Conformational Studies in the Cyclohexane Series. 3. The Dihalocyclohexanes

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The energies of axial and equatorial fluoro-, chloro-, and bromocyclohexanes as well as diaxial, axial−equatorial, and diequatorial 1,2-, 1,3-, and 1,4-dihalocyclohexanes were calculated using the hybrid density functional methods B3LYP and B3P86 as well as MP2 and QCISD and the 6-311G* and 6-311+G(2df,p) basis sets. The best agreement with experimental data was found with QCISD/6-311+G(2df,p). Solvent effects on the relative energies were calculated using the SCIPCM reaction field model. The effect of the halo substituents on the geometry of the cyclohexane ring was examined, and it was found that the effect of an axial substituent was local flattening of the cyclohexane ring, but no effect was found at the remote ring carbons, and no evidence of 1,3-diaxial interactions between the halogen and the axial ring hydrogens was found. In the case of the 1,2-dihalides, the calculations reproduce the preference for the diaxial form with X = Cl, but also predict that the energy difference between diaxial and diequatorial will be quite small when X = F. This appears to be related to the preference for the gauche form of 1,2-difluoroethane. The calculated relative energies of the 1,4-dihalocyclohexanes are in good agreement with electron diffraction data. A calculation of the electrostatic effects in the 1,4-dichlorocyclohexane reproduced the observed preference for the aa conformer.

1. Introduction

In view of the generally observed equatorial preference for groups attached to a cyclohexane ring,[1] compounds having a preference for axial conformers are of special interest. One group of such compounds are the dihalocyclohexanes. Here it is known that *trans*-1,2-dichlorocyclohexane prefers the diaxial conformation,[2] and it has been reported that *trans*-1,4-dichlorocyclohexane also prefers the diaxial conformation.[3,4] It is easy to see why the 1,2-dichloride prefers this conformation since it moves the two chlorines with partial negative charges away from each other, reducing the electrostatic repulsion. This overcomes the normal tendency for the groups to adopt the equatorial positions. However, the two C−Cl dipoles are fairly far from each other in the 1,4-dichloride, and therefore electrostatic interactions should be less important, whereas the expected conformational preference (ΔG) based on chlorocyclohexane would be about 1.3 kcal/mol, favoring the diequatorial form. Why does it still prefer the diaxial conformer? This question has been studied by several groups,[4] but a clear answer has not as yet emerged.

Although some experimental data are available for the relative energies, including solvent effects,[5] the previously available data are not adequate to completely define the conformational preferences. Thus, we have carried out ab initio geometry optimizations for the 1,2-, 1,3-, and 1,4-dihalocyclohexanes where the halogens are F, Cl, and Br. The B3LYP, B3P86, MP2, and QCISD theoretical models were used along with the 6-311G* and 6-311+G-(2df,p) basis sets. The density functional models MP2 and QCISD provide corrections for electron correlation, and the basis sets are reasonably flexible. The use of two DFT models allows a comparison of their ability to reproduce conformational energies.

There has been considerable interest in solvent effects on the relative conformational energies.[5] Therefore, we have also calculated the solvent effects using the SCI−PCM reaction field model.[6] Here, the solute is placed in a cavity in the solvent which corresponds to the 0.0004 e/au³ electron density surface for the solute. This generally reproduces the molar volumes of the solute to ±5%. The effective charges on this isodensity surface are derived from the ab initio charge distribution of the solute, and the interaction of the charges with the solvent are calculated, giving the free energy of solvation. This model has been applied to a number of equilibria, and has been found to give results in good agreement with experiment using nonassociating aprotic solvents such as cyclohexane, di-*n*-butyl ether, acetone, and acetonitrile.[7]

2. Halocyclohexanes

The conformational preferences for the dihalocyclohexanes must be compared with those for the monohalocyclohexanes to determine the role of electrostatic and other effects on the former. Therefore, the energies of the monohalocyclohexanes were calculated at the theoretical

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Table 1. Calculated Energies of the Halocyclohexanes

level	axial	equatorial	E_{rel}
a. X = F			
B3LYP/6-311G*	−335.19757	−335.19735	−0.13
B3P86/6-311G*	−336.21109	−336.21108	−0.01
ZPE (kcal/mol)	102.37	102.28	0.09
B3P86/6-311+G(2df,p)	−36.24297	−336.24340	0.26
μ (D)	1.86	2.23	
MP2/6-311G*	−334.16300	−334.16254	−0.28
MP2/6-311+G(2df,p)	−334.41468	−334.41473	0.03
QCISD/6-311G*	−334.23116	−334.23066	−0.31
QCISD/6-311+G(2df,p)[a]	−334.48284	−334.48285	0.01
$\Delta\Delta H$(298 K) (kcal/mol)			0.07
S(298 K) (eu)	78.87	79.15	−0.28
$\Delta\Delta G$(298 K) (kcal/mol)			0.15
b. X = Cl			
B3LYP/6-311G*	−695.55687	−695.55821	0.84
B3P86/6-311G*	−696.73990	−696.74094	0.65
ZPE (kcal/mol)	101.57	101.47	0.10
B3P86/6-311+G(2df,p)	−696.76692	−696.76792	0.63
μ (D)	2.25	2.58	
MP2/6-311G*	−694.14912	−694.14991	0.50
MP2/6-311+G(2df,p)	−694.39712	−694.39768	0.35
QCISD/6-311G*	−694.22501	−694.22595	0.59
QCISD/6-311+G(2df,p)[a]	−694.47301	−694.47372	0.45
$\Delta\Delta H$(298 K) (kcal/mol)			0.48
S(298 K) (eu)	81.16	81.73	−0.57
$\Delta\Delta G$(298 K) (kcal/mol)			0.65
c. X = Br			
B3LYP/6-311G*	−2809.47754	−2809.47901	0.92
B3P86/6-311G*	−2811.14775	−2811.14882	0.67
ZPE (kcal/mol)	101.16	101.07	0.09
B3P86/6-311+G(2df,p)	−2811.16832	−2811.16938	0.67
μ (D)	2.39	2.70	
MP2/6-311G*	−2806.99735	−2806.99818	0.52
MP2/6-311+G(2df,p)	−2807.22741	−2807.22810	0.43
QCISD/6-311G*	−2807.07092	−2807.07194	0.64
QCISD/6-311+G(2df,p)[a]	−2807.30098[a]	−207.30186	0.55
$\Delta\Delta H$(298 K) (kcal/mol)			0.56
S(298 K) (eu)	83.88	84.57	−0.69
$\Delta\Delta G$(298 K) (kcal/mol)			0.77

[a] Estimated value; see the text.

levels that will be used for the disubstituted compounds. The results are shown in Table 1. As will be noted below, the commonly used B3LYP density functional[8] often gives somewhat unsatisfactory results. As a result, the B3P86 density functional[9] also was used. It has been found to be more satisfactory than B3LYP for NMR shielding[10] and electronic excitation calculations.[11] A comparison of B3LYP, B3P86, and MP2 showed significant scatter in the calculated relative energies.

One of the more satisfactory of the variational procedures for correcting for the effects of electron correlation is QCISD.[12] In a study of the alkylcyclohexanes,[13] we found that this level of theory gave the best agreement with the experimental data. The QCISD/6-311G* energies were calculated using the MP2/6-311G* optimized geometries. Pople has shown in the development of his G2 model[14] that the effects of diffuse and higher polariza-

tion functions are approximately transferable between MP2 and QCISD. The higher level QCISD energies were then estimated as follows:

$$QCISD/6\text{-}311+G(2df,p) = QCISD/6\text{-}311G^* +$$
$$MP2/6\text{-}311+G(2df,p) - MP2/6\text{-}311G^*$$

The relative energies thus calculated were close to the larger basis set MP2 values.

To compare the relative energies calculated at this level with experimental data, it is necessary to correct for differences in zero-point energies and for the change in energy on going from 0 to 298 K. The vibrational frequencies were calculated at the B3P86/6-311G* level, and were not scaled.[15] The thermal corrections were made in the usual fashion, and the results are given in Table 1.

The difference in free energy between the axial and equatorial fluorocyclohexane conformers has been measured in the gas phase, giving $\Delta G = 0.25 \pm 0.02$ kcal/mol.[16] The calculated value, 0.15 kcal/mol, is in good agreement.[17] The solution-phase difference is 0.28 ± 0.02 kcal/mol.[18] Gas-phase values for chlorocyclohexane and bromocyclohexane are also available and are 0.65 ± 0.05 and 0.50 ± 0.10 kcal/mol, respectively.[19] They have also been studied by NMR in solution, giving $\Delta G° = 0.65$ and 0.77 kcal/mol, respectively. Again, the calculated values (0.65 and 0.77 kcal/mol) are in very good agreement with the experimental data.

If one makes the common assumption that, in the absence of other factors, the conformational energies are additive,[20] the preference for the diequatorial form over the diaxial form of the dihalocyclohexanes calculated at the QCISD level would be as follows (kcal/mol):

di-F	$\Delta H° = 0.14$	$\Delta G° = 0.30$
di-Cl	$\Delta H° = 0.96$	$\Delta G° = 1.30$
di-Br	$\Delta H° = 1.12$	$\Delta G° = 1.54$

Deviations from these values would give an approximate value for the contribution of electrostatic and other possible effects.

The structures of the compounds are also of interest. In an examination of the methylcyclohexanes,[13] we found that an axial methyl group led to local flattening of the cyclohexane ring, but no effect at the opposite ring carbon. This is also seen with the halocyclohexanes (Figure 1). The geometry at C3, C4, and C5 is essentially unchanged for all of the compounds, and the torsional angles involving these atoms have a normal value for a cyclohexane ring. However, the C−C−C bond angles at C2 and C6 are larger in the axial forms than in the equatorial forms, and the torsional angles involving these atoms are decreased. The structures of the halocyclohexanes have been studied via electron diffraction,[21] and there is generally good agreement between the calculated

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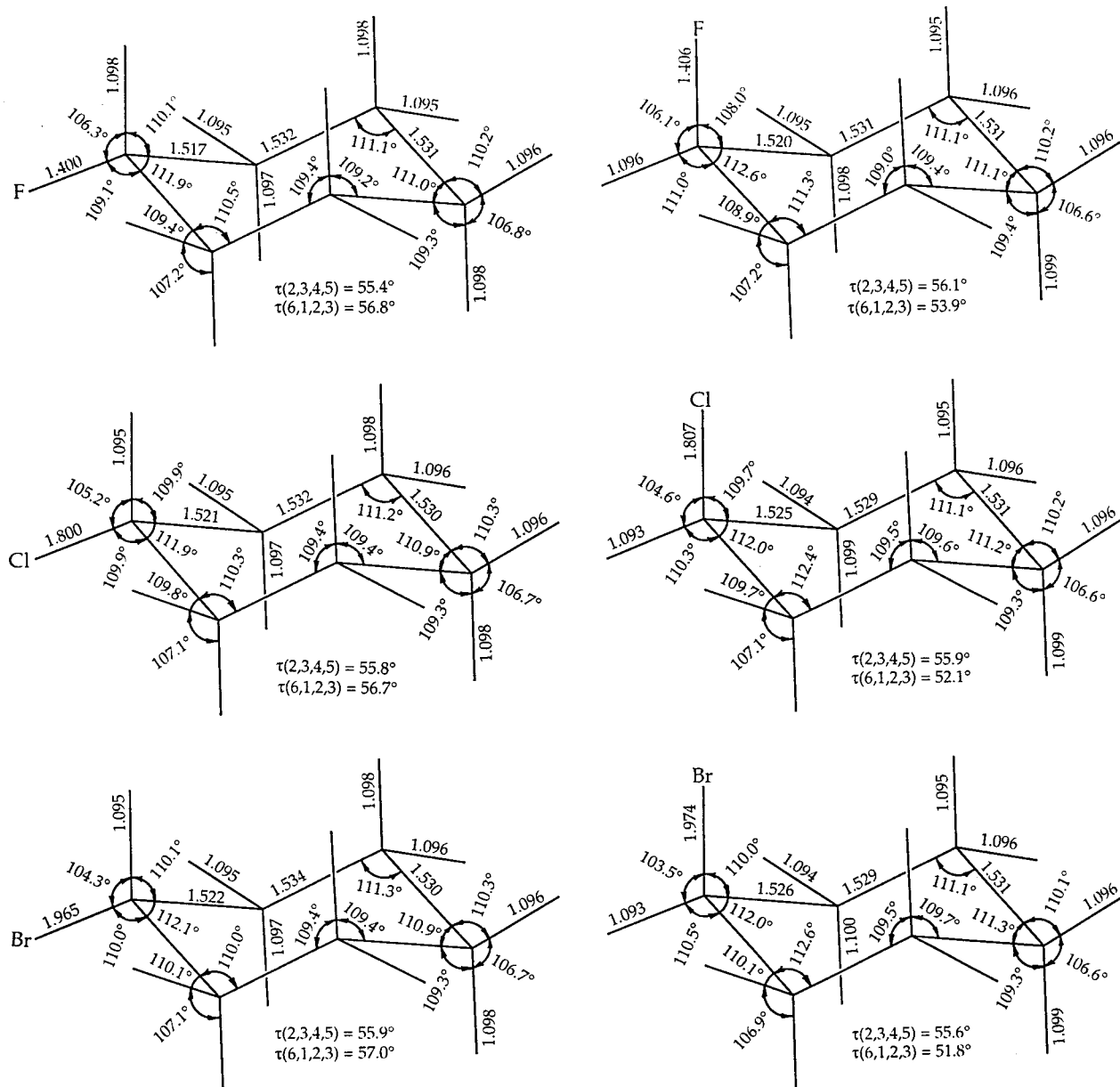
Figure 1. MP2/6-311G* calculated structures for the halocyclohexanes.

and experimental structures. However, a detailed comparison is not possible because of the limited information that could be obtained for compounds that have two significantly populated conformations.

A 1,3-diaxial interaction between an axial substituent and the axial hydrogens at C3 and C5 should lead to C−C−H bond angles in which the hydrogens bend away from the substituent. This is not found, and there is no indication of a 1,3-diaxial interaction. Rather, the gauche interaction between the halogen and the adjacent ring carbons appears to be the source of the destabilization of the axial forms.

3. 1,4-Dihalocyclohexane

The 1,4-dihalo compounds are the most interesting of the group. An early electron diffraction study found the aa and ee conformers of 1,4-dichloro- and 1,4-dibromocyclohexane to have about the same energy.[21] On the basis of NMR studies, it has been reported that the aa

conformer is preferred for both the dichloro and dibromo compounds in the gas phase and in nonpolar solvents, and that the ee conformer becomes the more stable in polar solvents.[5] A more recent electron diffraction study by Hedberg et al. found the two conformers of 1,4-dichlorocyclohexane to have the same free energy.[22] Why is the normal preference for equatorial conformers not found in this case?

When the electrostatic interactions are large, as with the difluoro compound, one might expect that the aa conformer would be preferred because it would be stabilized by the C···F nonbonded attraction. This is found in all of the ab initio calculations (Table 2). However, these interactions should be significantly decreased when the substituent is chlorine or bromine. Here, different theoretical levels lead to different predictions. The B3LYP density functional leads to the ee conformer having the

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Table 2. Calculated Energies of 1,4-Dihalocyclohexanes[a]

	aa di-X	ae di-X	ee di-X
		a. X = F	
B3LYP/6-311G*	−434.46655 (0.00)	−434.46486 (0.95)	−434.46403 (1.35)
B3P86/6-311G*	−435.61641 (0.00)	−435.61491 (0.94)	−435.61423 (1.37)
ZPE	97.68	97.57	97.55
B3P86/6-311+G(2df,p)	−435.65613 (0.00)	−435.65514 (0.62)	−435.65486 (0.80)
μ	0.00	2.81	0.00
MP2/6-311G*	−433.24727 (0.00)	−433.24530 (1.24)	−433.24418 (1.94)
MP2/6-311+G(2df,p)	−433.54711 (0.00)	−433.54574 (0.86)	−433.54502 (1.31)
QCISD/6-311G*	−433.31253 (0.00)	−433.31053 (1.25)	−433.30947 (1.92)
QCISD/6-311+G(2df,p)[b]	−433.61237 (0.00)	−433.61097 (0.88)	−433.61031 (1.29)
		b. X = Cl	
B3LYP/6-311G*	−1155.18472 (0.00)	−1155.18423 (0.31)	−1155.18519 (−0.29)
B3P86/6-311G*	−1156.67359 (0.00)	−1156.67277 (0.51)	−1156.67342 (0.11)
ZPE (kcal/mol)	96.08	95.92	95.88
B3P86/6-311+G(2df,p)	−1156.70390 (0.00)	−1156.70312 (0.49)	−1156.70374 (0.10)
μ (D)	0.00	3.06	0.00
MP2/6-311G*	−1153.21916 (0.00)	−1153.21839 (0.48)	−1153.21871 (0.28)
MP2/6-311+G(2df,p)	−1153.52286 (0.00)	−1153.51092 (0.59)	−1153.51095 (0.59)
QCISD/6-311G*	−1153.29981 (0.00)	−1153.29901 (0.50)	−1153.29982 (0.00)
QCISD/6-311+G(2df,p)[b]	−1153.59251 (0.00)	−1153.59154 (0.61)	−1153.59206 (0.28)
		c. X = Br	
B3LYP/6-311G*	−5383.02618 (0.00)	−5383.02577 (0.26)	−5383.02700 (−0.51)
B3P86/6-311G*	−5385.48939 (0.00)	−5385.48848 (0.57)	−5385.48930 (0.06)
ZPE	95.15	95.09	95.03
B3P86/6-311+G(2df,p)	−5385.50664 (0.00)	−5385.50578 (0.54)	−5385.50655 (0.06)
μ	0.00	3.14	0.00
MP2/6-311G*	−5378.91571 (0.00)	−5378.91491 (0.50)	−5378.91534 (0.23)
MP2/6-311+G(2df,p)	−5379.17244 0.00)	−5379.17161 (0.52)	−5379.17182 (0.39)
QCISD/6-311G*	−5378.99165 (0.00)	−5378.99010 (0.97)	−5378.99186 (−0.13)
QCISD/6-311+G(2df,p)[b]	−5379.24838 (0.00)	−5379.24680 (0.99)	−5379.24834 (0.03)

[a] The relative energies (kcal/mol) are given in parentheses and do not include the zero-point energy correction. [b] Estimated value, see the text.

Table 3. Calculated Relative Energies, 25 °C, kcal/mol[a]

	ΔH			ΔG		
compound	aa	ae	ee	aa	ae	ee
1,4-difluoro	0.0	0.8	1.2	0.0	0.3	1.1
1,4-dichloro	0.0	0.5	0.2	0.0	−0.1	−0.1
1,4-dibromo	0.0	1.0	0.1	0.0	0.4	−0.1
1,3-difluoro	1.1	−0.7	0.0	1.1	−0.5	0.0
1,3-dichloro	3.5	−0.2	0.0	3.8	−0.1	0.0
1,3-dibromo	4.4	0.0	0.0	4.7	0.2	0.1
1,2-difluoro	0.0	0.5	0.3	0.0	0.1	0.1
1,2-dichloro	0.0	1.0	0.6	0.0	0.6	0.3
1,2-dibromo	0.0	1.5	1.0	0.0	1.2	0.9

[a] The ΔH values are based on the QCISD/6-311+G(2df,p) energy differences, corrected for the differences in zero-point energies and the differences in $(H - H°)_{298}$. The ΔG values are derived from ΔH and the calculated entropy differences.

lower energy while the B3P86, MP2, and QCISD models lead to the aa conformer having the lower energy.

The QCISD/6-311+G(2df,p) energies for the 1,4-dihalo compounds were obtained as described above. The energy differences thus calculated were converted to $\Delta H°$ and $\Delta G°$ differences at 25 °C using the difference in calculated zero-point energies, and the thermal correction which was obtained in the usual fashion.[23] The values are given in Table 3. The calculated difference in free energy for the aa and ee 1,4-dichlorocyclohexanes is in very good accord with the observed energy difference (0.0 kcal/mol).[22]

The several theoretical methods that were used lead to significantly different structural parameters (Table 4). Some key values that will be important in calculating electrostatic interactions are compared with the results

Table 4. Calculated Structural Parameters

level	r(C−Cl)	r(C′−C)	r(C′−Cl)	r(Cl−Cl′)
		aa 1,4-Dichlorocyclohexane		
HF/6-31G*	1.821	2.982	3.913	5.326
B3LYP/6-311G*	1.851	2.983	3.924	5.362
B3P86/6-311G*	1.830	2.963	3.877	5.289
B3P86/6-311+G(2df,p)	1.822	2.958	3.869	5.273
MPW/6-311G*	1.825	2.964	3.878	5.288
MPW/6-311+G(2df,p)	1.817	2.960	3.869	5.271
MP2/6-311G*	1.807	2.962	3.842	5.223
observed[22]	1.802(5)	3.026(19)	3.880(15)	5.238(16)
		ee 14-Dichlorocyclohexane		
HF/6-31G*	1.806	2.925	4.599	6.345
B3LYP/6-311G*	1.833	2.931	4.627	6.399
B3P86/6-311G*	1.812	2.916	4.593	6.327
B3P86/6-311+G(2df,p)	1.804	2.912	4.583	6.327
MPW/6-311G*	1.809	2.916	4.590	6.339
MPW/6-311+G(2df,p)	1.801	2.913	4.580	6.321
MP2/6-311G*	1.796	2.921	4.581	6.316
observed[22]	1.787(3)	2.982(19)	4.598(10)	6.307(10)

of the recent study.[22] It can be seen that the MP2/6-311G* calculations give the more satisfactory agreement with the experimental values for r(C−Cl) and r(Cl−Cl′), and they are reasonably satisfactory for the other parameters.[24]

The relatively large experimentally measured solvent effect also is of interest. Both the ee and aa conformers have a zero dipole moment, and thus any solvent stabilization must come from higher electric moments. It has been proposed that the aa conformer has a large quadrupole moment,[5] whereas that for the ee conformer was assumed to be relatively small. The stabilization of the quadrupole moment might account for the solvent effect.

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(24) Cf. ref 22 for a more detailed comparison of calculated and experimental geometrical parameters.

Table 5. Effect of Solvent on the Relative Energies of aa and ee 1,4-Dihaloocyclohexane, B3P86/6-311G* SCI−PCM Calculations[a]

compound	$\epsilon = 2.0$	E_{rel}	$\epsilon = 36$	E_{rel}
aa di-F	−435.61825	−1.15	−435.62107	−2.92
ee di-F	−435.61646	−1.40	−435.61995	−3.59
aa di-Cl	−1156.67523	−1.03	−1156.67771	−2.59
ee di-Cl	−1156.67536	−1.21	−1156.67849	−3.18
aa di-Br	−5385.49103	−1.03	−5385.49346	−2.55
ee di-Br	−5385.49131	−1.26	−5385.49444	−3.23

[a] E_{rel} values (kcal/mol) are given with respect to $\epsilon = 1$.

However, the ab initio calculations find about the same quadrupole moments for the two conformers.

To see if higher moments might contribute to stabilization by polar solvents, SCI−PCM calculations were carried out for the aa and ee conformers for solvents with $\epsilon = 2$ (cyclohexane) and with $\epsilon = 36$ (acetonitrile). The results are given in Table 5. Significant solvent effects are found, and the difference between the stabilization of the aa and ee forms in acetonitrile is 0.6 kcal/mol in each case.

The energy difference for the aa and ee conformers of 1,4-dichlorocyclohexane has been measured by NMR spectroscopy at −65 °C in acetonitrile, and was found to be 0.4 kcal/mol with the ee form having the lower energy.[4] Using our calculated relative solvent stabilization of 0.6 kcal/mol would lead to a gas-phase energy difference of 0.2 kcal/mol, favoring the aa form. This is in good agreement with both the gas-phase experimental value and the calculated energy difference.

4. 1,3-Dihalocyclohexanes

There are few data concerning the conformational preference for the 1,3-dihalocyclohexanes, but they indicate a preference for the ee conformer.[25] This would be expected for electrostatic interactions since the C−X dipoles are aligned in a repulsive fashion in the aa conformer, and have a more favorable arrangement in the ee conformer. The ab initio calculations (Table 6) find the ee and ae isomers of the dichlorides and dibromides to have essentially the same energy, and the same dipole moment. The aa conformers have a much higher energy and, as expected, a larger dipole moment.

The results of the calculations for the difluorides are significantly different from those for the other halides. Here, the ae conformer has the lower energy, and the difference in energy between aa and ee has been reduced. The origins of these changes are not obvious, but may be related to the effect of fluorine on the 1,2-dihalides described below.

5. 1,2-Dihalocyclohexanes

The calculated energies of the 1,2-dihalocyclohexanes are given in Table 7, along with the calculated zero-point energies, the relative energies, and the dipole moments. Here, the aa and ee conformers correspond to trans and ae corresponds to cis. With the dichloride and dibromide, the aa conformer is calculated to have the lowest energy. The energy difference between aa and ee 1,2-dichlorocyclohexane is reported to be 0.61[26] or 0.72[27] kcal/mol. The

QCISD calculated energy difference corrected for the difference in zero-point energy is 0.6 kcal/mol, in very good agreement with these values.

On the other hand, the relative energies for 1,2-difluorocyclohexane are strongly dependent on the basis set used. The smaller basis sets indicate a strong preference for the diaxial conformer, whereas the large basis sets reduce the difference in energy markedly.

This is probably related to observations on the rotamer preference for 1,2-difluoroethane. It is known experimentally that the gauche form has a lower energy than the trans form.[28] Calculations using modest basis sets give the incorrect prediction that the trans rotamer has the lower energy, whereas the inclusion of the diffuse function in the basis set leads to the correct prediction.[29] The effect of the diffuse functions was examined via the use of electron density difference maps, which clearly showed the formation of an anti bent bond in the trans rotamer and a syn bent bond in the gauche form. The bent bonds are a result of the high electronegativity of the fluorine.

The diaxial form of 1,2-difluorocyclohexane is structurally related to *trans*-1,2-difluoroethane, whereas the diequatorial form is related to *gauche*-1,2-difluoroethane. We are attempting to obtain an experimental value for the energy difference to see if the calculated difference in ΔG is correct.

The dipole moments for all of the aa conformers are relatively small, whereas they are considerably larger for the ee conformers. Therefore, one would expect that the ee form would be preferentially solvated by polar solvents, and that the preference for the aa form would diminish. This has been found to be the case experimentally. The results of SCIPCM calculations for cyclohexane and acetonitrile solutions are shown in Table 8. The reported energy differences for the dichloride are 0.4 kcal/mol in cyclohexane and −0.5 kcal/mol in acetonitrile.[30] Taking the gas-phase energy difference as 0.7 kcal/mol, the solvent effect in going from the gas phase to solution is 0.3 kcal/mol in cyclohexane and 1.2 kcal/mol in acetonitrile. The calculated values, 0.5 and 1.4 kcal/mol, respectively, are in good agreement with the experiments.

6. The Role of Electrostatic Interactions

One explanation for the differences in energy between conformers is that they result from electrostatic interactions between C−X dipoles.[4] There are problems associated with modeling these interactions that include the question of which atomic charges are most appropriate for the purpose,[31] and whether a dielectric constant of 1 is appropriate for interactions between atoms on opposite sides of the cyclohexane ring.[32] It has been noted that just the interaction between the two C−Cl dipoles will not reproduce the observed effect.[4] We have chosen to use the CHELPG charges[33] that are derived from fitting the electrostatic potentials about the molecule in question

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Table 6. Calculated Energies of 1,3-Dihalocyclohexanes[a]

	aa	ae	ee
		a. Difluorides	
B3LYP/6-311G*	−434.46173 (0.92)	−434.46478 (−0.99)	−434.46320 (0.00)
B3P86/6-311G*	−435.61158 (1.14)	−435.61480 (−0.88)	−435.61340 (0.00)
ZPE	97.51	97.70	97.54
B3P86/6-311+G(2df,p)	−435.65168 (1.53)	−435.65495 (−0.52)	−435.65412 (0.00)
μ (D)	3.56	2.32	2.41
MP2/6-311G*	−433.24216 (0.63)	−433.24503 (−1.17)	−433.24317 (0.00)
MP2/6-311+G(2df,p)	−433.54235 (1.17)	−433.54538 (−0.73)	−433.54421 (0.00)
QCISD/6-311G*	−433.30748 (0.60)	−433.31033 (−1.19)	−433.30843 (0.00)
QCISD/6-311+G(2df,p)[b]	−433.60767 (1.13)	−433.61068 (−0.75)	−433.60947 (0.00)
		b. Dichlorides	
B3LYP/6-311G*	−1155.17740 (4.37)	−1155.18396 (0.25)	−1155.18436 (0.00)
B3P86/6-311G*	−1156.66622 (3.98)	−1156.67246 (0.07)	−1156.67257 (0.00)
ZPE (kcal/mol)	95.88	95.95	95.92
B3P86/6-311+G(2df,p)	−1156.69670 (3.95)	−1156.70288 (0.07)	−1156.70299 (0.00)
μ (D)	3.93	2.60	2.62
MP2/6-311G*	−1153.21140 (4.12)	−1153.21809 (−0.08)	−1153.21797 (0.00)
MP2/6-311+G(2df,p)	−1153.50456 (3.64)	−1153.51077 (−0.26)	−1153.51036 (0.00)
QCISD/6-311G*	−1153.29240 (4.17)	−1153.29901 (0.02)	−1153.29904 (0.00)
QCISD/6-311+G(2df,p)[b]	−1153.58566 (3.68)	−1153.59169 (−0.16)	−1153.59143 (0.00)
		c. Dibromides	
B3LYP/6-311G*	−5383.01771 (5.36)	−5383.02563 (0.39)	−5383.02625 (0.00)
B3P86/6-311G*	−5385.48075 (4.89)	−5385.48838 (0.11)	−5385.48855 (0.00)
ZPE (kcal/mol)	95.02	95.12	95.07
B3P86/6-311+G(2df,p)	−5385.49840 (4.67)	−5385.50570 (0.09)	−5385.50584 (0.00)
μ (D)	4.00	2.67	2.68
MP2/6-311G*	−5378.90676 (5.03)	−5378.91480 (−0.01)	−5378.91478 (0.00)
MP2/6-311+G(2df,p)	−5379.16427 (4.46)	−5379.17157 (−0.08)	−5379.17138 (0.00)
QCISD/6-311G*	−5378.98300 (5.15)	−5378.99100 (0.12)	−5378.99120 (0.00)
QCISD/6-311+G(2df,p)[b]	−5379.24051 (4.57)	−5379.24777 (0.02)	−5379.24780 (0.00)

[a] The relative energies (kcal/mol) are given in parentheses and do not include the zero-point energy correction. [b] Estimated value, see the text.

Table 7. Calculated Energies of 1,2-Dihalocyclohexanes[a]

	aa	ae	ee
		a. Difluorides	
B3LYP/6-311G*	−434.46385 (0.00)	−434.46129 (1.61)	−434.46160 (1.41)
B3P86/6-311G*	−435.61261 (0.00)	−435.61147 (0.72)	−435.61178 (0.52)
ZPE (kcal/mol)	97.62	97.56	97.46
B3P86/6-311+G(2df,p)	−435.65197 (0.00)	−435.65155 (0.26)	−435.65231 (−0.21)
μ (D)	0.91	3.19	3.59
MP2/6-311G*	−433.24331 (0.00)	−433.24191 (0.88)	−433.24161 (1.07)
MP2/6-311+G(2df,p)	−433.54296 (0.00)	−433.54227 (0.43)	−433.54243 (0.33)
QCISD/6-311G*	−433.30873 (0.00)	−433.30716 (0.99)	−433.30694 (1.12)
QCISD/6-311+G(2df,p)[b]	−433.60838 (0.00)	−433.60752 (0.54)	−433.70776 (0.39)
		b. Dichlorides	
B3LYP/6-311G*	−1155.18158 (0.00)	−1155.17921 (1.49)	−1155.18073 (0.53)
B3P86/6-311G*	−1156.67047 (0.00)	−1156.66833 (1.34)	−1156.66944 (0.65)
ZPE (kcal/mol)	96.01	95.86	95.73
B3P86/6-311+G(2df,p)	−1156.70107 (0.00)	−1156.69916 (1.20)	−1156.70009 ((0.61)
μ (D)	1.39	3.40	3.74
MP2/6-311G*	−1153.21677 (0.00)	−1153.21433 (1.53)	−1153.21518 (1.00)
MP2/6-311+G(2df,p)	−1153.50970 (0.00)	−1153.50787 (1.14)	−1153.50818 (0.95)
QCISD/6-311G*	−1153.29723 (0.00)	−1153.29477 (1.54)	−1153.29591 (0.83)
QCISD/6-311+G(2df,p)[b]	−1153.59016 (0.00)	−1153.58831 (1.16)	−1153.58891 (0.78)
		c. Dibromides	
B3LYP/6-311G*	−5383.02389 (0.00)	−5383.02026 (2.08)	−5283.02179 (1.32)
B3P86/6-311G*	−5385.48693 (0.00)	−5385.48362 (2.08)	−5385.48468 (1.41)
ZPE (kcal/mol)	95.02	95.03	94.87
B3P86/6-311+G(2df,p)	−5385.50430 (0.00)	−5383.50135 (1.85)	−5385.50224 (1.29)
μ (D)	1.32	3.41	3.74
MP2/6-311G*	−5378.91393 (0.00)	−538.91085 (1.93)	−5378.91148 (1.54)
MP2/6-311+G(2df,p)	−5379.17092 (0.00)	−5379.16858 (1.47)	−5378.16890 (1.27)
QCISD/6-311G*	−5278.98947 (0.00)	−5378.98630 (1.99)	−5378.98727 (1.38)
QCISD/6-311+G(2df,p)[b]	−5379.24646 (0.00)	−5379.24403 (1.52)	−5379.24469 (1.11)

[a] The relative energies (kcal/mol) are given in parentheses and do not include the zero-point energy correction. [b] Estimated value, see the text.

and reproduce the dipole moments. These charges have been found to be satisfactory for modeling intermolecular potentials.[34] In the absence of better information a dielectric constant of 1 was used.

The sum of all of the electrostatic interactions in the aa, ae, and ee conformations of 1,4-dichlorocyclohexane

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Table 8. Effect of Solvent on the Relative Energies of aa and ee 1,2-Dihaloocyclohexane, B3P86/6-311G* SCI−PCM Calculations[a]

compound	$\epsilon = 2.0$	E_{rel}	$\epsilon = 36$	E_{rel}
aa di-F	−435.61409	−0.93	−435.61627	−2.30
ee di-F	−435.61415	−1.49	−435.61790	−3.84
aa di-Cl	−1156.67163	−0.73	−1156.67336	−1.81
ee di-Cl	−1156.67142	−1.24	−1156.67460	−3.24
aa di-Br	−5385.48814	−0.76	−5385.48985	−1.84
ee di-Br	−5385.48663	−1.22	−5385.48967	−3.13

[a] E_{rel} values (kcal/mol) are given with respect to $\epsilon = 1$.

($\sum q_i q_j / r_{ij}, j > i$) was obtained. The values for aa, ae, and ee are −6.3, −4.0, and −4.2 kcal/mol, respectively. The similarity of the energies for the ae and ee conformers is in accord with the calculations in Table 2 that find the difference in total energy between these conformers to be similar to the difference between axial and equatorial chlorocyclohexane. The lower energy of the aa conformer is sufficient to overcome the expected 1 kcal/mol lower energy for ee on the basis of the energies of the conformers of chlorocyclohexane. This would still be the case if an "effective" dielectric constant[31] of 2 were used in estimating the electrostatic energies. Although these calculations can only be considered to be semiquantita-

tive, they do provide strong support for the view that the stabilization of the aa conformer is electrostatic in origin.

7. Calculations

The calculations were carried out using Gaussian-95[35] and standard basis sets.

Supporting Information Available: Tables of MP2/6-311G* calculated Cartesian coordinates for all of the compounds in this study and CHELPG charges for 1,4-dichlorocyclohexanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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