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THE *GAUCHE* EFFECT

ON THE NATURE OF THE INTERACTION BETWEEN ELECTRONEGATIVE SUBSTITUENTS IN *TRANS*-1,2-DISUBSTITUTED CYCLOHEXANES

NIKOLAI S. ZEFIROV,* V. V. SAMOSHIN, O. A. SUBBOTIN
and V. I. BARANENKOV
Department of Chemistry, Moscow State University, Moscow 117234, U.S.S.R.

and

SAUL WOLFE*
Department of Chemistry, Queen's University, Kingston, Ontario, Canada

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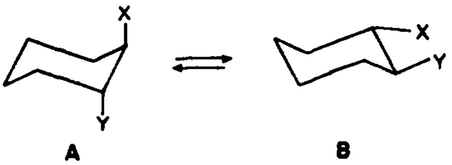
Abstract—The positions of the aa/ee conformational equilibria of a series of *trans*-1,2-disubstituted cyclohexanes containing electronegative substituents have been determined experimentally by NMR, and calculated theoretically by classical means. It is found that the classical analysis of the results, which takes into account explicitly steric and electrostatic interactions between *gauche* substituents, is not adequate, because residual attraction remains between the substituents.

trans-1,2-Disubstituted cyclohexanes are useful model compounds for the investigation of the factors governing conformational equilibria.[1-3] The results of such studies are usually discussed either in classical terms, i.e. in terms of "steric" and "electrostatic" interactions,[1] or in quantum mechanical terms at various levels of sophistication.[1-3] In the classical approach, one has to pose the following question: can one describe unambiguously the conformational behavior of a compound in terms of steric (E_{ster}) and electrostatic (E_{μ}) interactions alone, or is it necessary to introduce some additional "conformational effect" as a corrective term?[1-3] For example, the experimentally observed ΔG_{eq} values of *trans*-1,2-X,Y-disubstituted cyclohexanes[3] have been partitioned into three terms as shown in eqn (1),

$$\Delta G_{eq} = \Delta G_X + \Delta G_Y + \Delta G_{X/Y} \qquad (1)$$

where ΔG_X and ΔG_Y are the free energies of the conformational equilibria of the corresponding monosubstituted cyclohexanes, and the term $\Delta G_{X/Y}$ reflects the *gauche*-interaction of X and Y in the diequatorial conformation, B. This latter term can, in principle, be compared to calculated steric and electrostatic interaction terms. It is proposed that, when $\Delta G_{X/Y} = \Delta E_{ster} + \Delta E_{\mu}$, the conformational behavior can be understood in terms of classical effects alone. However, as has been demonstrated elsewhere,[3] when X and Y are atoms below the First Row (S, Br, I), some kind of nonclassical (i.e. unexpected) repulsive effect is found to exist and, for X/Y = F/I and MeO/OAc, some additional attractive effect has to be invoked.



These observations are in accord with the postulates of the "hockey-sticks" effect in the cases of the heavy atoms,[1-4] and the "*gauche*-effect" in the cases of the strongly electronegative atoms.[1-3,5] However, since the number of experimental points in the region corresponding to additional *gauche*-attraction is relatively small, and these points deviate only slightly from normal behavior,[3] it has seemed desirable to extend such work to additional 1,2-*trans*-disubstituted cyclohexanes containing electronegative substituents, e.g. F, Cl, OAc, OCH_3 (for a preliminary communication, see Ref. 6).

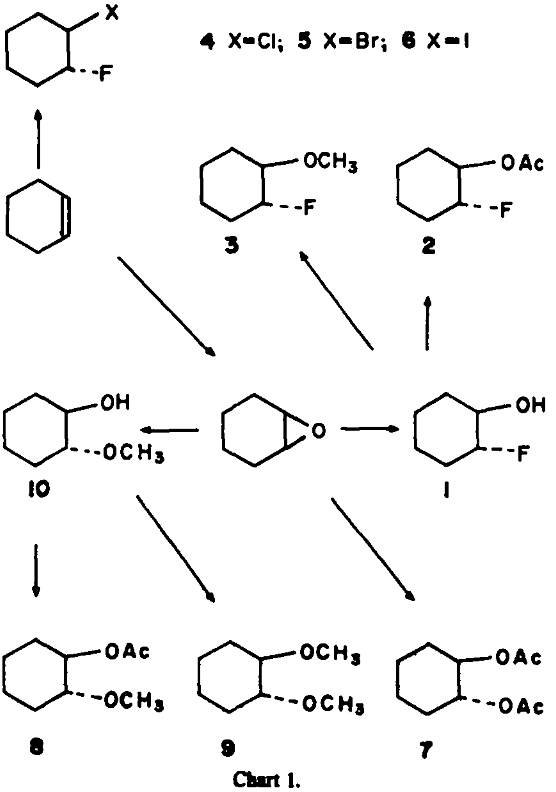


Chart 1.

RESULTS

(A) *Syntheses*

All oxygen-containing compounds were obtained from cyclohexene oxide. The *trans*-1-fluoro-2-halogenocyclohexanes **4–6** were prepared by addition of the appropriate N-halosuccinimide to cyclohexene in the presence of anhydrous HF/ether. These syntheses are summarized in Chart 1.

(B) *Determination of the positions of the conformational equilibria*

The positions of the A⇄B conformational equilibria of these compounds were measured in two ways: (a) by integration of appropriate peaks of ^{13}CMR spectra of the two conformers at −80°; (b) by measurement of the width of averaged peaks at 30° in the ^{1}HMR spectra. Details of the first procedure have been presented in Ref. 7. In some cases, an *upper limit* for the minor conformation was estimated. The ^{13}CMR data are summarized in Table 1.

The width of the averaged peak in the ^{1}HMR spectrum can be employed to calculate the amounts of the two conformation, using the Eliel eqn (2):

$$W = W_{aa} \cdot n + W_{ee} \cdot (1 - n). \qquad (2)$$

The H–CF proton signal in compounds **1–6** has $J_{HF} \sim$ 49–52 Hz and one of the resulting signals is usually found to overlap with other peaks. In these cases, determination of peak widths was performed on peaks which were clearly separated from others, and which included the required vicinal coupling constants. The reported widths are the average of three experimental spectra and have an accuracy of ±0.4 Hz. A major problem with this method relates to the choice of W_{aa} and W_{ee}. The widths $W_{aa} = 7$ Hz and $W_{ee} = 23$ Hz have been observed in the model 5-t-butyl-*trans*-2-fluorocyclohexanols.[8] We adopted the first of these, but W_{ee} has been set equal to 23.5 Hz to agree with the experimentally observed width for compound **1** in $CHCl_3$. The calculated values of ΔG_{eq} are also included in Table 1. It has to be emphasized that neither method permits precise ΔG_{eq} values to be assigned to strongly shifted (anancomeric) equilibria; the error in ΔG_{eq} increases as the equilibrium constant increases even though the errors in the experimentally determined parameters ($W_{1/2}$ or intensity) are the same.

(C) *Empirical regularities in the conformational equilibria*

It will be noted, first, that there is good correlation between the data obtained by the two methods of the present work (see also Refs. 9–11), and also between the present results and available literature data (Table 1). Secondly, for all compouhnds there is a definite increase in the proportion of *ee*-conformation, **B**, with an increase in the polarity of the solvent. Thirdly, the **W**-values in MeCN provide additional confirmation of the *trans*-configurations of the compounds. Unfortunately, the low-temperature ^{13}CMR method does not permit data to be obtained in a range of solvents of different polarity. Nevertheless, the results obtained in CS_2 and in CH_2Cl_2 follow the trends already noted.

The data of Table 1 also demonstrate a "benzene effect"[3,12] because, in this solvent, *ee*-conformations are preferentially stabilized in comparison to CCl_4 and CS_2. It is remarkable that $CHCl_3$ appears to be a more "polar" solvent than benzene in the cases of the oxygen containing compounds, while the opposite is observed in the case of the dihalogeno compounds. This is, perhaps, related to a more effective solvation of the oxygen-containing compounds via coordination such as $CCl_3H \cdots O$. It is also of interest to contrast the "benzene effects" exhibited by *trans*-2-fluorocyclohexanol, **1**, and *trans*-2-chlorocyclohexanol.[13]

The $-\Delta G_{eq}$ values for compound **1** increase in the direction $CS_2 \rightarrow CCl_4 \rightarrow C_6H_6$, and then decrease in $(CD_3)_2CO$ and CH_3CN. These observations may be related to the presence of an intramolecular O–H···F H-bond in nonbasic solvents.[14] Thus, there is a strong band at $3618 \pm 3\ cm^{-1}$ in the IR spectra of 0.01M and 0.005M solutions of **1** in CCl_4, which is assigned to the intramolecular H-bond. This assignment takes into account the analogous situation in 2-chloroethanol[15] and *trans*-2-chlorocyclohexanol.[16] The IR spectrum of **1** also exhibits a low intensity shoulder on the $3618\ cm^{-1}$ band and at higher frequency, corresponding to a "free" OH group. The slightly increased content of the *aa*-conformation in $(CD_3)_2CO$ and CH_3CN is compatible with the presence of an *intermolecular* H-bond (C–O–H···S), leading to an increase in the negative charge on the oxygen and, thence, to an increase in *gauche*-electrostatic repulsion of the substituents.[17]

Examination of the data for compounds **2**, **3** and **7–9** indicates that the conversion of X/OCH_3 to X/OAc leads to an increased preference for the diequatorial conformation, **B**; the magnitude of this effect is greater than $A_{OAc}–A_{OCH_3} = 0.15$ kcal/mol. Two speculations can be offered to account for this result: (a) the existence of a *gauche*-electrostatic attraction between the CO carbon of an OAc group and a vicinal electronegative substituent (*cf* Ref. 18); (b) smaller coulombic repulsion between the O atom of OAc and a vicinal *gauche*-substituent as compared to the O atom of Me (see Ref. 17; for analogous observations on MeO- and AcO-monosubstituted cyclohexanes, see Ref. 19).

(D) *Calculation of the steric and electrostatic interactions of the* gauche-*substituents*

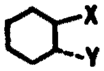
As discussed earlier,[3] to demonstrate the presence of a conformational "effect", it is necessary to compare observed $\Delta G_{X/Y}$ values with calculated values of steric and electrostatic interactions of *gauche*-substituents. However, the parameters required for such calculations vary greatly in the literature. The present calculations have been performed using "best" or "average" values, as well as ranges of parameters which permit an estimation of limiting (maximal and minimal) values. The *A*-values that have been employed are shown in Table 3.

A variety of potentials based upon the two-parameter 6-12-potential or two- or three 6-exp potentials have been employed in the literature for the calculation of steric interactions.[20–23] Usually the parameters vary according to the particular class of compound, and it is probably impossible to choose *a priori* a generally applicable "best" potential. In the present work, the well-known Hill potential[20] (eqn 3) has been used because of its successful application to a wide range of structurally different compounds.[3,23–26]

$$E_v = \epsilon \cdot (-2.26\alpha^{-6} + 8.28 \times 10^5 \exp(-\alpha/0.0736)). \qquad (3)$$

The E_v values shown in Table 2, have been calculated using Hill's parameters[27]. This procedure seemed

Table 1. NMR and conformational equilibrium data for *trans*-1,2-disubstituted cyclohexanes

No	 X	Y	$-\Delta G_{ee-aa}$, kcal/mol							Literature data (Ref.)	*gauche*-effect[d]: $\Delta G_{eq}^{exp} - \Delta G_{eq}^{calc}$
			^{13}CMR, -80°C		^{1}H-NMR (% of *aa*-conformer)						
			CS_2	CH_2Cl_2	CCl_4	CS_2	$CHCl_3$	C_6H_6	CH_3CN		
1	F	OH	–	>1.5	1.65±0.23 (6.1)	1.43±0.22 (8.5)	(large)[a] (0)	2.0_9 (3.0)	1.1_9[b] (12.1)	0% *aa* (8)	–
2	F	OAc	>1.13	>1.37	1.28±0.17 (10.6)	1.34±0.2 (9.7)	1.9_7 (3.6)	1.4_8 (7.9)	2.4 (1.8)	–	–
3	F	OCH_3	0.89±0.17	–	0.81±0.09 (20.6)	0.81±0.09 (20.6)	1.1_9 (12.1)	0.9_8 (16.4)	1.8_0[c] (4.8)	–	-1.33
4	F	Cl	0.60±0.09	1.22	0.59±0.08 (27.3)	0.65±0.08 (25.5)	0.9_3 (17.6)	0.9_6 (17.0)	1.8_0[c] (4.8)	0.74-0.81(46) -60 -90°C	-0.65
5	F	Br	0.64±0.06	1.20	0.42±0.07 (33.3)	0.65±0.21 (25.5)	0.9_8 (16.4)	1.1_9 (12.1)	1.3_9 (9.1)	0.65, Et_2O, -80°C(9)	-0.60
6	F	I	0.76±0.12	1.33	0.54±0.07 (29.1)	0.75±0.09 (22.4)	0.8_6 (19.4)	1.1_6 (12.7)	2.2_2 (2.4)	0.65±0.025, CS_2, -90°C(10)	-0.59
7	OAc	OAc	>1.50	>1.50	–	–	–	–	–	1.77, CCl_4, 30°C (11)	–
8	OAc	OCH_3	0.70±0.1	1.22	–	–	–	–	–	0.52±0.15, CS_2, 30°C(1)	–
9	OCH_3	OCH_3	0.28±0.004	1.06	–	–	–	–	–	–	-0.66

[a] W = 23.5Hz; [b] in $(CD_3)_2CO$ $-\Delta G_{ee-aa} = 1.30$ kcal/mol(10.3% of *aa*-conformer); [c] in CD_3CN; [d] using the optimal set from Table 2, kcal/mol.

Table 2. Calculation of ΔG_{eq} for the *trans*-1,2-X, Y-disubstituted cyclohexanes (energies in kcal/mole)

Compound			ΔE_V	ΔE_ρ	$\Delta G_{X/Y}$	ΔG_X	ΔG_Y	ΔG_{eq}	$\Delta G'_{eq}$
	X	Y	eq(3)	eq(4)				eq(1)	eq(5)
3	F	OCH_3	-0.08_6	2.0_4[a]	1.9_5	-0.11	-0.34	1.5_0	
			-0.08_6	1.3_3[b]	1.2_4	-0.25	-0.55	0.4_4	
			-0.08_6	1.0_4[c]	0.9_5	-0.385	-0.785	-0.2_2	-0.4_0
4	F	Cl	-0.10_2	1.8_2[a]	1.7_2	-0.11	-0.39	1.2_2	
			-0.10_2	0.9_0[b]	0.8_0	-0.25	-0.50	0.0_5	
			-0.10_2	0.6_6[c]	0.5_6	-0.385	-0.66	-0.4_9	-0.6_0
5	F	Br	-0.09_2	1.9_1[a]	1.8_2	-0.11	-0.31	1.4_0	
			-0.09_2	0.7_8[b]	0.6_9	-0.25	-0.48	-0.0_4	
			-0.09_2	0.4_9[c]	0.4_0	-0.385	-1.0	-0.9_8	-1.0_7
6	F	I	-0.05_2	1.3_7[a]	1.3_2	-0.11	-0.407	0.8_0	
			-0.05_2	0.6_1[b]	0.5_6	-0.25	-0.48	-0.1_7	
			-0.05_2	0.3_1[c]	0.2_6	-0.385	-0.59	-0.7_1	-0.8_0
9	OCH_3	OCH_3	-0.08_8	1.7_4[a]	1.6_5	-0.34	-0.34	0.9_7	
			-0.08_8	1.5_7[b]	1.4_8	-0.55	-0.55	0.3_8	
			-0.08_8	1.0_5[c]	0.9_6	-0.785	-0.785	-0.6_1	-0.7_9
	F	H	-0.04_8	0.1_4[c]	0.0_9				
	OCH_3	H	-0.04_9	0.1_4[c]	0.0_9				
	Cl	H	-0.06_0	0.0_8[c]	0.0_2				
	Br	H	-0.05_7	0.0_6[c]	0.0_0				
	I	H	-0.04_1	0.0_4[c]	0.0_0				

[a] using the maximal parameters, [b] using the optimal parameters,
[c] using the minimal parameters.

reasonable because the use of different parameters from different sources would have required a demonstration that these are internally consistent.[23,24] In addition, the magnitudes of the steric interaction terms obtained in this way are small in comparison with the electrostatic interaction terms (Table 2).

The electrostatic interactions have been calculated using a point charge model[12,28] in which these interactions are represented as a sum of the pairwise coulombic interactions of the charges on the X and Y atoms (eqn 4).

$$E_\mu = 332 \cdot e_X \cdot e_Y / r_{X/Y} \cdot \epsilon. \qquad (4)$$

These charges were calculated either from experimental dipole moments, μ, and bond lengths, C–X, or from published quantum mechanical data. Both "extremal" and "optimal" literature magnitudes of such charges are collected in Table 4.

One drawback of the classical molecular mechanics calculations relates the value assigned to the dielectric constant, ϵ. Assignments of this parameter ranging from 1[24] to 4[25] have been used, without any obvious justification for the particular choice. In the present work ϵ has been set equal to 1, the value advocated in Refs. 24 and 29. As will be seen, increasing this parameter does not alter the main features of our results.

When eqn (1) is analyzed, it is seen that the correcting terms $\Delta G_{X/H}$ and $\Delta G_{Y/H}$ should be added to the general scheme. These take into account the fact that there is one less X···H or Y···H *gauche*-interaction in a 1,2-disubstituted cyclohexane than in a monosubstituted cyclohexane (eqn 5).

$$\Delta G_{eq} = (\Delta G_X - \Delta G_{X/H}) + (\Delta G_Y - \Delta G_{Y/H}) + \Delta G_{X/Y}. \qquad (5)$$

However, this correction also introduces new uncertainties because of our uncertainty concerning the charges on the H atoms. As will be seen later, this correction is useful only for the calculation of the *minimal set* of ΔG_{eq} values.

Finally, the geometries of the molecules under investigation have been calculated as described in Ref. 3. The results are summarized in Table 2.

DISCUSSION

The relationship between ΔG_{eq}^{calc} and ΔG_{eq}^{exp} is shown in Fig. 1 (this treatment is slightly different from that of Ref. 3). It will be noted that the line which corresponds to $\Delta G_{eq}^{calc} = \Delta G_{eq}^{exp}$ divides Fig. 1 into two regions: one can be termed the region of additional attraction and the other the region of additional repulsion (see Ref. 3). With this interpretation, the distance of the ordinate for an experimental point from the line is the energy associated with the additional *gauche*-interaction, i.e. the "conformational effect".[1–3]

The results are very striking. All of the compounds of the present work lie distinctly in the region of additional attraction. Therefore, *the conformational behaviour of all of these compounds can be rationalized only by invoking the existence of additional* gauche-*attraction* (i.e. *a* "*gauche*-effect"[3,5]). In the case of **3** the magnitude of this effect is 1.33 kcal/mol by ^{13}CMR, and 1.25 kcal/mol by ^{1}HMR (Table 1).

However, it will be clear that the theoretical parameters discussed above could have been manipu-

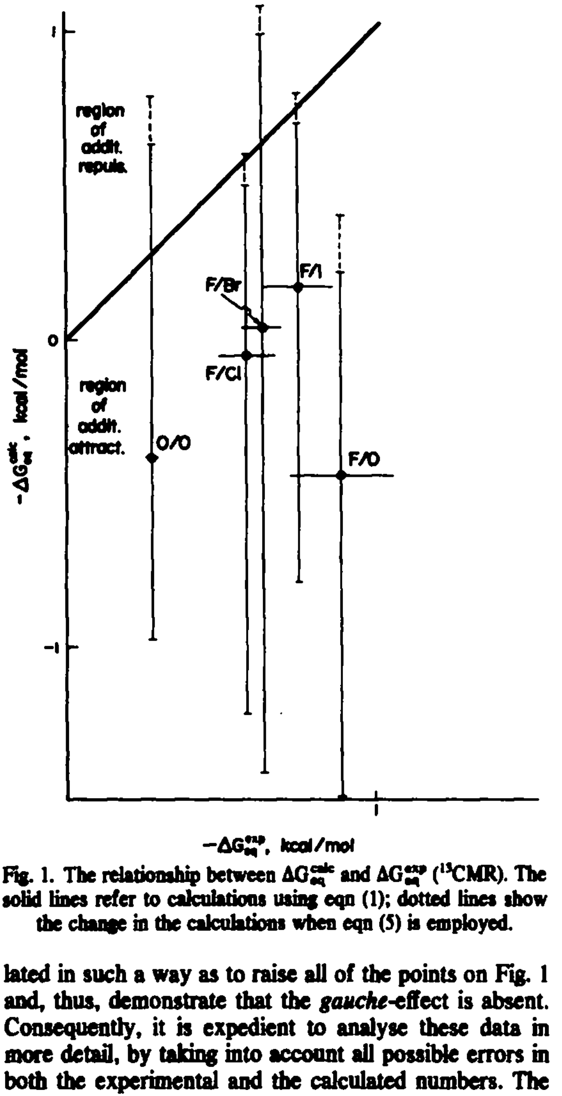


Fig. 1. The relationship between ΔG_{eq}^{calc} and ΔG_{eq}^{exp} (^{13}CMR). The solid lines refer to calculations using eqn (1); dotted lines show the change in the calculations when eqn (5) is employed.

lated in such a way as to raise all of the points on Fig. 1 and, thus, demonstrate that the *gauche*-effect is absent. Consequently, it is expedient to analyse these data in more detail, by taking into account all possible errors in both the experimental and the calculated numbers. The error bounds obtained in this way are included in Fig. 1. Calculations based on eqn (1) show that all possible combinations of parameters leave the points for compounds 3, 4 and 6 in the region of the additional attraction. However, with eqn (5), some of the error bounds intersect the borderline slightly. Thus, manipulation of the parameters does not lead to an unambiguous answer in these cases. It should be clear, however, that forcing agreement in this way is in itself an unsatisfactory procedure, because there is no obvious justification for the particular set of parameters that lead to the disappearance of the effect (see also Ref. 2).

For compound 3, *regardless of the parameters or equation employed* for the calculation, additional *gauche*-attraction remains, whose lower limit is greater than 0.5 kcal/mol. In addition, it is expedient to discuss the factors which can lead to the shift of points on Fig. 1 either up or left, and hence to the decrease of the effect magnitude. Firstly, it is the increasing of the dielectric constant, ϵ (*vide infra*). Evidently, an artificial overstatement of ϵ could raise the points up quite drastically. However the calculation with $\epsilon = 3$ (a very large value) and the "best" parameters of Tables 3 and 4 still leads to an additional attraction of 0.4 kcal/mol.

Secondly, it is the solvent problem. Indeed, the calculated energies refer to the vapour phase, but the experimental energies compared are *not* the vapour-state values but the *non-polar solvent* values. In fact, the approximation $\Delta G_{vap} \simeq \Delta G$ in non-polar solvents is frequently used in literature (see refs. in Ref. 12*b*). However Abraham *et al.* have shown that the difference between these energy values for the 1,2-dihalogenocyclohexanes can be rather appreciable.[12] In order to estimate the ΔG_{vap} value we have used two approximate methods. Firstly, the eqn (6)[12b] have been used.

$$\delta\Delta G_{(vap\text{-}CS_2)} \approx \delta\Delta G_{(CS_2\text{-}acetone)}. \tag{6}$$

We have found $\Delta G_{(CD_3)_2CO} = -1.23$ kcal/mol for 3, and hence, using $\Delta G_{CS_2} = -0.81$ kcal/mol, the value ΔG_{vap} is equal to -0.4 kcal/mol. Secondly, we have employed the method elaborated by Pentin *et al.*:[12b] the extrapolation of the plot of ΔG_{solv} *vs* $(\epsilon - 1)/(2\epsilon + 1)$ to $\epsilon_{solv} = 1$. This method gave the value $\Delta G_{vap} \approx -0.33$ kcal/mol. Thus, the account of the solvent influence and the use of the vapour-phase value decreases the value of an additional *gauche*-attraction from 1.33 to about 0.8 kcal/mol but still does not change the general conclusion. The existence of additional *gauche*-attraction between vicinal electronegative substituents thus seems to be a real phenomenon, and this phenomenon has to be explained in any discussion on the conformational behaviour of such compounds.

In addition we must emphasize the difficulty of principle which accompanies all attempts to decrease the value of the effect of additional *gauche*-attraction by the manipulation of the parameters. As it has been shown elsewhere[3] many points lie in the borderland, and such operation will shift many borderline cases distinctly in the region of additional *gauche*-repulsion. Thus, instead of explanation of additional attraction molecular mechanics calculation would be challenged to explain the additional repulsion and vice versa.

CONCLUSIONS

We believe that the significance of these results is the following. It is well established[30] that MO theory at the *ab initio* level reproduces faithfully the stereochemical behaviour of all classes of molecular systems, including the behaviour of molecules with electronegative substituents. However, until very recently,[31] it has not been possible to interpret the results of such calculations in a manner likely to be acceptable to the majority of organic chemists. In our opinion, the perturbational molecular orbital (PMO) procedure[31] merits much more attention than it has so far received. The reluctance of experimental chemists to accept and use the ideas and predictions of this procedure is due to two factors; the first is the unfamiliar language in which the theory is couched; the second is the conviction, held by most experimentalists, that the current qualitative language of organic chemistry can always be adapted or modified as the need arises.

We hope that the present work will lead to a reappraisal of the second factor and, therefore to a greater interest in the PMO method because, in this work, we have attempted to show that the concepts of steric and electrostatic effects, which are central to qualitative organic chemical thinking, cannot explain our results.

EXPERIMENTAL

NMR spectra were obtained using T-60(^{1}H, 60 MHz), CFT-20(^{13}C, 20 MHz) and XL-100-15(Varian, both ^{1}H 100 MHz and

Table 3. Conformational energies of substituents ($-\Delta G_X$, kcal/mole)

	F	Cl	Br	I	OCH_3
minimal	0.11 [34]	0.39 [34,35]	0.31 [34]	0.407 [34,35]	0.34 [36]
optimal	0.25 [35]	0.50 [34,35]	0.48 [34,35]	0.48 [34,37]	0.55 [34,37]
maximal	0.385 [38]	0.66 [38]	1.0 [39]	0.59 [7]	0.785 [38]

Table 4. Charges on the atoms (in electrons)*

	F	Cl	Br	I	OCH_3
maximal	-0.306[#,40]	-0.236[#,40]	-0.252[#,40]	-0.186 [41]	-0.26 [42]
optimal	-0.21 [3]	-0.17 [3]	-0.15 [3]	-0.12 [3]	-0.247 [43]
minimal	-0.20 [44]	-0.13 [44]	-0.10 [44]	-0.065 [44]	-0.202 [45]

* e_H=+0.013 if the hydrogen is antiperiplanar to halogen and e_H=+0.005 for the syn-clinal conformation [12].

\# calculated from maximal μ_{C-X} and minimal r_{C-X}.

^{13}C 25.16 MHz). The FT ^{13}C spectra were recorded using either full or partial ^{13}C-{^1H} decoupling. An impulse time of 80 mcs with an interval of 3–5 sec for XL-100-15 (90° corresponds 140 mcs) and 7–10 mcs for CFT-20 (90° corresponds 21 mcs) was used. The number of impulses was 1000–5000. The error range in the temp. measurements is ±1.5°. Concentrations of 6 mol% (molar ratio 1:16) for ^{13}CMR, 9 mol% (molar ratio 1:10) for ^{1}HMR of **1**–**3** and 6.3 mol% (molar ratio 1:15) for **4**–**6** were used. The syntheses of **1**, **8** and **10** were performed as described in the literature.[32,33] Satisfactory analytical data were obtained for all new compounds (±0.3 for C and H: ±0.4 for halogens).

General procedure for the synthesis of **4**, **5** *and* **6**

To a stirred soln of liquid HF (30 ml) ether (90 ml) at −80° were added, in portions, N-halosuccinimide (0.13 mol) and cyclohexene (0.09 mol; 0.13 mol in the case of **6**), over a period of 10 min. The mixture was stirred for 2 hr at −80° and 2 hr at 0° and then poured carefully onto ice-cold $NaHCO_3$ and extracted with ether. The ether was washed with water (and, in the case of **6**, also with 2% thiosulfate), dried, and evaporated. The products were isolated by distillation with the following results: **4**, 26% yield, b.p. 43–44°/9 mm, n_D^{20} 1.4516 (after additional purification by chromatography on $Al_2O_3/CHCl_3$); **5**, 45% yield, b.p. 52–53°/9 mm, n_D^{20} 1.4847; **6**, 55% yield, b.p. 69.5–70.5/9 mm, n_D^{20} 1.5332 (after additional washing with thiosulfate and redistillation with addition of 0.5 g of K_2CO_3).

1,2-trans-*Diacetoxycyclohexane*, **7**. A mixture of cyclohexene oxide (2.5 g), Ac_2O (11 g) and 1 drop of conc. H_2SO_4 was refluxed for 2.5 hr. The usual work up gave 1.5 g (30% after distillation) of **7**, b.p. 120°/12 mm, n_D^{20} 1.4492. Compound **2** was obtained by acetylation of **1** with acetyl chloride in ether; 90% yield, b.p. 74–75°/10 mm, n_D^{20} 1.4349. Compound **3** was obtained by methylation of **1** with MeI and Ag_2O, and purified by chromatography on $Al_2O_3/CHCl_3$; 71% yield, b.p. 41°/11 mm, n_D^{19} 1.4257. Compound **9** was obtained by methylation of **10** with MeI and Ag_2O; 65% yield, b.p. 67–68°/21 mm, n_D^{21} 1.4413.

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