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STERIC AND ELECTROSTATIC INTERACTIONS IN HEXACYCLIC RING SYSTEMS

THE ORIGIN OF THE BUTTRESSING EFFECT

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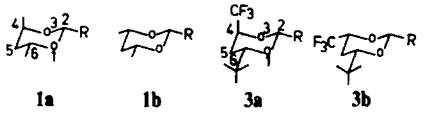
Abstract—Ring deformation in a number of 2-trichloromethyl-1,3-dioxanes could be traced in their ^1H NMR spectra from anomalies in coupling constants. No distortion occurs when the 2-substituent is a dichloromethyl or a tertiobutyl group, or when a 4-axial substituent is lacking. It was impossible to deduce the ring geometry from the vicinal coupling constants, but the nature of the ring deformation has been ascertained by NMR data ($^3J_{exo}$, $\Delta\delta$) and dipole moment calculations. Flexible conformations are not the origin of the observed anomalies. The rotomeric populations in 2-dichloromethyl-1,3-dioxanes has been evaluated and the origin of the buttressing effect, as caused by different substitution, has been disclosed.

INTRODUCTION

Most of the saturated hetero- and carbocyclic 6-membered ring systems occur in a chair form, but the precise shape (geometry) of the latter depends on the number and kind of build-in hetero atoms and on the presence of substituents. The influence of axial substituents on the ring geometry has been the subject of several studies. It is known[1,2] that mutual repulsion between two axial substituents considerably decreases ring torsional angles at the substituted side of the ring, whereas the angles increase at the opposite side (reflex effect). In most cases no appreciable torsional distorsions occur if only one axial substituent is present, but as a result of a valence-angle deformation, the *syn*-axial protons tend to bend out, and molecular-mechanics-based calculations[3] have shown that this may amount to 0·5°. If, by the presence of equatorial alkyl substituents, these *syn*-axial H atoms are tertiary, this might result in an additional destabilization[4,5] of the axial substituent. Although this effect is experimentally well documented, little is known about the nature of the resulting ring deformation. Eliel,[5] in an investigation of *r* - 2 - *p* - trifluoromethylphenyl - *trans* - 4 - *trans* - 6 - dimethyl - 1,3 - dioxane, has invoked a bending out of 20° in order to fit calculated and experimentally determined dipole moments. However these models allow no ^1H NMR study of the effect and therefore we have now investigated a series of compounds avoiding this restriction. Chart 1 depicts the selected 1,3-dioxanes. We feel it more relevant to compare the coupling constants between di- and trichloromethyl substituted compounds, rather than to interpret directly absolute values in single cases. We furthermore considered trifluoromethyl substituted 1,3-dioxanes, for the following two reasons:



R = -CCl$_3$	**1a**	**1b**	**3a**	**3b**
-CHCl$_2$	**2a**	**2b**	**4a**	**4b**
-Me	**5**			
-*t*Bu	**6**			
-φ	**7**			

Chart 1.

(i) In view of the high groupmoment of trifluoromethyl (2·03 D) we anticipate that small ring deformations will result in observable changes of the molecular dipole moment and,

(ii) the stereospecificity of ^{19}F–^1H long-range couplings[6] is possibly a criterium for tracing changes in ring geometry.

It was hoped to gain insight in the nature of this so-called buttressing effect, since as can be seen in Fig. 1, the unfavourable van der Waals interactions can arise at two sites. They will occur between H_{ax} and the Me group (**1A**) in the case of a valence angle deformation, or between H'_{ax}, H'_{eq} and the Me group, when a torsion angle is changing (**1B**).

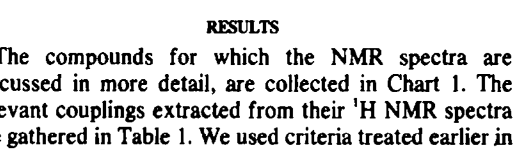


Fig. 1. Possible ring deformations due to an axial substituent and potential steric interaction sites.

RESULTS

The compounds for which the NMR spectra are discussed in more detail, are collected in Chart 1. The relevant couplings extracted from their ^1H NMR spectra are gathered in Table 1. We used criteria treated earlier in the literature,[7] in order to assign relative configurations in the different pairs of isomers. Chemical derivatizations were used to ascertain the *cis*-relation between the trichloromethyl and the 6-alkyl group in **1a**, **1b**, **3a** and **3b**. In alkaline buffered medium, the catalytic hydrogenolysis of the Cl atoms in this group proceeds with retention of configuration at the acetal centre.[8] The configuration of the 2-Me group was established by comparing the ^1H NMR spectra of the resulting reduction products with authentic samples.[7]

When we compare the vicinal couplings of **1a** with those of **2a** in Table 1, it is clear that both J(4e, 5a) and

Table 1. Coupling data in Hz[a] for compounds of Chart 1

	1a[b]	**1b**[b]	**2a**[b]	**2b**[b]	**3a**[c]	**3b**[c]	**4a**[c]	**4b**[c]	[c]**5**[e]	**6**[d]	**7**[b]
$^2J_5$	13·2	13·2	13·4	13·4	14·2	12·9	14·2	13·0	13·0	—	13·1
$^3J_{(4e,5a)}$	5·8	—	6·0	—	7·2	—	7·4	—	5·8	6·2	6·0
$^3J_{(4e,5e)}$	2·5	—	1·6	—	3·4	—	2·2	—	1·2	1·4	1·3
$^3J_{(4a,5a)}$	—	11·2	—	11·4	—	11·8	—	11·3	—	—	—
$^3J_{(4a,5e)}$	—	2·5	—	2·4	—	2·3	—	2·6	—	—	—
$^3J_{(6a,5a)}$	10·9	11·2	11·4	11·4	11·4	11·8	11·8	11·3	11·2	11·6	11·7
$^3J_{(6a,5e)}$	3·2	2·5	2·5	2·4	$3·9_5$	2·3	3·2	2·6	2·4	2·8	2·4
$^3J_{(H_4,F)}$					8·8	5·8	9·4	6·0			
$^4J_{(H_{2a},F)}$					1·2	—	1·4	—			
$^4J_{(H_{5a},F)}$					0·9	—	0·8	—			
$^5J_{(H_{6a},F)}$					1·4	—	1·6	—			
$J_{H_{2a}-H'}$			3·75	4·35			3·70	4·40			

[a] Spectra obtained at 300 MHz, 2% vol, TMS internal.
[b] CCl_4.
[c] CS_2.
[d] $CDCl_3$.
[e] D. Tavernier, Ph.D. thesis, R.U.G.-Gent, 1971.

J(6a, 5a) decrease slightly, whereas J(4e, 5e) and J(5e, 6a) increase substantially. A same trend is discerned by comparing **3a** with **4a**. Also the stereochemical-controlled H–F long-range couplings show changes up to 0·2 Hz at the moment $CHCl_2$-2 is changed for CCl_3-2 (**4a** vs **3a**). The *exo* coupling (an interesting criterium[9] to uncover the axial or equatorial nature of a substituent) is 0·6 Hz lower in **3a** than in other compounds with an axial trifluoromethyl group.[7]

Between the *cis*-, and *trans*-dichloromethyl compounds there is a systematic difference in the H_{2a}–$H_{2'}$-coupling. In the *trans* compound (the one with an axial substituent in 4-position) this coupling is always smaller, and by lowering the temperature this effect is even more pronounced (Fig. 2).

A further anomaly is the dipole moment of **3a**. The experimentally determined value is 3·25 D, whereas calculation for a typical dioxane chair predicts only 2·64 D.*

DISCUSSION

The possible presence of non-chair conformations. Two different explanations come into mind in an attempt to rationalize observed deviations between the measured and calculated dipole moment or observed anomalies in coupling constants: the molecule prefers genuine (twist-) boat conformation(s)[10] or, although the ring has become distorted, a basic chair conformation is still recognizable. This distortion however is not necessarily of a kind as one of those met in the typical forms that lay on a path for ring reversal. In order to trace the presence of any flexible or intermediate forms, we followed by calculation the course of the dipole moment during ring reversal.† By considering the C_s and C_2^2 inversion modes, we obtained all twist and boat forms lying on the pseudorotation route of the flexible forms (Figs. 3 and 4). The highest dipole value obtained is 3·10 D. We must conclude that, if flexible forms are present, they would be the sole forms present in actual compounds. This is in striking contradiction with the NMR-coupling parameters, for which the observed deviation from the typical chair values are by far too small.[11] Also NMR-shift data make a preponderent population of flexible forms for **1a** and **3a** most unlikely. When we look at the dispersion-induced deshielding of axial protons by a *syn*-axial substituent[12] (Table 2), it is obvious that, although in most cases the effect is somewhat smaller than expected, the position of the 4-trifluoromethyl and 4-Me substituent remain substantially axial in nature.

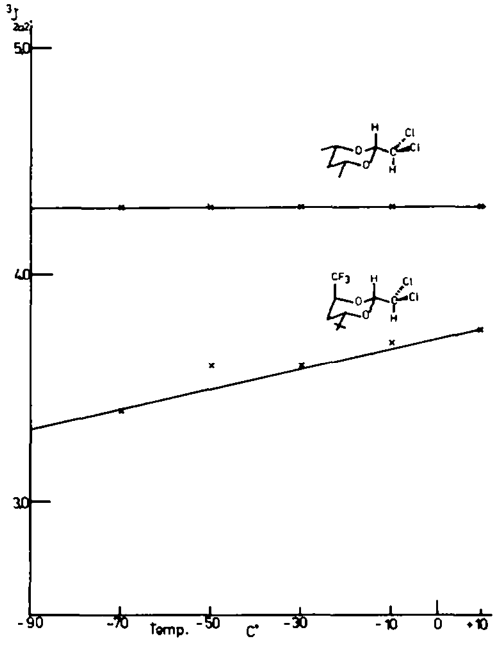


Fig. 2. Temperature dependence of $^3J_{2a2'}$.

Ring distorsion. A more detailed interpretation of the nature of the ring distorsions by the use of a Karplus-approach is in the present compounds unfeasible. In view of the strong orientational dependence of electronegative substition on the coupling constants, the situation is indeed too complex to result in a straightforward treatment. It is for instance striking that especially the

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*For more details on this calculation see Appendix 1. The atomic coordinates needed for this were based upon data obtained by X-ray diffraction on 2-*p*-chlorophenyl-1,3-dioxane.

†See Appendix 1 for the mode of calculation.

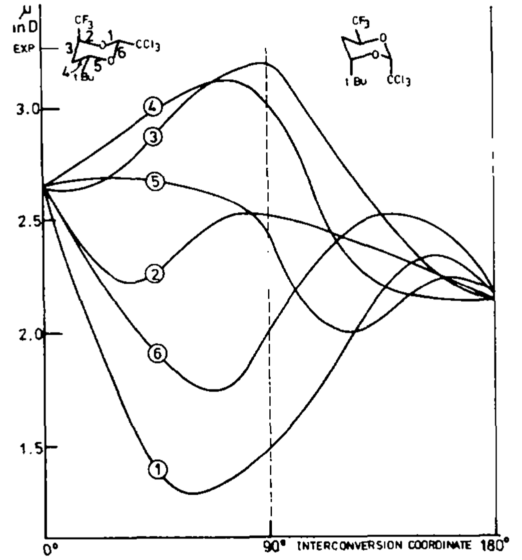

Fig. 3. The calculated dipole moment in function of the interconversion coordinate* along the C_2 route. The numbers in each graph refer to the ring torsion angle which becomes first zero. The dashed line corresponds to the twist-boat forms.

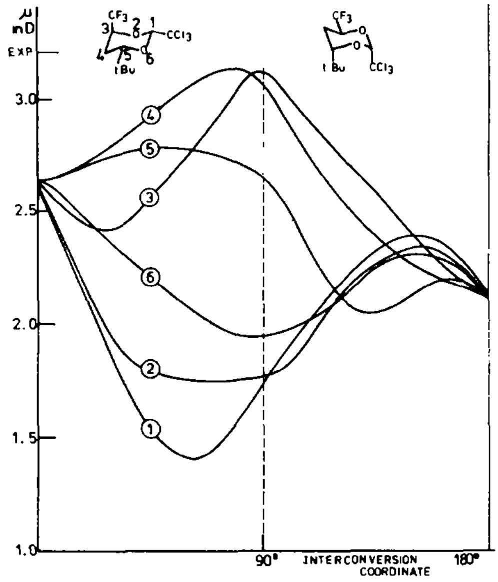

Fig. 4. The calculated dipole moment in function of the interconversion coordinate* along the C_s route. The numbers in each graph refer to the atom which equatorial substituent reaches a flagpole position. The dashed line corresponds to classical boat forms.

*H. M. Picket and H. L. Strauss, *J. Am. Chem. Soc.* **52**, 7281 (1970).

couplings with the 5e-proton seem to be affected. This could mean that a re-orientation of this proton with respect to the ring O atom (or their unshared electron pairs)[13,14] is very important. That the influence of the electronegativity of the CF_3 or CH_3 group is less important can be deduced from the parallelism **3a–4a** and **1a–2a** (Table 3).

In Table 3 we collected, together with the Δ*J*-data of **1a**, **2a**, and **3a**, **4a**, the sign of the predicted changes in coupling constants due to a re-orientation of the two O atoms with respect to the coupling protons. From the variation of the effect of the electronegativity of a substituent on the $^3J_{HH}$ constant with the orientation of that substituent relative to the interacting protons,[15] it follows however that both a flattening or a puckering of the ring would result in similar changes.

A priori two different phenomena may operate: (i) puckering of the O–C–O moiety and flattening at the opposite site of the ring, and* (ii) the reversed situation, where the O–C–O part is flattened and the carbocyclic ring fragment is puckered.

The experimental evidence points in the direction of the

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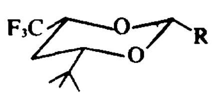
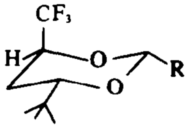
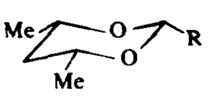
*In general a distortion at a certain part of the ring results in a reverse effect in the region opposite to the original site of distortion.[2]

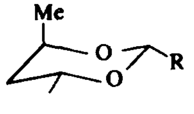
Table 2. Downfield-shift effects of axial substituents on *syn*-axial protons.





	H-2a	H-6a	H-2a	H-6a	Δδ(2a)	Δδ(6a)
R= H	4·59	3·12	4·97	3·39	0·38	0·27
CHCl₂	4·69	3·32	5·02	3·52	0·33	0·20
CCl₃	4·78	3·41	5·07	3·60	0·29	0·19





R= Me[a]	H-2a	H-6a	H-5a	H-6a		
CHCl₂	4·50	3·54	4·85	3·79	0·35	0·25
CCl₃	4·76	3·84	5·03	4·07	0·27	0·23
	4·70	3·86	4·94	4·08	0·24	0·22

[a] Value taken from ref. 12b.

Table 3. Observed and predicted changes in coupling constants.

	$\Delta J_{I_e-II_e}$	$\Delta J_{III_e-IV_e}$	Predicted signs.[15]
$\Delta J(4e, 5a)$	−0·2 Hz	−0·2 Hz	$-\Delta J$
$\Delta J(4e, 5e)$	+0·9 Hz	+1·2 Hz	$+\Delta J$
$\Delta J(6a, 5a)$	−0·5 Hz	−0·4 Hz	$-\Delta J$
$\Delta J(6a, 5e)$	+0·7 Hz	+0·8 Hz	$+\Delta J$

first possibility. In this respect, the low *exo* coupling between the fluoromethyl group and the 4e proton is important. It clearly uncovers an outwards bending of the trifluoromethyl group and therefore a flattening of the aliphatic moiety. Furthermore is the second proposition in contradiction with the dipole moment calculation of **3a**. Indeed, a flattening of the O–C–O moiety significantly lowers the resulting dipole moment, (*cf* Figs 3 and 4 species 1, 2 and 6) in conflict with the experimentally determined higher value.

Therefore it is clear that the dioxane ring is distorted in a way that the trifluoromethyl group is bending out, while the O_1–C_2 and C_2–O_3 torsional angles increase, in agreement with the calculated and measured dipole moments.* It follows from Fig. 5 that puckering of the O–C–O moiety is in that respect especially effective.

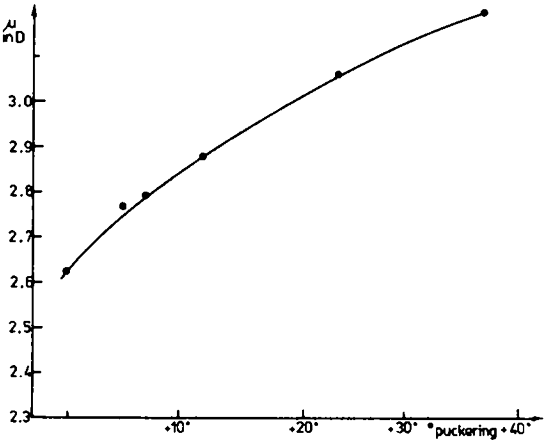


Fig. 5. Influence of ring puckering in the O–C′–O moiety on the molecular dipole moments.

Further proof for the flattening of the carbocyclic moiety are the Δδ data of Table 2. It is known that deshielding increases with increasing van der Waals interaction.[17] The decrease in Δδ is thus the result of a net increase of the interatomic distance of the relevant protons, caused by a pronounced flattening of that part of the ring.

We conclude that large equatorial substituents induce local ring distorsion and the *syn*-axial substituents in γ position are especially effective for the transmission of this distortion to the opposite part of the ring.

The rotameric distribution of the dichloromethyl group in 2-dichloromethyl-1,3-dioxanes. In order to investigate the Cl–O interaction in 2-dichloromethyl-1,3-dioxanes, an analysis of the rotameric population of this group is rewarding. The rather low value for J(2a, 2′) suggest a significant contribution of the H-"up" rotamer. As a rough approximation we may interpolate this coupling value between J_{anti} and J_{skew} measured in 1,1,2,2-tetrachloroethane, respectively 10·5 and 2·2 Hz.[20,21]

This results in 73% of **a** in the *cis*-4,6-disubstituted compounds and 82% of **a** in the *trans*-substituted ones. Since the hydrogen "up" conformation is entropically stabilized for 0·40 kcal.mol^{-1} at room temperature this result in a small ethalpic difference between a chlorine "up" and "down" in **2b** and **4b**. This conclusion is corroborated by the temperature independence of J(2a, 2′) in these compounds (Fig. 2). It is also known[21] that in 1,1,2,2-tetrachloroethane the difference in enthalpy between the two rotamers is small in apolar media. This is in agreement with some empirical rules formulated by Wolfe *et al.*[22]

Changing the 4-substituent from an equatorial to an axial position results in a decreased value for J(2a, 2′) and in a strong temperature dependency of this coupling (Fig. 2). Therefore we find an increased population of rotamer a in *trans*-4,6-disubstituted compounds. There may be two explanations† for this favouring of **a**:

(i) The 4-axial substituent bends the 2-hydrogen outwards, increasing the van der Waals strain between this hydrogen and the Cl atom. (Fig. 1A)

(ii) A flattening of the O–C–O part of the ring increases the oxygen p-lobe chlorine "up" repulsion more than the p-lobe chlorine "down" interaction. (*Cf.* Fig. 1B)

Origin of the buttressing effect. This is reduced to a choice between the two explanations given for the observed changes of the rotameric populations in the 2-dichloromethyl-1,3-dioxanes.

Comparison of the ^{1}H coupling constants between *r* - 2 - *trans* - 4 - *cis* - 6 - trimethyl - 1,3 - dioxane and the corresponding 2-tertiobutyl derivative reveals that they are almost identical. Therefore it can be concluded that even in 2-tertiobutyl substituted 1,3-dioxanes no perceptible deformation occurs‡ when a 4-axial Me group is present. This demonstrates that if no repulsive interaction between the equatorial substituent and the ring occurs, there is no buttressing effect. We therefore conclude that the occurence of a buttressing effect in cyclohexane is closely related to these substituent-vicinal-ring-hydrogens repulsive interactions. In tertiobutylcyclohexane this results in a rotation of the tertiobutyl Me groups out of the perfectly staggered conformation (17°).[16]

When introducing Cl atoms instead of Me groups on the α-carbon of 2-substituted dioxanes, an electrostatic repulsion is created between the Cl atoms and the oxygen lone pairs, and the buttressing effect becomes again important. The only way to escape this strain is puckering of that part of the ring. That the interaction between the geminal hydrogen and the equatorial substituent is less important is shown by the fact that the van der Waals non-bonded radius of a Me group is 0·2 Å greater than that of a Cl atom.[26]

In the present context we have also looked at the

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*Our observations make a puckering in the C_1 part of tertiobutylcyclohexane reasonable. From ^{1}H NMR studies of deuterated derivatives and using a Karplus equation no clear-cut distinction could be made, since both puckering[16,18] and flattening[19] have been proposed.

†An alternative explanation, in which a difference in a solvation would stabilize the most polar rotamer at lower temperature,[23] is ruled out because in the *cis*-isomers the coupling constant $^3J^{exo}$ is temperature independent. (The dipole moment differences between "up" and "down" conformations are in both isomers comparable).

‡Earlier studies have shown that 2-tertiobutyl-dioxanes are not distorted,[24] even when further equatorial methyl groups are present.[25]

aptitude of a 2-phenyl group in causing buttressing effects. No deviations of the vicinal coupling constants could be traced in the C–C–C part of *r* - 2 - phenyl - *trans* - 4 - *cis* - 6 - dimethyl - 1,3 - dioxane. This corroborates data gathered from four component equilibria studies of 2-phenyl substituted 1,3-dioxanes.[27]

EXPERIMENTAL

1,1,1-*Trifluoro-5,5-dimethyl-2,4-hexanediol.* The preparation starting from ethyl trifluoroacetate and pinacolone has been given,[32] yield 60%. IR (heat):
3450(vs), 1240(s), 1180(s), 1160(s), 1050(s) cm^{-1}; NMR (60 MHz, $CDCl_3$): δ = 3·30(m, 1H), 4·17(m, 1H), 1·8(m, 2H), 0·9(s, 9H).

1,1,1-*Trifluoro-5,5-dimethyl-2,4-hexanedione*: IR (neat): 1660(s), 1610(m), 1140(m), 1200(m), 1380(m) cm^{-1}; NMR (60 MHz, CCl_4): δ = 5·94 (s, 1H), 14·5(s, 1H), 1·20(s, 9H).

r - 2 - *Trichloromethyl* - trans - 4 - *trifluoromethyl* - cis - 6 - *teriobutyl* - 1,3 - *dioxane* (**3a**) *and* r - 2 - *trichloromethyl* - cis - 4 - *trifluoromethyl* - cis - 6 - *tertiobutyl* - 1,3 - *dioxane* (**3b**). The ring closures were carried out as described.[33] A mixture of 5·52 g (0·02 mole) diol, 3·8 g (0·02 mole) freshly distilled chloral and 2·5 ml conc. H_2SO_4 were heated slowly up to 70° and kept for a further 2 hr at this temp. After the mixture was cooled to room temp it was poured onto ice and extracted with chloroform (3 × 10 ml). The chloroform layer was washed ($NaHCO_{3ab}$) dried, evaporated and distilled (b.p. 150°/12 mmHg). Only two diastereomeric dioxanes were formed and separation by preparative GlC (20 m 5% QF_1 on Chromosorb G (45/60 mesh, 290°) afforded analytically pure **3a** and **3b**.

Compound **3a**: IR (neat, cm^{-1}): 680(m), 810(s), 900(m), 1100(s), 1140–1230(s), 1350(m), 1400(m); NMR (300 MHz, CS_2): δ = 5·05(s, 1H), 4·45(m, 1H), 2·04(m, 1H), 1·78(m, 1H), 3·60(m, 1H), 0·97(s, 9H); (Found: C, 35·98; H, 4·32. Calc. for $C_{10}H_{14}O_2F_3Cl_3$: C, 36·44, H, 4·28%).

Compound **3b**: IR (neat, cm^{-1}): 660(m), 800(m), 890(m), 1020(m), 1040(m), 1090(s),1120–1220(s), 1290(s), 1390(s); NMR (300 MHz, CS_2): δ = 4·78(s, 1H), 4·09(m, 1H), 1·70(m, 1H), 1·64(m, 1H), 3·41(m, 1H), 0·98(s, 9H); (Found: C, 36·20, H, 4·22. Calc: *cf.* **3a**.)

r - 2 - *Dichloromethyl* - trans - 4 - *trifluoromethyl* - cis - 6 - *tertiobutyl* - 1,3 - *dioxane* (**4a**) *and* r - 2 - *dichloromethyl* - cis - 4 - *trifluoromethyl* - cis - 6 - *tertiobutyl* - 1,3 - *dioxane* (**4b**). The two isomeric products **4a** and **4b** were obtained by selective hydrogenolysis of **3a** and **3b** on a contaminated carbowax GLC column, using hydrogen as eluent. Subsequent purification was carried out on a QF_1 column:

4a NMR (300 MHz, CS_2): δ = 5·02(d, 1H), 5·42(d, 1H), 4·32(m, 1H), 2·0(m, 1H), 1·73(m, 1H), 3·42(m, 1H), 0·94(s, 9H); (Found: C, 40·97; H, 5·14. Calc. for $C_{10}H_{15}O_2F_3Cl_2$: C, 40·69, H, 5·12%).

4b NMR (300 MHz, CS_2): δ = 4·69(d, 1H), 5·47(d, 1H, 4·0(m, 1H), 1·64(m, 1H), 1·61(m, 1H), 3·32(m, 1H), 0·95(s, 9H); (Found C, 10·75, H, 5·15. Calc.: see **4a**.)

2-*Trichloro-, and* 2 - *dichloromethyl* - 4,6 - *dimethyl* - 1,3 - *dioxanes.* A crude mixture of diastereomeric *erythro*-; and *threo*-2,4-pentanediols, (yield 90%, from Ra–Ni 7W-reduction of acetylacetone) was treated with chloral as described above. The mixture of dioxanes (90°/12 mmHg, yield 30%) were separated by preparative GLC (QF_1).

Compound **1a**. NMR (300 MHz, CCl_4): δ = 4·94(s, 1H), 4·45(m, 1H), 4·08(m, 1H), 1·90(m, 1H), 1·41(m, 1H), 1·40(d, 3H), 1·31(d, 3H); (Found: C, 35·56, H, 4·79. Calc. for $C_7H_{11}O_2Cl_3$: C, 36·00, H, 4·75%).

Compound **1b**. NMR (300 MHz, CCl_4): δ = 4·70(s, 1H), 3·86(m, 2H), 1·53(m, 1H), 1·35(m, 1H), 1·31(d, 3H): (Found: C, 35·77, H, 4·73. Calc.: see **1a**).

The dichloromethyl derivatives were obtained by GLC on Carbowaxcolumn. Purification yielded analytically pure **2a** and **2b**.

Compound **2a**. NMR (300 MHz, $CDCl_3$): δ = 5·33(d, 1H), 5·03(d, 1H), 4·44(m, 1H), 4·07(m, 1H). 1·87m, 1H), 1·39(d, 4H), 1·27(d, 3H): (Found: C, 38·92, H, 6·56. Calc. for $C_7H_{12}O_2Cl_2$: C, 38·80, H, 6·42%).

Compound **2b**. NMR (300 MHz, $CDCl_3$): δ = 5·56(d, 1H), 4·76(d, 1H), 3·84(m, 2H), 1·56(m, 1H), 1·32(m, 1H), 1·20(d, 6H): (Found C, 38·97, H, 6·39. Calc.: see **2a**). .

r - 2 - *Methyl* - *trans* - 4 - *trifluoromethyl* - *cis* - 6 - *tertiobutyl* - 1,3 - *dioxane.* This product was obtained by hydrogenolysis of the corresponding **3a** as described.[8] A soln of 1·2 g (0·0037 mole) of **3a** in 35 ml EtOH was mixed with a soln of $NaHCO_3$ 1·2 g (0·0088 mole) in 25 ml water and hydrogenated over 0·3 g of 5% Pd/C under an initial pressure of 2·8 kg/cm^2. After 2 hr, the mixture was filtered and the filtrate worked up in the usual manner. Distillation (175°/12 mm Hg) afforded in 70% yield the 2-methyl derivative.[7] NMR: (60 MHz, $CDCl_3$): δ = 5·00(q, 1H), 4·43(m, 1H), 3·55(m, 1H), 1·90(m, 2H), 1·20(d, 3H), 0·98(s, 9H).

r - 2 - *Methyl* - cis - 4 - *trifluoromethyl* - cis - 6 - *tertiobutyl* - 1,3 - *dioxane.* The same procedure as applied above was used to convert the trichloromethyl group in a Me group in **3b**.[7] NMR (60 MHz, $CDCl_3$): δ = 4·79(q, 1H), 4·08(m, 1H), 3·34(m, 1H) 1·64(m, 2H), 1·32(d, 3H), 0·98(s, 9H).

r - 2 - *Tertiobutyl-, and* r - 2 - *phenyl* - trans - 4 - cis - 6 - *dimethyl* - 1,3 - *dioxane* (6 *and* 7). These two dioxanes were obtained by treatment of 2,4-pentanediol under acidic conditions (*p*-toluenesulfonic acid) in benzene with an excess of pivaldehyde or benzaldehyde, followed by continuous removal (Dean Stark trap) of the water formed. After the theoretical amount of water has been obtained, the mixture was treated with $NaHCO_3$, filtered and fractionated. The spectral features of the pure isomers (GLC, QF_1) agree with those published for similar compounds.[12b]

Compound 6. NMR (100 MHz, $CDCl_3$): δ = 4·30(s, 1H), 4·27(m, 1H), 3·85(m, 1H), 1·75(m, 1H), 1·31(d, 3H), 1·27(m, 1H), 1·16(d, 3H), 0·87(s, 9H).

Compound 2. NMR (300 MHz, $CDCl_3$): δ = 7·35(m, 2H), 7·33(m, 3H), 5·66(s, 1H), 4·32(m, 1H), 4·07(s, 1H), 1·95(s, 1H), 1·42(d, 3H), 1·34(s, 1H), 1·23(d, 3H).

Dipole moments of **3a** were measured[39] with a WTW instrument DMO 1, equipped with a DFL-2 cel. Benzene was used as the solvent and the temp was 25·0°.

The calculations of the theoretical dipole moments (see Appendix 1) were carried out on a Siemens 4004 computer system at the "Centraal Digitaal Rekencentrum" of the State University of Gent (Director Ir. C. Lagrain).

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APPENDIX 1

Calculation of the molecular dipole moments[28]

The molecular electrical dipole moments are calculated by summation of the contributing bond moments having the following values: C–O 0·9D[29]; H–C 0·3D[29]; C–CF_3 2·03D[30]; C-CCl_3 1·27D[30].

We derived the atomic coordinates, by transformation of these from the internal molecular coordinates (bond lengths, valence angles, torsional angles). For a non-deformed chair we used the basic dioxane skeleton as determined by X-ray diffraction analysis of 2-*p*. chlorophenyl-1,3-dioxane.[31] (d: O1–C2 1·41, O3–C4 1·44, C4–C5 1·50 Å; valence angles: $\hat{O}1$: 111°, $\hat{C}2$: 111°, $\hat{C}4$: 109·5°, $\hat{C}5$: 108°: torsional angles: CO–CO: 63°, CO–CC: 59°, OC–CC: 55°)

To simulate the ring inversions we wrote a computer program allowing continuous variation of the ring torsional angles, as follows.

(a) *The* C_2-*inversion mode*[2]. During C_2-inversion of a symmetric ring compound, all intermediates possess this C_2-symmetry. In going from the chair to the twist conformation, the ring passes through the half-chair and 1,3-diplanar forms (and *vice versa* in reversed order, ending up with the reversed chair). In order to simulate the entire process, we expressed the changes of the different ring torsional angles as a function of the changes of one typical torsional angle, e.g. the one which is the first to become zero starting from the chair. This implicates the following transformation-equations:

$$\begin{array}{ll} T1 \Rightarrow T1 + \Delta T & T4 \Rightarrow T4 + 0{\cdot}12\,\Delta T \\ T2 \Rightarrow T2 - 0{\cdot}65\,\Delta T & T5 \Rightarrow T5 + 0{\cdot}10\,\Delta T \\ T3 \Rightarrow T3 + 0{\cdot}10\,\Delta T & T6 \Rightarrow T6 - 0{\cdot}65\,\Delta T \end{array}$$

The parameters in this equations were computed in such a way, that they reproduce as good as possible the (idealized) geometries (chair, half-chair, 1,3-diplanar and twist-boat[2]) of the intermediate conformations. The sign of ΔT depends on the sign of T1.

(b) *The* C_s-*inversion mode*. During this inversion mode, a plane of symmetry is retained for symmetric ring compounds. The intermediate forms involved, are the 1,2-diplanar and the boat form. The analogous transformation-equations become now:

$$\begin{array}{ll} T1 \Rightarrow T1 + \Delta T & T4 \Rightarrow T4 - 0{\cdot}02\,\Delta T \\ T2 \Rightarrow T2 - 0{\cdot}5\,\Delta T & T5 \Rightarrow T5 + 0{\cdot}5\,\Delta T \\ T3 \Rightarrow T3 + 0{\cdot}2\,\Delta T & T6 \Rightarrow T6 - \Delta T. \end{array}$$

They are again parameterized in order to generate the idealized intermediates.