Tetrahedron Vol. 35, pp. 691–695
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0040–4020/79/0301–0691/$02.00/0

EFFECTS OF METHYL GROUPS ON THE GEOMETRY AND CONFORMATIONAL EQUILIBRIUM OF 1,3-DIOXANES

ULRICH BURKERT*
Fachbereich Chemie der Universität Konstanz, Postfach 7733, D-7750 Konstanz, West Germany

(*Received in UK* 4 *September* 1978)

Abstract—The geometries and energies of polymethyl-1,3-dioxanes were studied by molecular mechanics calculations. Buttressing effects of the Me groups are discussed. The chair/twist conformational equilibrium of 1,3-dioxanes having two syn-axial Me groups in the chair were calculated, and a twist form (the 1,4-twist) is found to be more stable than the chair only for **9** and **14**, chair and 2,5-twist form are of comparable energies for **10** and **13**, and the chair is considerably favored in **11** and **12**. The chair/1,4-twist energy difference of **1** was calculated to be only 16.4 kJ mol^{-1}. Ring inversion of **1** goes through a transition state with C–C–C–O coplanar with a calculated activation enthalpy of 28.3 kJ mol^{-1}.

In conformational analysis of 1,3-dioxanes methods like acid-catalyzed equilibration of diastereomers, heat of combustion measurements, and the analysis of chemical shifts and (geminal and vicinal) coupling constants observed in ^{1}H and ^{13}C NMR spectra have been employed extensively.[1] When applied to simple 1,3-dioxanes, the equilibration method provided data about conformational free energies (A values)[2] of substituents at the three possible positions, and by the first order method of conformational energy calculations, in which transferability of interaction increments is assumed, these A values were used to calculate equilibrium constants in more highly substituted 1,3-dioxanes. Heat of formation measurements complement the equilibration approach in the determination of conformational enthalpies. Differences between calculated and experimental relative energies were explained qualitatively, discussing deformations of the 1,3-dioxane ring, but also postulating non-chair conformations to be preferred whenever syn-axial Me/Me interactions would occur in the chair form.[3] The values of vicinal coupling constant in the CCC part of the ring also were interpreted on these grounds, assuming buttressing effects of alkyl substituents on ring hydrogen atoms,[4] and non-chair conformations for molecules exhibiting 1,3-synaxial Me group interactions in the chair form.[5–7]

Just as the method of interaction increment addition, ball-and-stick type molecular models are a first order approach to conformational analysis. There is no doubt that such models give a very rough approximation of the geometry of a 1,3-dioxane even without alkyl substituents, for one because the models assume ideal tetrahedral bond angles, although these are known to be usually larger for CCC and OCO, and often also CCO angles. This effects that the 1,3-dioxane ring, like cyclohexane,[8] is flatter than the model would indicate. The model also does not account for steric interactions, and one can only make qualitative estimates of the geometry changes, and no estimate at all about the energy changes following these, when strong repulsions occur. These non-ideal bond angles and molecular relaxations are the reason why transferability of interaction increments is usually non fulfilled, or at least restricted to closely related molecules. A much better model is available in molecular mechanics calculations.[9] The energy minimization procedure does all the molecular relaxation, and with a properly parameterized force field one can get good agreement of calculated and experimental geometries and energies. We have developed a force field for ethers, which we have applied in this study to polymethyl - 1,3 - dioxanes, especially looking at subtle geometry changes due to buttressing effects, and the existence of non-chair conformations.

Method. The force field has been described in detail elsewhere.[10,11] The hydrocarbon parameters are those of Allinger (1973 force field).[12] Electrostatic interactions are included as charge interactions between charges calculated by the CNDO/2 method. A weak van der Waals potential for lone pairs is employed, 1,4-interactions of lone pairs are excluded.[10] For the CCOC torsional potential a function

$$V_{tor} = \frac{1}{2}V_1(1+\cos\omega) + \frac{1}{2}V_3(1+\cos 3\omega)$$

with $V_1 = 1.70$ kcal mol^{-1} and $V_3 = 0.66$ kcal mol^{-1} is used for all torsion angles between 0° and 180°,[11] for the other torsion angles the procedure described before is followed.[10,12] The calculations were performed with a modified version of Allinger's program, with full optimization of geometries.

Buttressing phenomena. A recent electron diffraction study shows 1,3-dioxane **1** to be flattened as compared to the idealized geometry (torsion angles: $\omega_{COCO} = 58.9°$, $\omega_{COCC} = 56.0°$, $\omega_{CCCO} = 57.4°$),[13] but less than cyclohexane (54.6°).[8] Our calculation agrees with this result in the CCC part of the ring, but it indicates a stronger pucker in the OCO part also found in several derivatives.[10] The ring flattening has the effect that the axial H atoms on C-4 and C-6 are turned out from the ring, which decreases the HCCH anti torsion angle to 173°, while the torsion angle between the equatorial H atoms grows (Fig. 1). The vicinal anti ^{1}H NMR coupling in **1** was determined to be 12.4 Hz, the ordering of the gauche coupling constants ($J_{4e,5e} = 1.2$ Hz, $J_{4a5e} = 2.3$ Hz, $J_{4e,5a} = 4.9$ Hz)[1] agrees with that expected from the calculated torsion angles with a Karplus type relationship.

Distortions of the cyclohexane ring by Me and t-Bu substituents has been studied by means of molecular mechanics with several force fields,[14–16] and the results

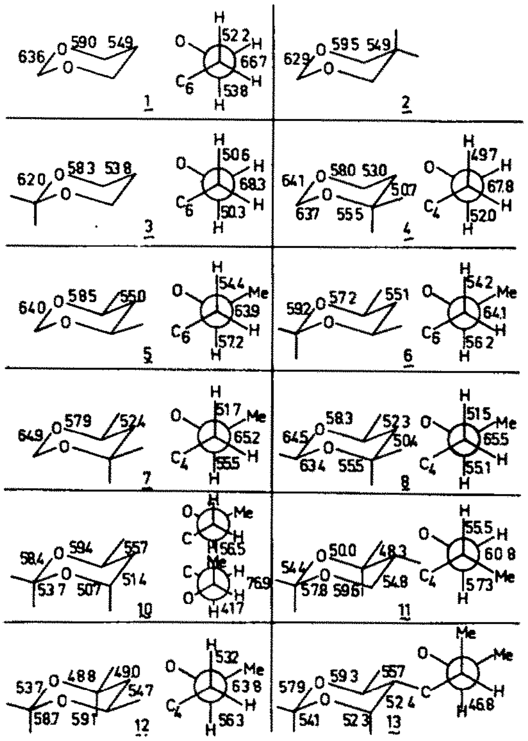


Fig. 1. Ring torsion angles and exocyclic torsion angles in the CCC region of 1,3-dioxane chair conformations.

are in most cases in good agreement with experimental data from electron diffraction and X-ray crystallographic studies. Thus, 1,1-dimethylcyclohexane exhibits a further flattening of the ring region around the sterically hindered quaternary carbon. The endocyclic CCC bond angle at this carbon decreases to roughly the tetrahedral value (109.9°).[14] Because of the buttressing equatorial Me group the repulsion of the axial Me group by the synaxial hydrogen atoms cannot be relieved by bending the axial Me group out from the ring. The only possibility for the minimization of transannular strain is a considerable flattening of the ring.

We calculated that geminal dimethylation at C-2, C-4 or C-5 of 1,3-dioxanes leads to a decrease of the endocyclic bond angle at the quaternary atom of 2°, and has some effect on the ring torsion angles. In **2** the ring is only slightly flatter in the OCO region than in **1**, while the rest of the ring remains as in **1**. Disubstitution at C-2 or C-4 effects flattening of the whole ring (**3** and **4**), in **4** the ring is flattened especially strong at the site of substitution. This flattening around the quaternary carbon is not observed in **2**, because transannular van der Waals repulsions of the axial Me groups are less severe there because of the lacking axial hydrogens. The axial H atoms in the CCC part of **3** and **4** tilt out from the ring not only because of the ring flattening, but also because of the repulsion with the syn-axial Me group, which is documented by the HCH bond angle on C-4 (C-6), which decreases from 107.0° in **1** to 105.4° in **3** and 105.7° in **4**.

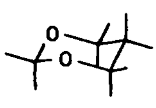
Me groups at the 4- and 6-positions of 1,3-dioxane have been used as anchor groups to study the conformational free energies of substituents at C-2, but Eliel has pointed out that the Me groups buttress their *iso* hydrogens into the ring, thus increasing the repulsion of the axial substituents at C-2 and causing an overestimation of conformational free energies determined this way.[4] This buttressing is also found in X-ray structures of 2 - aryl - *r* - 4,*c* - 6 - *dimethyl* - 1,3 - dioxanes,[17] and in our calculated structures of these molecules.[10] The decrease of the anti-coupling constant J_{4a5a} to 9.5–10.0 Hz[7,18] and the increase of the gauche coupling J_{4a5e} to 3.1–3.6 Hz has also been ascribed to this effect,[4] our calculated structure of *cis* - 4,6 - dimethyl - 1,3 - dioxane **5** can however not substantiate this belief. The ring torsion angles are hardly changed at all as compared to **1**, the axial protons on C-4 and C-6 are buttressed in over the ring, but instead of *de*creasing the anti-torsion angle, this brings it closer to 180°, compensating for the ring flattening in **1**. On the other side the gauche HCCH torsion angle to the equatorial hydrogen on C-5 is *in*creased by 3.4°. A buttressing of the hydrogens on C-5 by the Me groups is not observed, they retain their bond angle of 107.7° also found in **1**, and their torsion angles to the ring atoms. The geometry variations upon introduction of the Me groups at C-4 and C-6 can therefore not account for the changes in the coupling constants relative to **1**.

For *cis*-2,2,4,6-tetramethyl-1,3-dioxane **6** Eliel *et al.* have suggested a repulsion of the axial protons on C-4 and C-6 by the axial C-2 Me group, which roughly balances the buttressing due to the equatorial Me groups.[4] This is exactly what we find in the calculated structure, the HCCH anti-torsion angle is 1.0° smaller, while the torsion angle between the equatorial and the axial hydrogen is 0.7° larger than in **6**. The anti-coupling is increased to 10.6 Hz, and the gauche coupling decreased to 3.1 Hz, as compared to **5**, which like in the preceding case is the opposite from what is expected from a Karplus type relation. The same happens in 4,4,6 - trimethyl - 1,3 - dioxane **7**, where the axial Me group on C-4 repells the axial hydrogen on C-6. The torsion angles of **6** and **7** are very similar, as are the coupling constants (10.5–11.7 Hz/3.2–2.6 Hz).[4,7]

An additional equatorial Me group at C-2 of **7** has, according to the calculations, no effect on the torsion angles (**8**). This is contrary to a proposition[4] that the equatorial C-2 Me group would buttress the axial C-4 Me, and increase the repulsion of the axial C-6 hydrogen from the axial 4-Me, which has been made to explain an unusual, small anti-coupling of 8.5 Hz and a gauche coupling of 6.1 Hz determined by these authors.[4] In an earlier study more usual coupling constants of 11.2 and 2.6 Hz had been reported,[7] which are in agreement with our result that no major changes of the geometry will occur which are due to such a transannular buttressing.

Chair-twist equilibria. The ^{1}H NMR coupling constants of *trans* - 2,4,4,6 - tetramethyl - 1,3 - dioxane **9**, which have been reported to exhibit a strong temperature dependency (9.3/5.3 Hz at −83.5° and 7.8/6.8 Hz at 39° in CS_2 solution),[5] indicate an anti-arrangement of two coupled protons. The temperature dependency caused Nader and Eliel[5] to suggest an equilibrium either of a chair with an axial 2-Me group and a twist conformation, or of different twist conformations. Pihlaja *et al.*[19] reported for the same compound couplings of 11.8 and 4.4 Hz from a second order analysis of the spectrum at 33.5° in CCl_4 solution. Ruling out the chair with the C-2 Me in the axial position on energetic grounds, and the other chair because of the large coupling constant, they concluded that **9** exists in the 1,4-twist form exclusively.[19]

The calculation agrees fully with this interpretation of the NMR results, the most stable conformation is the



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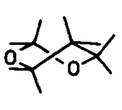
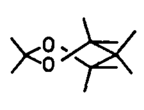


1,4-T



2,5-T

proposed[19] 1,4-twist, with energies of 7.18 kJ mol^{-1} for the chair with an equatorial C-2 Me group, and 10.45 kJ mol^{-1} for the other chair form. The 2,5-twist form was calculated to have an energy of 13.73 kJ mol^{-1}, which rules it out as a major contributor to the equilibrium, and also sets a lower limit to the pseudorotation barrier of the twist forms. The chemical equilibrium of **9** and its *cis* isomer was reported to be so much on the side of the *cis* form that by glc no *trans*-isomer could be detected in the equilibrium mixture, and a lower limit of 22.8 kJ mol^{-1} for the Gibbs energy difference was suggested.[5] According to a microcalorimetric study of the BF_3 catalyzed equilibration the enthalpy difference is 24.1 kJ mol^{-1}.[21] Our calculated value for this energy difference is only 12.9 kJ mol^{-1}, only slightly more than half the experimental value. Probably the *cis*-isomer was calculated too unstable, but the reason for this is at the moment unclear. This point is under further study, both on the theoretical and experimental side.

An important argument in favor of twist conformations for 1,3-dioxanes with two axial Me groups in the chair was the failure to freeze out a conformational process in the NMR spectrum of such compounds, but Friebolin has shown[22] that axial Me groups at C-2 or C-4 decrease the ring inversion barrier of 1,3-dioxanes by about 8 kJ mol^{-1} and 5.4 kJ mol^{-1}, respectively. For 4,4,6,6 - tetramethyl - 1,3 - dioxane he reports a signal broadening at −150°, which would be consistent with chair conformations inverting with a barrier of $\Delta G^{\neq} <$ 30 kJ mol^{-1}.[22]

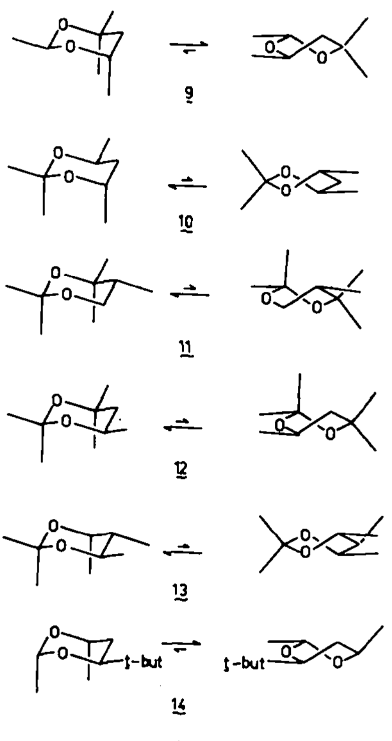


Fig. 2. Chair-twist equilibria in 1,3-dioxanes.

The ^1H NMR spectrum of *trans* - 2,2,4,6 - tetramethyl - 1,3 - dioxane **10** does not show any temperature dependency down to −50°,[19] and this, together with the coupling constants of 7.4 Hz for both the *trans*- and *cis*-couplings has been interpreted as an indication of a 2,5-twist form as the prevailing conformation.[19] Our calculation prefers however the chair form by 0.79 kJ mol^{-1} over the 2,5-twist, which is the only non-chair energy minimum. The calculated equilibrium with 42% twist form and 58% chair is in full agreement with the ^1H NMR coupling constants. In the highly deformed chair the coupling constants are of course much different from those in **1**. The ring is considerably flatter in the OCO part of the ring than an analog lacking the axial 2-Me group, **8**. The repulsion of the axial Me groups buttresses the equatorial *iso*-hydrogen and alters its torsion angles to the hydrogens on C-5 by more than 10° as compared to **1**, whereas the torsion angles of the C-5 hydrogens to the other *iso*-hydrogens are fairly close to those in **1**. From the torsion angles calculated for **6** and the corresponding observed coupling constants a Karplus type equation would follow

$$^3J = 11.1 \cos^2 \omega + 0.61 \text{ Hz}.$$

The coupling constants expected from this equation for the rapidly inverting chairs are

$$J_{trans} = (J_{aa} + J_{ee})/2 = (J_{174^\circ} + J_{77^\circ})/2 = 6.3 \text{ Hz}$$

and

$$J_{cis} = (J_{ae} + J_{ea})/2 = (J_{56^\circ} + J_{42^\circ})/2 = 5.3 \text{ Hz},$$

for the 2,5-twist form the expected couplings are

$$J_{trans} = J_{33^\circ} = 8.3 \text{ Hz}$$

and

$$J_{cis} = J_{150^\circ} = 8.8 \text{ Hz}.$$

With this admittedly simplistic approach one would expect an equilibrium with 33% twist and 66% chair form.

The enthalpy difference between **10** and its *cis*-isomer is calculated to be 20.9 kJ mol^{-1}, which is in moderate agreement with Pihlaja's experimental values of 13.9 kJ mol^{-1} [20] and 12.65 ± 6.6 kJ mol^{-1} [23] from heat of combustion measurements. Note that heats of vaporization had been estimated only by Pihlaja, which brings our result within experimental error of his measurements. The deviation is also in the other direction than in the case of **9**, where the calorimetric data had indicated a larger than calculated enthalpy difference of *cis*- and *trans*-isomer.

The conformations of 2,2,4,4,5 - pentamethyl - 1,3 - dioxane **11** and 2,2,4,4,6 - pentamethyl - 1,3 - dioxane **12** cannot be elucidated from the ^1H NMR coupling constants, because these (10.3 Hz/4.9 Hz for **11** and 10.9 Hz/2.5 Hz for **12**)[19] fit a deformed chair conformation with an equatorial Me group and a 2,5-twist form equally well. For both molecules the calculation favors the chair form considerably, for **11** by 12.1 kJ mol^{-1}, for **12** by 14.2 kJ mol^{-1}, over the 2,5-twist, and only slightly more over the 1,4-twist. It appears that the second geminal Me grouping, which introduces a bulky group into a pseudoaxial position of the twist forms, destabilizes these forms sufficiently to make the chair the highly favored conformation. On the other hand, in 2,2,*r* - 4,5,*t* - 6 - pentamethyl - 1,3 - dioxane **13** the equilibrium between the chair and twist conformations is balanced; the 2,5-twist form is only 0.7 kJ mol^{-1} less stable than the chair with an equatorial 5-Me group. The 1,4-twist is a high energy conformation with 12.8 kJ mol^{-1}. The ^{1}H NMR coupling constants (7.8 and 5.3 Hz)[19] are in agreement with such an equilibrium.

For *r*-2,*c* - 6 - dimethyl - *t* - 4 - t - butyl - 1,3 - dioxane **14** the preference for the 2,5-twist conformation was proposed by Tavernier and Anteunis[24] to explain the sum of the observed coupling constants. The 1,4-twist form with the t-Bu group in a pseudoequatorial position is however calculated to be more stable than the 2,5-twist, and 10.7 kJ mol^{-1} more stable than the most stable chair. The 1,4-twist form can very well explain the large difference between the coupling constants on the t-Bu side (10.3 and 5.7 Hz) and the Me side (7.5 and 6.4 Hz)[24] of the 1,3-dioxane ring.

Some general rules evolve for the conformations of polymethyl 1,3-dioxanes. A non-chair conformation is favored if a 1,3-synaxial Me/Me interaction occurs in the most stable chair, the twist form is the 1,4-twist conformation, *and* if no Me group is in a pseudoaxial position in the 1,4-twist. Geminal Me groups will prefer the bisectional position; if this is possible only in the 2,5-twist form, the chair and twist forms are of comparable energies. If a Me group must adopt a pseudoaxial position in the twist form, the chair form predominates in the equilibrium.

Other arguments in favor of twist conformations (the ^{13}C and ^{1}H chemical shift,[7,25] and the sum of vicinal coupling constants,[19,24] and others[3]) are not very convincing because the strong van der Waals repulsions and bond angle deformations in the chair forms have complex effects on these quantities. In fact the chemical shifts and coupling constants observed for 2 - (4 - bromophenyl) - *r* - 2,4,4,*c* - 6 - tetramethyl - 1,3 - dioxane, which exists as a deformed chair in the crystal,[26] agree well with those of **12**, confirming the chair conformation of **12**, and the validity of our conclusions.

Chair-twist conformational energy difference and ring inversion in 1,3-*dioxane*. Because of the non-additivity of conformational energies the chair-twist energy difference of **1** loses much of its attractivity, and merely gives the proportion of **1**, but not of other 1,3-dioxanes, which adopts the non-chair conformations. Estimates in the literature, arrived at from the application of increment addition schemes, range from about 25.7 kJ mol^{-1} to about 36.9 kJ mol^{-1},[1,3] these values must be reduced by the amount of van der Waals strain due to Me groups in the twist conformations.[1,3] Pickett and Strauss found in a force field calculation of 6-membered rings an energy difference of only 18.7 kJ mol^{-1},[27] with our force field we calculate an energy difference of chair and 1,4-twist conformation of only 16.4 kJ mol^{-1}, while the 2,5-twist has a higher energy (24.8 kJ mol^{-1}), which is in very good agreement with a value proposed by Anteunis of 25.7 kJ mol^{-1}.[28] This author also proposed that the chair/twist energy difference is smaller than this value, when the 1,4-twist form has more weight in the conformational mixture, like in *trans* - 4,6 - diisopropyl - 1,3 - dioxane, for which he gives an enthalpy difference of 14.1 kJ mol^{-1} between chair and twist boats.[28] In our calculated energies, the 2,5-twist is favored in angle bending energy, but 1,4-van der Waals and torsional energies favor the 1,4-twist form much more.

For the ring inversion process three different routes are feasible depending on the torsion angle which changes its sign close to the transition state. Earlier studies have indicated that the transition state is close to the geometry with O-3 to C-6 coplanar.[22,29] We have applied the torsion angle "driving" method of Wiberg and Boyd[30] to the ring inversion of **1**, and found the same result with a barrier of 28.3 kJ mol^{-1} ($\Delta H^{\ddagger}$) at the geometry with $\omega_{CCCO} = 0°$. This is considerably less than the experimental Gibbs energy of activation of 40.2 kJ mol^{-1}. The difference cannot be entirely due to entropy and solvent effects, so the force field apparently underestimates the energy of the eclipsed arrangement in the transition state, and possibly also the near-eclipsed arrangement of the 1,4-twist form. If this is the case, the chair/twist equilibrium in polymethyl-1,3-dioxanes is even less on the side of the twist form, and this would also improve the agreement with the experimental energy difference of **9** and its *cis*-isomer. The other transition states for 1,3-dioxane ring inversion with COCO and CCOC coplanar are calculated to have considerably higher energies (43.6 kJ mol^{-1} and 49.4 kJ mol^{-1}) than the one with CCCO coplanar, which makes it doubtful that these are the transition states in derivatives of **1**, depending on the substitution pattern.[22,29]

CONCLUSIONS

Alkyl groups were found to introduce only minor geometry changes in the geometry of 1,3-dioxanes, which not always are sufficient to explain the variations in vicinal coupling constants. We suppose that other factors of Me substitution play an equally important role as the buttressing of ring H atoms. 1,3-synaxial Me/Me interactions appear not to be sufficient to shift the chair-twist conformational equilibrium totally towards the twist form, rules for the necessary substitution pattern have been given. The chair/twist energy difference is calculated to be smaller than proposed earlier on grounds of additivity of conformational energies. The molecular mechanics method, which accounts for molecular relaxation to minimize strain, was found to be a valuable tool for the interpretation of experimental data of conformational equilibria of strained 1,3-dioxanes.

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