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CONFORMATIONAL ANALYSIS—CX

APPLICATIONS OF THE MOLECULAR MECHANICS METHOD TO ORGANIC HALIDES[a,b]

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Abstract—Available structural and thermochemical information concerning small halide molecules (fluorides, chlorides, bromides, and iodides) has been fit to by an extension of the current hydrocarbon force field. It is found that the fit to structural information is good to approximately within experimental error, and predictions are made for many compounds. Heats of formation and energy differences between isomers, conformers, etc. are generally well calculated, but there are some small, though definite, systematic errors. These may be due to solvent effects. The calculations are then extended to dihalides, by inclusion of an electrostatic term and additional parameters involving halogen-halogen interactions. While dihalides and certain tetrahalides can be usually fit very well, the same parameters are not adequate for the treatment of other polyhalides.

Various molecular-mechanical force fields have previously been applied to unsubstituted and substituted hydrocarbons.[2] Among others, fields were proposed for the treatment of organic mono-[3] and poly-halides.[4] Most of these fields, however, have not been shown to contain adequate hydrocarbon force fields. Furthermore, they were used only in connection with a small number of molecules or molecular types; more often than not it is unclear whether a given scheme is trustworthy outside of its original domain, or even if it applies, in the limit, to the parent structures.

It is our aim to adopt a more systematic approach and examine the extensibility to halides of one particular hydrocarbon force field.[5] Here, the total energy of a molecular species is written down as a sum of steric contributions (stretch, stretch-bend, bend, torsion-bend, torsion and van der Waals energies) which are meant to be carried over without formal change but with supplementary halide constants. In addition, electrostatic interactions—customarily disregarded when treating hydrocarbons—have now to be included. Currently, there are two ways of dealing with these. One is the so-called monopole-approximation,[6] in which the intramolecular distribution of charge is first estimated, then the electrostatic term built up as sum of charge-charge interactions. In the alternative dipole-approximation,[7] group moments are attributed to those bonds in the molecule whose polarization is considered decisive, and the electrostatic term is composed of dipole–dipole interactions. Naturally, the first approach is less prone to arbitrariness and, once a technique for the evaluation of charges has been set up, should leave no place for *ad hoc* parameterizations.

In view of our experience with charge calculations,[8] we felt that the scope of the dipole approach should be examined first. Less labor is here involved, and for certain ends further effort may not be justifable. Furthermore, limitations of the dipole approach, when encountered, should single out significant features of charge distribution, and thus guide the derivation of a monopole-type technique.

In the simplest scheme, only C^{α}-X and C^{α}-C^{β} group moments are included, which means that, in monohalides, electrostatic effects are disregarded altogether.

MONOHALIDE FORCE FIELD

If only C^{α}-X and C^{α}-C^{β} polarizations are included, and if the interaction of dipoles that are based on a common atom is considered as accounted for (implicitly) by the appropriate bending constant, then no electrostatic term occurs in the monohalide energy expression. The steric terms, enumerated in Table 1, merit some comment.

Parameters were chosen such that the scheme, in its entirety, reproduces in so far as consistent data are available—experimental geometries and energetic relationships in a series of haloalkanes. The van der Waals parameters for the halogens were arrived at by beginning with the corresponding rare gas, and increasing the van der Waals radius by 0·05 Å, and rounding off. The polarizability of the halogen was taken to be the same as that of the corresponding rare gas.[10,11] The natural lengths of the bonds C-Cl, C-Br and C-I, were taken as the electron-diffraction distances[12] in halomethanes; for CH_3F, only a microwave value was available,[13] and this was used.[d] Stretching force constants are based on current tabulations.[15,16]

Bending constants are close to the experimental values;[15,17] "natural" angles were arrived at by fitting available structural data for small molecules. One may note in passing that angles HCX, CCX and HCH (112·8 or 111·1, dependent on structure[5]) do not fulfill the stereometric tetrahedron relationships. This is also the case with the measured angles, which is suggestive of bent C-X bonds.

The torsional term is formulated throughout as threefold, despite the fact that some conceivable barriers (e.g. C^1C^2 in $XCH_2CH_2CH_3$) are of another periodicity. In justifying this choice, which was made for conformity with the alkane calculations, let us stress that torsion, as incorporated in molecular mechanical techniques, is just a corrective term to 1–4 nonbound interactions (see

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[d] The ED lengths of C-Cl, C-Br and C-I coincide with one or the other of the two available[12,14] MW values.

Table 1. Haloalkane force field[a]

Hill's Equation[b] Constants

$$E_v = -2.25\epsilon(r^*/r)^6 + 8.28\,(10^5)\,\epsilon \exp(-r/0.0736r^*)$$

Atom	r^*	ϵ
F	1.60	0.056
Cl	1.95	0.214
Br	2.10	0.296
I	2.25	0.400

Bond Stretching

$$E_s = 71.94\,k_s(l-l_o)^2[1-2(l-l_o)]$$

Bond	l_o	k_s
C-F	1.385	5.6
C-Cl	1.781	3.4
C-Br	1.939	2.6
C-I	2.139	2.2

Angle Bending

$$E_b = 0.021914\,k_b(\Theta-\Theta_o)^2[1-0.006(\Theta-\Theta_o)]$$

Atom	Θ_o(HCX)	k_b(HCX)	Θ_o(CCX)	k_b(CCX)
F	108.5	0.95	109.2	1.22
Cl	107.6	0.71	109.8	0.96
Br	107.0	0.64	109.1	0.90
I	106.4	0.54	108.9	0.82

Torsion

$$E_t = (V/2)(1+\cos 3\omega) \quad \text{for } 0 \leq \omega \leq 60$$

V	
0.71	HCCF, CCCF
0.80	HCCCl, CCCCl HCCBr, CCCBr

[a] Parameters for the hydrocarbon skeleton have been listed elsewhere.[5] Energies (E, ϵ, V) in kcal mole^{-1}, distances (r^*, r, l) in Å, angles (Θ, ω), in degrees, stretching (k_s) and bending (k_b) force constants in mdyn A^{-1} and mdyn A rad^{-2}, respectively. The CCC stretch-bend force constant (0.12) is also used for CCX, as is HCC (0.04) for HCX, where X is a halogen. Torsion-bend terms, except CCCC are suppressed.

[b] Ref. 9

Appendix in Ref. 9). Thus, it need not have the same periodicity as the total energy change on internal rotation. We also use threefold terms for calculation on polyhalides (below).

Monohalides

The force field parameters were derived to reproduce experimental geometries, and the results for sixteen representative haloalkanes are listed in Table 2. Available literature data are also given, and one should note that their scatter precludes further refinement of the force-field. Apart from C^{α}-C^{β} bonds, which are calculated to be somewhat long, structural features do fall in the expected ranges.

In haloethanes, the barrier to internal rotation is of interest. This may be equated to the difference between the minimum energies for the eclipsed and staggered forms. However, some of the recent experimental barriers were derived spectroscopically from torsional vibration modes, and these are not strictly comparable with a theoretical number which is based on relaxation in all degrees of freedom. In an alternative computational approach, therefore, the eclipsed structure is obtained from the staggered by a rigid rotation. One thus deals with two quantities, relaxed and non-relaxed.[24,25a]

Relevant data are assembled in Table 3. The experimental values scatter over wide ranges; indeed, they were obtained by variegated techniques (MW, IR, Raman) and may refer to different physical processes. It is best, perhaps, to compare the non-relaxed theoretical barriers with quantities derived recently[27] from Raman torsional vibrations: Cl, 3·66 *vs* 3·72; Br, 3·82 *vs* 3·72; I, 3·88 *vs* 3·66 kcal mole^{-1}. Our value for CH_3CH_2F, 3·22, is very close to the far-IR barrier,[28] 3·33 kcal mole^{-1}. Agreement is good throughout.

A phenomenon which has been suspected of involving charge-effects is the slight gauche preference[3,29] in 1-halopropanes (F, Cl, Br). Unfortunately, the accuracy of the published energy differences (g-a) is very low: F,[30] $-0{\cdot}47 \pm 0{\cdot}31$; Cl,[31,32] $-0{\cdot}3 \pm 0{\cdot}2$, $0 \pm 0{\cdot}5$, or $-0{\cdot}05 \pm 0{\cdot}15$; Br,[32] $-0{\cdot}1 \pm 0{\cdot}2$ kcal mole^{-1} (it is not always clear in the original papers if account has been taken of the statistical double weight of g). In contrast with the experimental evidence, our force field furnishes positive differences (F, 0·22; Cl, 0·39; Br, 0·49; I, 0·60). The values for F and Cl correspond to a gauche preponderance (because of entropy) and are reconcilable with experimental quantities; for Br and I, however, the anti conformation is computed to be slightly more abundant.

Now, it has been suggested[29,30] that the extra stabilization of the gauche conformation is due to an intramolecular X-C^1/C^3-H dipole–dipole interaction. In the present context, C-H polarization is disregarded, and it seems best to defer the problem for now. One may, however, check the conformer populations in the 1-halobutanes. Experimental (electron diffraction) values have been published[33,34] for the Cl and Br-derivatives. Using current notation,[33,34] the computed and (experimental) percentages are: for Cl, aa 34(11), ga 33 (37), ag 21 (11), gg 11 (17), gg′ 1 (24); and for Br, aa 37 (36), ga 29 (24), ag 23 (24), gg 10 (16), gg′ 1 (0). It is hard to decide whether the experimental numbers are really reliable; in 1-chlorobutane, in particular, the reported population of gg′ seems much too high, which casts doubts on the validity of the other values. As for the bromo compound, our results agree surprisingly well with the experimental, and are probably more realistic than those predicted[3] by another force field.

Table 4 contains data on the conformational energy of axial halocyclohexanes. The calculated energies consistently exceed the experimental ones but, clearly the two series of values are not immediately comparable. The latter are free-energy differences in solution, whereas the former are equated with enthalpy differences between isolated molecules. The theoretical values can be transformed approximately by Onsager's formula,[25b] to a medium of dielectric constant $\epsilon \neq 1$. We have done this in a rough way, using experimental dipole moments, the computed geometry, and Pauling's contact radii.[10] The results, for $\epsilon = 2{\cdot}63$ (CS_2), are given in the last line of Table 4. They are still high, but additional corrections—for entropy and perhaps for "solvent pressure"[38] are also required. Although not readily computable, both are expected to lower the theoretical value further.

The foregoing review illustrates the main handicap to

Table 2. Structure of representative haloalkanes

	F		Cl		Br		I	
	Comp.	Exp.	Comp.	Exp.	Comp.	Exp.	Comp.	Exp.
CH_3X[a]								
C–H	1.095	1.1	1.095	1.1	1.095	1.09–1.1	1.095	1.09–1.1
C–X	1.384	1.384–1.385	1.781	1.780–1.781	1.939	1.936–1.939	2.139	2.139
HCH	110.5	110.0	111.2	111.5	111.7	111.0–111.7	112.1	111.4–112.1
HCX	108.4	108.4	107.6	107.3	107.2	107.1–107.9	106.7	106.7
CH_3CH_2X[b]								
C–C	1.530	1.505–1.533	1.532	1.520	1.533	1.518	1.532	
C–H	1.1	1.09–1.1	1.1	1.09	1.1	1.09	1.1	
C–X	1.387	1.379–1.398	1.787	1.788	1.949	1.950	2.151	
HCH	107.8–108.8	108.8–108.8	107.6–109.1	108.5–109.2	107.3–109.5	108.9–109.9	107.3–109.9	
HCX	107.8	106.1	106.6		106.1	105.4	105.5	
CCX	109.4	109.4–109.7	111.1	111.0	111.32	111.2	111.5	
$CH_3CH_2CH_2X$[c]								
C–C	1.531		1.534	1.521	1.534	1.508	1.534	
C–X	1.390		1.795	1.798	1.961	1.957	2.166	
CCC	112.8		112.3	112.7	112.4	114.2	112.5	
CCX	108.9		110.2	109.4	110.3	110.0	110.4	
HCX	107.2		105.6	105.3	105.0		104.2	
$(CH_3)_3CX$[d]								
C–C	1.533	1.516	1.538	1.530	1.538		1.538	
C–X	1.393	1.43	1.80	1.803	1.975		2.184	
CCC								

Exp. data: [a] Ref. 12–14 and 18. Somewhat different values are given in Ref. 19; [b] Ref. 20; [c] Ref. 21; [d] Ref. 22. The MW spectrum of $(CH_3)_3CBr$ has been reported[23] but not analyzed.

Table 3. Barriers (kcal mole^{-1}) to internal rotation in CH_3CH_2X

	F	Cl	Br	I
Computed				
relaxed	2.98	3.40	3.52	3.56
non-relaxed	3.22	3.66	3.82	3.88
measured[a]	3.30–4.26	3.56–3.72	3.57–3.72	3.22–3.66

[a] Ref. 20, 26, 27, 28.

Table 4. Axial-equatorial free energy and energy differences for halocyclohexanes

	F	Cl	Br	I
Experimental $\Delta\Delta G^\circ$				
a	0.15	0.43	0.38	0.43
b	0.28	0.53	0.48	0.47
c	0.36	0.62	0.58	0.46
Calculated ΔE				
	0.44	0.82	1.02	1.22
corrected[d]	0.40	0.71	0.87	1.00

[a] Best values, 1967, Ref. 35;

[b] PMR in CS_2, Ref. 36;

[c] ^{13}C-Magnetic resonance, Ref. 37.

[d] See text

developing a force field for halides: experimental data, when available, are often of low accuracy or of a type not readily comparable to calculation. Even heat of formation data, a forceful aid in fixing hydrocarbon parameters,[39] are here sufficiently inaccurate to be of little use. It is, indeed, an easy matter to reproduce the reported values to within their claimed limits of accuracy. As our field is meant to be an extension of the hydrocarbon force field, we write here also[2]

H_f^0 = R + computed energy + ½RT for each external degree of freedom (translation, rotation), plus ½RT for each torsional degree where complete rotation is possible (excluding methyl).

Hydrocarbon parameters previously derived are used, together with new, best-fit, halide values (Table 5). It is gratifying to find, as Table 6 shows, that the extension performs smoothly.

SOME DI- AND TETRAHALOETHANES

When carrying out calculations on polyhalides, one expects to reproduce not only structure and energy relationships, but also the measured dipole moments. In the dipole–dipole approximation, these three factors are linked, directly or indirectly, with the values assigned to the bond moments.

The additional constants that we need are gathered in Table 7. The BrCBr "natural" value is somewhat lower than the experimental,[42] but a higher value could not be made to work. XCX bending constants have practically no effect on the computation, and we estimated them roughly from a theoretical relationship, $K_b(BAB) \approx 0{\cdot}1\, K_s(AB)$, derived[43] for triatomics AB_2 of valence angles 90–135°.

The electrostatic contribution to the total energy is taken as the sum of the dipole–dipole interactions. Only the C-X bond dipoles are included, and each term is calculated by Jeans' formula[41] with $\epsilon = 1$. The derivation

Table 5. Bond and structure parameters for heat of formation

X	C	F	Cl	Br	I
Bond C-X[a]	3.220	-45.92[b]	-9.589	0.873	14.324
CH_3-X	1.299	-	-	-	-
C-CH_2-X	0	0	0	0	0
	-1.700	-2.12[b]	-3.765	-3.944[d]	-2.248
	-4.827	-	-8.504[c]	-7.613	-6.447[c]

[a] Bond C-H, -5.054

[b] Fluorine parameters are based on two observations only

[c] Based on one observation, Me_3CX

[d] Based on one observation, $CH_3CHBrCH_3$

Table 6. Calculated and experimental heats of formation[a]

Compound	Calc.	Exp.	Calc-Exp	Exp. Accuracy
PrF	-67.6	-67.6	0.0	0.6
i-PrF	-69.4	-69.4	0.0	0.4
EtCl	-25.90	-26.1	-0.2	0.4
PrCl	-30.93	-31.0	-0.2	0.2
i-PrCl	-34.06	-33.6	-0.7	1.0
BuCl	-35.92	-35.1	-0.8	2.0
t-BuCl	-43.7	-43.7	0.0	0.6
$C_6H_{11}Cl$	-38.73	-39.1	-0.4	0.8
EtBr	-15.29	-15.2	-0.1	0.5
PrBr	-20.27	-20.5	-0.3	1.0
i-PrBr	-23.5	-23.5	0.0	0.6
BuBr	-25.35	-25.6	0.2	0.3
t-BuBr	-31.9	-31.9	0.0	0.3
EtI	- 1.90	- 2.0	0.1	0.4
PrI	- 6.89	- 7.1	0.2	1.8
i-PrI	- 8.44	- 9.8	1.4	1.5
t-BuI	-17.4	-17.4	0.0	0.6
$C_6H_{11}I$	-13.14	-12.2	-0.9	1.0

[a] All exp. data recorded in Ref. 40 have been included in the analysis, except methyl halides – where the structural type pertains to one sole molecule – and long-chain halides (> butyl) which were not calculated.

Table 7. Additional force field parameters

Bending				
X		Θ^0(XCX)	K_b(XCX)	
F		109.1	1.07	
Cl		111.7	1.08	
Br		109.7	0.98	
Torsion				
V				
0.71		FCCF		
0.76		FCCCl, FCCBr		
0.80		ClCCCl, ClCCBr, BrCCBr		
Electrostatic[a]				
By Jeans' formula[41] with $\epsilon = 1$				
Bond	μ^*(D)		Cl, Br	F
C-F	1.95	f_{gem}	0.91	1.
C-Cl	2.00	f_0	0.43	-
C-Br	2.15	f_{60}	0.825	0.667
		f_{120}	0.525	-
		f_{180}	0.825	0.825

[a] See text for details.

of the electrostatic parameters is best illustrated by some examples.

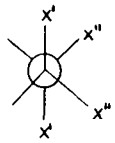
Consider first CH_3CHCl_2. The gas-phase dipole moment of this molecule is 2·07 D,[44] and the ClCCl angle is calculated 110·8 (exp.[42] 109·5 ± 1·5). Working backwards, $\mu_{C\text{-}Cl}$ (C-Cl geminal to another C-X) = 1·82 D. Alternatively, one may express $\mu_{C\text{-}Cl}$ as a product $\mu^{\bullet}_{C\text{-}Cl} f_{gem}$, where $\mu_{C\text{-}Cl}$ is some basic moment, and f_{gem} is a multiplicative factor typical of the particular structural feature. Picking $\mu_{C\text{-}Cl}$ = 2·0 D (dipole moment of C_2H_5Cl), we have f_{gem} = 0·91.

Take next the gauche form of $ClCH_2CH_2Cl$. Its dipole moment should be around[25] 2·55 D, and the dipolar ClC/CCl angle is calculated to be 79·7°, so that here $\mu_{C\text{-}Cl}$ = 1·65 D. Denoting the factor for *gauche* relationship by f_{60}, one has 1·65 = 2·00 f_{60}, and f_{60} = 0·825.*

C-Cl group moments in other rotamers of $ClCH_2CH_2Cl$ can be based on experimental estimates of conformational energies: anti is lower than *gauche* by[45] *ca.* 1·2 kcal mole^{-1}, while the Cl···Cl and Cl···H barriers are higher than anti by 4·5 and 2·8 kcal mole^{-1}, respectively. The bond moment for the C-Cl bond required in each case to give the quoted energy difference was 1·65 (anti), 0·86 (Cl···Cl), 1·05 (Cl···H). The corresponding factors are f_{180} = 0·825, f_0 = 0·43, f_{120} = 0·525.

It turns out that the same factors can be used for bromine-containing ethanes, provided one puts $\mu^{\bullet}_{C\text{-}Br}$ = 2·15 D. Data for fluorinated and iodinated ethanes are scarce, and only a few constants for F (and none for I) are included in Table 7.

As mentioned, all factors are meant to be multiplicative† so that, e.g. in skew 1,1,2,2-tetrahaloethane,



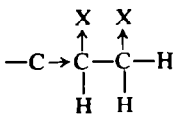
$$\mu(C\text{-}X') = \mu^{\bullet}_{C\text{-}X} f_{gem} f_{60} f_{180}$$
$$m(X\text{-}X^{o}) = \mu^{\bullet}_{C\text{-}X} f_{gem} f^{2}_{60}$$

We carried out by this technique calculations on all molecules of types CH_3CHX_2, XCH_2CH_2Y and X_2CHCHY_2 for which we had found at least some experimental numbers. Energies and dipole moments are given in Table 8. In most cases, geometrical data are lacking, and no comparisons are possible.

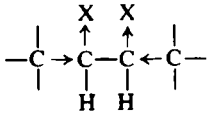
How should one feel about the results of Table 8? Numerically, they are satisfactory, and the force field that produced them has the gratifying feature of containing, as particular cases, force fields for monohalides and for unsubstituted hydrocarbons. Yet, no no guides have evolved for computing constants for other structural types, and the physical relevance of the bond-moment parameters seems doubtful. The present treatment of polyhalides is best considered as a step towards the development of a better computational scheme. As such, it has to be pushed to the limits of its applicability, so that finer details of the molecular substructure—which will have to be incorporated in an improved treatment—can be discerned.

EXTENSIONS AND LIMITATIONS

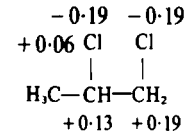
The next step is to check whether the field of Tables 1 and 7 can be used for molecules more complicated than those hitherto discussed. No difficulty is envisaged in extending the treatment of CH_3CHX_2 to $CH_3CH_2CHX_2$, etc. for here the halogens are remote enough from the inserted chain. As for vicinal dihalides, it turns out that the scheme applies, provided one assigns a moment of 0·43 D to the bond $C^{\alpha} \leftarrow C^{\beta}$, i.e.



or



In 1,2-dichloropropane, for example, this corresponds to the charge distribution



As the experimental reports are seldom unambiguous, it would be instructive to examine some results.

cis - 1,2 - *Dichlorocyclohexane* (molecule used in fixing the C-C bond moment). Calculated dipole moment 3·14 D, exp.[44] 3·10–3·15 D.

trans - 1,2 - *Dichlorocyclohexane.* Although most conformational studies of this compound have been conducted in solution,[60] a gas-phase value for the dipole moment is available; it is[44] about 2·3 D over a large temperature range. Judging from the dipole moments of the 4 - tert - butyl derivatives, 1·2 (diaxial) and 3·3 D (diequatorial), the material is a mixture of conformations. If the numbers above are assumed to hold simultaneously in the gas phase at 25°C, one derives for *trans* - 1,2 - dichlorocyclohexane (Eee) − E(aa) = 0·2 kcal mole^{-1}.‡

We calculate ΔE = 0·21, μ_{aa} = 1·12, μ_{ee} = 3·37, about 59% aa at 25°C, with an overall dipole moment of 2·33 D.

trans - 1,2 - Dibromocyclohexane. We calculate E(ee) − E(aa) = 0·24 kcal mole^{-1}, μ_{ee} = 3·54, μ_{aa} = 1·24. For comparison, one may cite the dipole moments of the 2,3-*trans*-dibromodecalins, 3·28 (ee) and 1·15 (aa), or those of the 1,2 - dibromo - 4 - t - butylcyclohexanes, 3·3 (ee) and 1·19 D (aa). ΔE has been measured only in solution; extrapolations to the gas phase lead to very high values,[60,63] 1·3–1·5 kcal mole^{-1}.

*A theoretical analysis[46] seems to suggest additive, rather than multiplicative factors. However, in an additive construction for heavily halogenated ethanes (e.g. X_2CHCHX_2) computed bond moments turn out too low to reproduce the experimental dipole moments.

†Note that, in this construction, f_{gem} and f_{60} (as well as $\mu^{\bullet}_{C\text{-}X}$ which are arbitrary) do not depend on the assumption ϵ = 1. In contrast, the other factors to be listed (f_{180}, f_0, f_{120}) are derived from energy relationships, and cannot be carried over to fields where other values of ϵ are incorporated in Jeans' formula.

‡A previous estimation of conformer ratios from dipole moments[61] was based on the assumption μ_{aa} = 0·4 D, and cannot be accurate. Also, ratios of integrated IR peaks lead to[62] ΔE = 0·6 or 0·7 kcal mole^{-1}, but these high values imply that the dipole moments of the separate conformers exceed 1·2 and 3·3 D by far.

Table 8. Polyhaloethanes (energies in kcal mole^{-1})

Molecule and Structure	Conformational Energy Calc.	Conformational Energy Exp.	Dipole Moment Calc.	Dipole Moment Exp.
CH_3CHCl_2			2.07	2.07
stg.	0	0		
ecl.	4.13	4.13[a]		
$ClCH_2CH_2Cl$			1.15	1.1–1.2
g	1.23	1.2 ± 0.1[b]		
a	0	0		
Cl···Cl	4.49	4.50[c]		
Cl···H	2.82	2.81[c]		
$Cl_2CH{\cdot}CHCl_2$			1.33	1.29–1.37
s	0.30	0.2–0.3[d]		
a	0	0		
Cl···Cl, Cl···Cl	2.78	-		
Cl···Cl, Cl···H	0.86	-		
CH_3CHBr_2			2.27	2.14[e]
stg.	0	0		
ecl.	4.33	4.33[a]		
$BrCH_2CH_2Br$			0.97	0.95–1.16
g	1.54	1.4–1.7[f]		
a	0	0		
Br···Br	6.00	5.85–6.18[g]		
Br···H	2.99	-		
$Br_2CHCHBr_2$			1.31	1.30[l]
s	0.46	0.6–1.1[h]		
a	0	0		
Br···Br, Br···Br	4.96	-		
Br···Br, Br···H	1.65	-		
$BrCH_2CH_2Cl$			1.09	1.1[k]
g	1.35	1.43 ± 0.10[i]		
a	0	0		
Br···Cl	5.46	4.54–4.74[g]		
Br···H, Cl···H	3.46	-		
CH_3CHF_2			2.27	2.24–2.30
stg.	0	0		
ecl.	3.20	3.2[l]		
FCH_2CH_2F			1.62	-
g	0.13	< 0.2[m]		
a	0	0		
$ClCH_2CH_2F$			1.62	1.84[o]
g	0.47	0.46–0.50[n]		
a	0	0		
$BrCH_2CH_2F$			1.74	-
g	0.40	0.3–1.0[p]		
a	0	0		

Experimental dipole moments are from Ref. 44, except when noted otherwise.

[a] New far-Raman value.[47]

[b] Selected value.[45]

[c] Selected value,[45] based on dipole moments. The thermodynamic approach yields[48] 4.13 and 2.76.

[d] From dipole moments and IR.[49,50] Extrapolation of solution values gives a higher energy,[51] 0.54–0.84.

[e] Measured in benzene.

[f] Some literature values are[52,53] 1.4 (dipole moments), 1.45 (IR), 1.63 (ED), 1.60 (extrapolated from solution NMR). The selected value[45] is 1.77 ± 0.15, but there are grounds to expect a narrower range,[54] 1.63–1.70.

[g] Based on dipole moments.[45]

[h] This value, extrapolated from solution data,[51] is undoubtedly too high, as are some other values included in the same research.

[i] Measured in hexane (in ether, μ = 1.70 D).

[j] IR value.[50] Extrapolation of solution data yields[53] 1.50 ± 0.20.

[k] Measured at 65°C.

[l] Most recent determination, by Stark-laser and IR-MW, gave[55] 3.199.

[m] See Ref. 45 and 54. Still, some authors claim that only the gauche form is detectable or that it predominates strongly.[56] A recent MW study suggests[57] 0.43.

[n] From dipole moments[58] and extrapolated solution data[53] (see also Ref. 57). A lower value has been estimated from IR.[59]

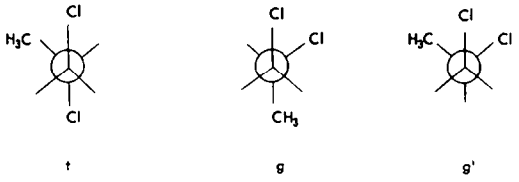
[o] Measured at 35°C.

[p] IR suggests[59] 0.30 ± 0.08, while NMR leads to[53] 1.00.

meso - 2,3 - *Dichlorobutane.* The *gauche* form is calculated to lie 1·43 kcal mole^{-1} higher than the *trans* (exp.[64] 1·30 ± 0·30), which corresponds to 85% *trans*. $\mu_t = 0·0$, $\mu_g = 3·0$, and the computed overall moment is 1·18 D. The predicted barriers are 4·13 (asymm.) and 7·08 kcal mole^{-1} (symm.) above the *trans*. For comparison, ultrasonic relaxation revealed one barrier,[65] 5·13 ± 0·06 above *gauche*.

meso - 2,3 - *Dibromobutane.* Here we find E(g) − E(t) = 1·25 kcal mole^{-1} (exp.[64] 1·43 ± 0·22 or 1·52 ± 0·30), μ_t = 0·0, $\mu_g = 3·15$, μ (overall) = 1·46 D.* Barriers are 4·05 (asymm.) and 8·31 kcal mole^{-1} (symm.) above the trans, vs the one barrier measured,[65] 6·43 ± 0·38 above the *gauche*.

1,2 - *Dichloropropane.* This molecule has three conceivable minimum energy conformations, and has been investigated several times. In early dipole moment work,[67]



the presence of g′ was disregarded; later it was assumed that g′ could be excluded on energy grounds, and this led to the estimate[68] E(g) − E(t) = 0·95 − 1·05 kcal mole^{-1}. More recent gas-phase IR and NMR measurements suggest[69] E(g) − E(t) = 1·2, E(g′) − E(t) = 1·9 kcal mole^{-1}. The dipole moment is about 1·46 D, both in CCl_4 at 25°C[70] and in the gas phase at 70°.[68]

On the whole, the experimental data quoted above are in line with each other, except for the controversial g′. We find that g and g′ are rather close in energy, E(g′) − E(g) = 0·04, and that E(g) − E(t) = 1·12 kcal mole^{-1}. This corresponds to the following populations at 25°: 77% t, 12% g, 11% g, altogether 23% of *gauche* forms. The computed dipole moments are $\mu_t = 0·61$, $\mu_g = 2·96$, $\mu_g = 2·62$, and the weighted, overall value is 1·44 D.

1,2-*Dibromopropane.* We find E(g) − E(t) = 1·30, E(g′) − E(g) = 0·12 kcal mole^{-1} (exp. energy difference between "*gauche*" and t: 1·25 in the vapor,[71] 1·44 in CCl_4[70]). The calculated dipole moment, 1·36 D at 25°, is higher than the values measured, 1·06 in CCl_4 at 25°,[70] 1·13 D in the vapor at 80·6.[71]

There are not enough data to check 1,3-dihalides, but a very interesting limitation of the force field comes to light when dealing with 1,4-dihalides.

A case in point is *trans* - 1,4 - dichlorocyclohexane. When the C-Cl dipoles alone are included in the electrostatic term ($\mu_{C\text{-}Cl} = \mu^{*}_{C\text{-}Cl} = 2D$), E(ee) − E(aa) = −1·02 kcal mole^{-1}; when C^{α}–C^{β} moments are also taken into account (moment of 0·43 D assigned to bonds C^1C^2, C^1C^6, C^3C^4 . C^4C^5), E(ee) − E(aa) = −0·79. Both values seem wrong: E(ee) is known to exceed E(aa) in solvents of $\epsilon > 3$,[63] and there is no reason to expect a reversal of order in the gas phase. There thus exists an effect that stabilizes the axial conformer and has not been accounted for in our calculation. Now, CNDO calculations suggest that the axial hydrogens in the diaxial conformer are more positive than usual.[63] Here, C^1-Cl is close in space to C^3-H_{ax} and C^5-H_{ax} (as is C^4-Cl to C^2-H_{ax} and C^6-H_{ax}) which provides four stabilizing interactions. No equivalent obtains in the diequatorial structure.

Another type of limitation can be illustrated by the case of Cl_3CCCl_3. The steric contribution to the total energy is 5·31 (staggered) and 18·07 kcal mole^{-1} (eclipsed). The difference between these two numbers, 12·8 kcal mole^{-1}, is about what one expects for the rotational barrier,[72] so that the electrostatic terms should roughly cancel. However, if one adheres to the factors of Table 7,

$$\mu_{C\text{-}Cl}(\text{stg.}) = 2f^2_{gem} f^2_{60} f_{180} = 0·93$$
$$\mu_{C\text{-}Cl}(\text{ecl.}) = 2f^2_{gem} f_0 f_{120} = 0·20$$

the electrostatic term turns out to be very large (8·02) for the staggered, and very small (0·36 kcal mole^{-1}) for the eclipsed conformation. As a consequence, the computed barrier has the unrealistically low value of 5·1 kcal mole^{-1}.

These examples suffice to indicate what the difficulty is. Unlike the saturated hydrocarbons, and unlike the monohalides, polyhalides fall into a large number of structural types, and the electrostatic contribution to their molecular-mechanical energy is structure-dependent. This dependency upon structure is a result of the charge distribution. Thus it would seem that each molecule must be dealt with as a special case, at least when there are two or more halogens in the same molecule. To do this properly, some kind of charge distribution calculation is required. This can either be done quantum mechanically, or classically. In principle either of these methods should be applicable, in practice, this remains to be demonstrated.

*The dipole moment has been reported as[66] 2·20 D (gas, 22°). This high value implies, however, almost equal populations of *gauche* and *trans*, and ΔE about zero.

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