kcal mol^{-1} for the diaxial conformer and 0·895, −1·125(×2), and 1·611 kcal mol^{-1} for the diequatorial conformer, giving an extra stabilisation in the diaxial form of only +0·13 kcal mol^{-1}, an order of magnitude lower than the observed result.

The dipole–dipole interaction may be calculated similarly. The Jean's formula for the interaction of two dipoles,[22] reduces for the case of two equal anti-parallel dipoles, to the expression (3) where W is in kcal mol^{-1},

$$W = 14{\cdot}41\mu^2(3\cos^2\theta - 1)/r^3 \qquad (3)$$

μ is in D, and r the inter-dipole distance in Å and where θ is the angle between the dipole moments and r. For the calculation we use a C–Cl bond dipole of 1·5 D[24] and r and θ are obtained from the midpoints of the C–Cl dipoles. This gives an energy of interaction of 0·20 and 0·58 kcal mol^{-1} for the diaxial and diequatorial conformers respectively, giving an extra stabilisation of the axial conformer of 0·38 kcal mol^{-1}. Again the calculated energy of interaction is too small to explain the observed effects. Note that the two calculations do not give identical results because the charge densities used are not equivalent to a bond dipole of 1·5 D (this would be obtained by both the carbon and chlorine having charges of + and −0·177 electrons).

Clearly therefore electrostatic interactions between the C–Cl dipoles are not the prime cause of the extra stabilisation of the axial conformer. Obviously all steric interactions are the same in equilibria (I) and (III), except the long range ones between the chlorine atoms which again are much too small to explain the observed effect.

However, inspection of Table **3** shows an alternative explanation. We note that in the diaxial conformer the hydrogen atom (2*ax*-H) in a planar *trans*-arrangement with the axial chlorine becomes more positive than usual. This hydrogen atom is however in close proximity to the axial 4-chlorine atom, resulting in an attractive interaction. In the diequatorial conformer although the 2*ax*-H is also positively charged it is now much further away from the 4-chlorine and therefore does not contribute any extra stabilisation. [The interaction of this hydrogen and the 1-chlorine atom is of course included in equilibrium (I)].

The attractive 1,3-interaction in the axial conformer can be readily calculated from equation (2) and is −0·26 kcal mol^{-1} with the same geometry as before and the charge densities of Table **3**. Furthermore there are four such interactions in the diaxial conformer, giving therefore a nett attractive interaction of −1·0 kcal mol^{-1}. This is in reasonable agreement with the observed stabilisation energy (1·8 kcal mol^{-1}) when one considers all the approximations made in the calculation. We conclude therefore that attractive 1,3-interactions between the negatively charge halogen and a positive hydrogen atom play a major role in the extra stabilisation of the 1,4-diaxial conformers.

This interaction also explains the extra stabilisation of the axial conformer of (V), in which according to Stolow the dipole–dipole interaction stabilises the equatorial conformer. The electronegative chlorine and oxygen substituents withdraw electrons from the neighbouring axial hydrogens in both conformers but only in the axial form will 3*ax*- and 5*ax*-H interact strongly with the 1-chlorine atom. The analogous interaction with the acetal oxygens will be very similar in both conformers and we would expect therefore an extra stabilisation of the axial conformer of roughly half that of (III). The observed value of 0·66 kcal mol^{-1} needs to be corrected for solvent effects but supports this interpretation.

We note finally that for substituents of large dipole moments the dipole–dipole term may be appreciable. For example in (IV) the C=O dipole (3·1 D)[23] is twice that of the C–Cl moment of (III) and thus the dipole–dipole interaction in (IV) may be an appreciable part

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* The methods are of course not identical if one uses an ' effective dielectric constant ' in the Jean's formula.[22] The extent of the unreality of such a concept for intramolecular interactions may be seen by the analogy with the charge interactions. On this basis the quantum-mechanical Hamiltonian should include the term $\rho_i\rho_j/\varepsilon r_{ij}$.

[22] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' pp. 460—462, Wiley-Interscience, New York, 1965.

[23] A. L. McClellan, ' Tables of Experimental Dipole Moments,' Freeman, London, 1963.

[24] J. W. Smith, ' Electric Dipole Moments,' Butterworths, London, 1955, p. 92.

of the stabilisation energy (0·85 kcal mol^{-1} in CCl_4 solution).

Clearly however it is necessary to remove the effects of the solvent from such comparative studies in order to obtain data which can be used to test these ideas quantitatively.

We acknowledge grants from the S.R.C. towards the purchase of the A56/60 and HA-100 spectrometers, and thank Mrs. J. Farrell for some initial work on this project and Mr. T. M. Siverns and Mrs. A. Spencer for technical assistance.

[2/2346 *Received*, 16*th October*, 1972]