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Empirical force field calculations. Part 28[1]. Conformations and pseudorotations of 1,3-dioxolane and some methyl-substituted derivatives

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Abstract. The conformations and pseudorotations of 1,3-dioxolane (**1**), *cis*- and *trans*-4,5-dimethyl-1,3-dioxolane (**2** and **3**) and the corresponding 2,2-dimethyl derivatives (**4**, **5** and **6**) have been studied with molecular mechanics using the MM2 force field. Free pseudorotation occurs in **1** and **4** (ΔE = 1.5 kJ/mol) and pseudolibration in **2**, **3**, **5** and **6** (ΔE = 6, 7, 11 and 14 kJ/mol, respectively). The steric energies of **3** and **6** are lower than those of **2** and **5** since the 4- and 5-methyl groups can both occupy a pseudo-equatorial position in the minimum energy conformation of the *trans* isomers. Estimates of ΔH_f° (25°C, gas, kJ/mol) are: **2**, −376.1; **3**, −380.5; **4**, −387.2; **5**, −464.4; **6**, −470.1. Vicinal proton coupling constants were calculated from the appropriate torsion angles and averaged over the pseudorotation circuit. They are in good agreement with experimental values. The 1,3-dioxolanes can be used as model compounds for borate monoesters of vicinal diols. The ^{13}C chemical shifts of C(2) in 1,3-dioxolanes correlate well with the ^{11}B chemical shifts in the corresponding borate monoesters.

Introduction

The rates of formation[2] and the stabilities[3] of borate esters of dihydroxy compounds have been studied extensively. Little is known about the conformations of these cyclic compounds. So far, only a few X-ray investigations have been carried out on borate diesters[4]; large side-chains may influence the ring conformations strongly. Therefore, we decided to use 1,3-dioxolanes as model compounds for the corresponding borate monoesters and to perform molecular mechanics calculations on a number of 1,3-dioxolanes as an extension of our studies on the simple vicinal diols[1]. This decision is based on the correlation between ^{13}C chemical shifts of C(2) in the 1,3-dioxolanes and the ^{11}B chemical shifts of the corresponding borate monoesters (Fig. 1). Such a correlation is indicative of conformational similarity[14]. The correspondence of Raman spectra of 1,3-dioxolanes with those of borate esters[15] supports this view. The computational results for 1,3-dioxolanes presented in this paper will be compared with experimental and calculated data for borate esters in a forthcoming paper.

The compounds studied are 1,3-dioxolane (**1**), *cis*- and *trans*-4,5-dimethyl-1,3-dioxolane (**2** and **3**), 2,2-dimethyl-1,3-dioxolane (**4**) and *cis*- and *trans*-2,2,4,5-tetramethyl-1,3-dioxolane (**5** and **6**). The results are compared with ^{1}H NMR data.

Experimental

Calculations

The calculations were performed using DELPHI, the Delft molecular-mechanics computer program[16], and Allinger's MM2 empirical force field[17]. We did not use the refined MM2(82) force field[18] because of the complicated dependency of the natural bond length l'_0 of the C−O bond on certain torsion angles, especially with respect to the derivation of first and second derivatives in our

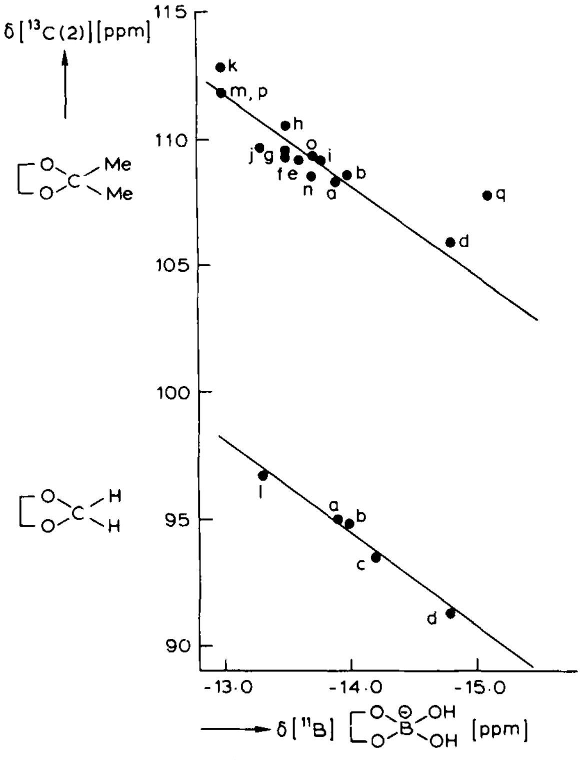

Fig. 1. Correlation of ^{13}C chemical shifts (Me_4Si as internal standard) of C(2) in 1,3-dioxolanes vs. *^{11}B chemical shifts (0.1 M boric acid as external reference) of the corresponding borate monoesters[3b,5]. The letters refer to the parent diols. The borate binding site is given in parentheses: glycol[6] (a); 1,2-propanediol[6] (b);* meso *2,3-butanediol[6] (c); pinacol[6] (d); glycerol (1,2)[5b] (e);* D*-glucitol (1,2/5,6)[7] (f); (3,4)[7] (g);* D*-mannitol (1,2/5,6)[8] (h);* D*-ribonic acid (2,3)[9] (i); (4,5)[9,10] (j);* meso *tartaric acid[5b] (k); galactaric acid (2,3/4,5)[11] (l); β-*D*-fructopyranose (1,2)[12] (m); (2,3)[12b] (n); (4,5)[12] (o); α-*D*-glucofuranose (1,2)[8,13] (p); (5,6)[13] (q) (mean ^{13}C chemical shifts for g, j, m, o and p).*

full matrix *Newton–Raphson* scheme. The improvement of the results for small cyclic dioxygen compounds using MM2(82) instead of MM2 is limited. The dielectric constant (ε) was set at the standard value[17a] of 1.5; some results using a value of 80 are also reported. The calculations for **2** and **5** and for **3** and **6** were carried out for the *S,R* and *S,S* configurations, respectively. The pseudorotation paths were obtained by torsion angle driving, using the *Lagrange* multiplier method[19]. The minima and transition states were found by unconstrained optimization. Because of symmetry, it is not necessary to investigate the complete pseudorotation paths.

The conformational changes observed during the pseudorotation of the five-membered rings are described by the changes in the ring torsion angles θ_i (i = 0–4; Fig. 2). According to *Altona* et al.[20], θ_i can be approximated with two parameters, namely the phase angle of pseudorotation φ (0–2π) and the maximum torsion angle θ_{max} ($\approx 40°$):

$$\theta_i = \theta_{max} \cdot \cos(\varphi + 0.8 \cdot i \cdot \pi) \qquad (1)$$

The phase angle φ can be calculated from:

$$\tan(\varphi) = (\theta_2 + \theta_4 - \theta_1 - \theta_3)/(3.0777 \cdot \theta_0) \qquad (2)$$

In this way, half chairs or twist forms (T) are obtained at $\varphi = 0.2n\pi$ (n = 0, 1, 2–9) and bent forms or envelopes (E) at $\varphi = (0.1 + 0.2n)\pi$ (Fig. 2). θ_0 is assigned to the unique endocyclic torsion angle around C(4)–C(5). The designations T and E are preceded by superscripts and/or subscripts which indicate which ring atoms lie above and/or below the plane formed by the remaining ring atoms (Fig. 2). An alternative way to describe the pseudorotation is to use a puckering amplitude q along with a phase angle of pseudorotation[27]. We prefer the use of φ in conjunction with torsion angles.

Energy values *versus* phase angles of pseudorotation for **1–6** are presented in Figs. 3–8. A table containing steric energies, exact values of the phase angles of pseudorotation, point groups and the values of the endocyclic torsion angles of all relevant optima can be obtained from the authors upon request. Steric energies (kJ/mol) of the global minima are: **1**, 70.4996 (ε 1.5), 60.8069 (ε 80); **2**, 78.7768 (ε 1.5), 69.0209 (ε 80); **3**, 74.8844 (ε 1.5), 66.3076 (ε 80); **4**, 78.5655 (ε 1.5); **5**, 87.1389 (ε 1.5); **6**, 80.5709 (ε 1.5). The minima and transition states are characterized by six zero-eigenvalues of the final force constants matrix. The transition states have one negative eigenvalue. The supplementary material also contains data on the planar forms characterized by two negative eigenvalues.

The vicinal proton coupling constants $^3J(4,5)$ were calculated from the dihedral angles H–C(4)–C(5)–H using the semi-empirical equation of *Haasnoot* et al.[21], especially derived for rings containing oxygen. Because the pseudorotational barriers for **1–6** are low, $^3J(4,5)$ has to be averaged[22]:

$$^3J(4,5) = \int_0^{2\pi} {}^3J(4,5)(\varphi) \cdot x(\varphi)\, d\varphi \qquad (3)$$

This integration was carried out numerically with steps of 0.1π. The fractions $x(\varphi)$ with a certain phase angle of pseudorotation φ were calculated, using the *Boltzmann* equation (T = 25°C), from the energies obtained by molecular mechanics. The calculated and experimental $^3J(4,5)$ values are compared in Table I.

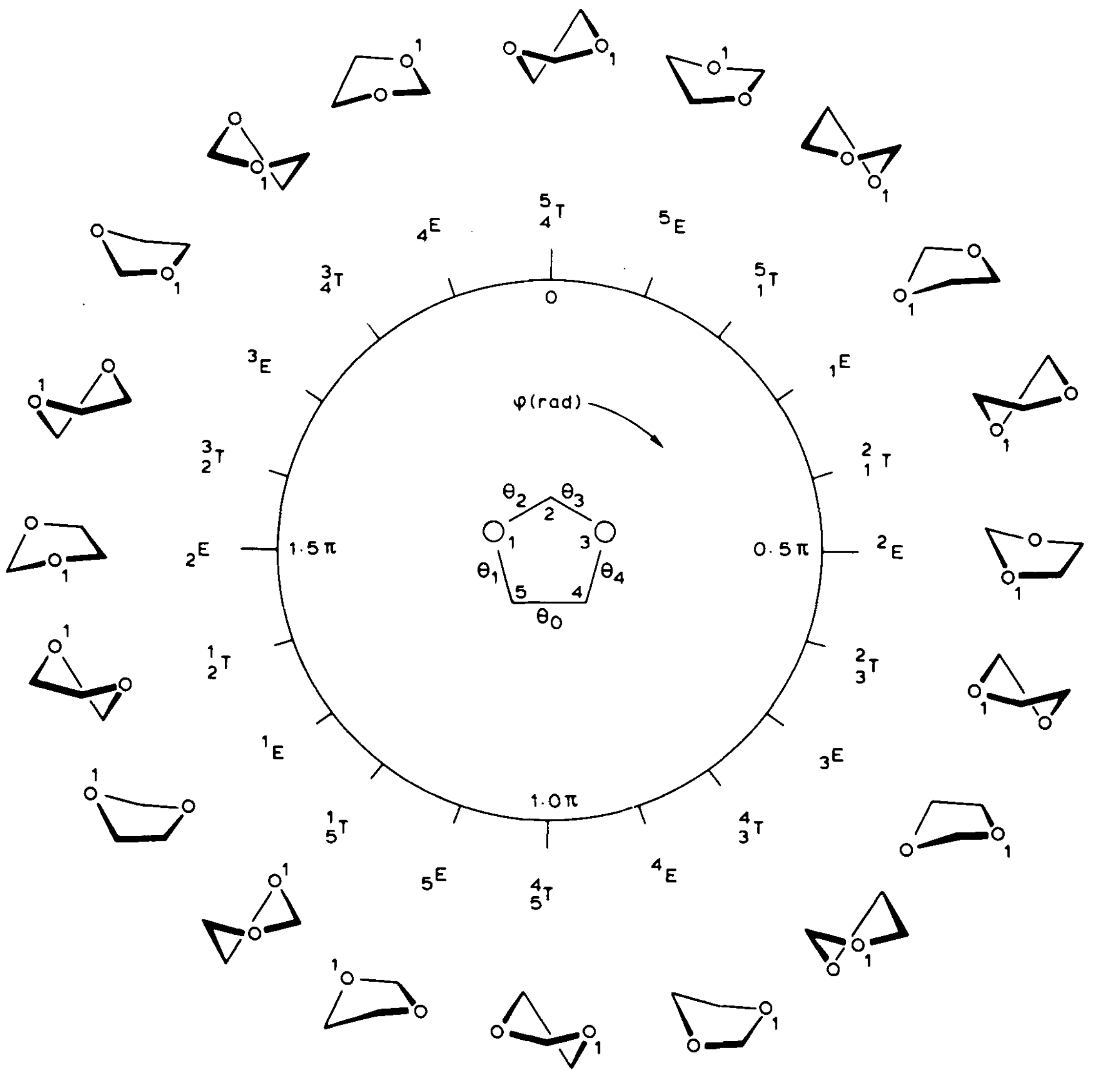

Fig. 2. Pseudorotation in 1,3-dioxolane.

Table I Experimental and calculated vicinal proton coupling constants of 1,3-dioxolanes **1–6**.

1,3-Dioxolane	$^3J(4,5)$ (Hz)			
	Calculated			Experimental
	Min [φ(rad)/π]	Max [φ(rad)/π]	Averaged[d]	
1	5.6/5.2 (0.0 and 1.0)	5.8/9.0 (0.5 and 1.5)	5.7/7.1	6.3/6.8[a]
2	4.2 (0.0 and 1.0	6.9 (0.5 and 1.5)	5.6	6.2
3	1.2 (1.0)	9.0 (0.0)	7.4	8.1
4	5.6/5.2 (0.0 and 1.0)	5.7/9.0 (0.5 and 1.5)	5.7/7.0	6.3/6.3[a,b]
5	4.6 (0.0 and 1.0)	6.9 (0.5 and 1.5)	5.6	5.9[c]
6	1.9 (1.0)	9.0 (0.0)	8.6	8.4[c]

[a] Using ^{13}C satellites[5,6]. [b] Reference 23a. [c] Reference 31a. [d] Using Eqn. 3.

The heats of formation ΔH_f° were calculated from the steric energies of the global minima (ε 1.5) and the increments of the MM2 force field[17a]. The heat content to account for the admixture of higher energy conformations (POP, kJ/mol) was calculated from the energy profiles of the pseudorotation paths in the same way as for $^3J(4,5)$: **1**, 0.7; **2**, 1.5; **3**, 1.0; **4**, 0.8; **5**, 0.8; **6**, 1.7. The heat content due to free and slightly hindered internal rotations (TOR) was taken to be equal to $\frac{1}{2}RT$ for **1** and **4** (free pseudorotors) and equal to one time 1.5 kJ/mol for the other compounds. The resulting ΔH_f° values (kJ/mol) are: **1**, −299.4; **2**, −376.1; **3**, −380.5; **4**, −387.2; **5**, −464.4; **6**, −470.1. *Allinger* et al.[17b] have given a calculated value for **1** of −299.7 kJ/mol but, as far as we can see, they ignore the quantity POP.

^{1}H NMR

The ^{1}H NMR spectra of solutions of **1–3** in $CDCl_3$ were recorded using a Nicolet NT-200 WB spectrometer at 25°C with Me_4Si as internal standard. The chemical shifts δ (±0.01 ppm) and coupling constants J (±0.1 Hz) were determined with the LAME spin simulation program (RMS < 0.1). ^{1}H NMR data not given in Table I: **1** δ(2) 4.90, δ(4) 3.88, $^2J(4,4')$ −10.0, $^1J(^1\mathrm{H},^{13}\mathrm{C})$ 149.0; **2** δ(2) 5.11 and 4.80, δ(4) 4.10, δ(Me) 1.16, $^3J(\mathrm{Me}_4, 4)$ 6.3, $^4J(\mathrm{Me}_4, 5)$ −0.2, $^5J(\mathrm{Me}_4, \mathrm{Me}_5)$ 0.0; **3** δ(2) 4.94, δ(4) 3.57, δ(Me) 1.28, $^3J(\mathrm{Me}_4, 4)$ 6.1, $^4J(\mathrm{Me}_4, 5)$ −0.2, $^5J(\mathrm{Me}_4, \mathrm{Me}_5)$ 0.0. These values are in agreement with literature data[23] as far as available. Compounds **2** and **3** were prepared according to *Garner* and *Lucas*[24].

To test the significance of the calculated steric energies, an equilibration was carried out for a solution of formaldehyde (**F**; 9.2 M) and *meso* and *racemic* 2,3-butanediol (**M** and **R**; 1.0 M each) in D_2O/D_2SO_4 (50/50, v/v) at 25°C:

$$\mathbf{M} + \mathbf{F} \overset{\mathrm{H}^+}{\rightleftharpoons} \mathbf{2} + \mathrm{H_2O}$$

$$\mathbf{R} + \mathbf{F} \overset{\mathrm{H}^+}{\rightleftharpoons} \mathbf{3} + \mathrm{H_2O}$$

The experimental value of $\Delta(\Delta G)$ (3.8 kJ/mol) is compared with the calculated enthalpy differences[25], obtained from molecular mechanics:

$$\Delta(\Delta G)_{\mathrm{expt}} = -R \cdot T \cdot \ln([\mathbf{2}] \cdot [\mathbf{R}])/([\mathbf{3}] \cdot [\mathbf{M}]) \quad (4)$$

$$\Delta(\Delta H)_{\mathrm{calcd}} = \bar{E}_{\mathbf{2}} + \bar{E}_{\mathbf{R}} - \bar{E}_{\mathbf{3}} - \bar{E}_{\mathbf{M}} \quad (5)$$

Discussion

Pseudorotation was used by *Kilpatrick* et al.[26] to describe the dynamic deformation[27] or conformational flexibility[28] of the puckered cyclopentane ring. Introduction of heteroatoms and substitution increase the pseudorotational energy barrier $(\Delta E)^{27-29}$ and result in a pseudolibration $(\Delta E > RT)^{29}$ or even in a rigid conformation $(\Delta E \gg RT)$. Furthermore, deviations from the ideal pseudorotation path, as defined by Eqn. 1, occur (mainly ring flattening). Dipole measurements[30], ^{1}H NMR[23,29a,29c,31], IR[32] and microwave spectroscopy[33] and X-ray diffraction[34] have demonstrated that 1,3-dioxolanes are indeed puckered. However, in general, these techniques do not provide explicit information with respect to the actual conformations of the minima and transition states on the pseudorotation paths[35].

1,3-Dioxolane (**1**)

The pseudorotation path of **1** is rather simple due to the C_s symmetry in the equivalent minima ^2E and $_2E$ (θ_0 = 0°) and the C_2 symmetry in the equivalent transition states ${}^5_4T$ and ${}^4_5T$ (θ_0 = ±39°) (Fig. 3). The symmetry elements of ^2E, $_2E$, ${}^5_4T$ and ${}^4_5T$ are also symmetry elements of the pseudorotation. Going from the minima to the transition states, the increase in torsion and valency angle energy (2.5 and 1.3 kJ/mol) is only partly compensated for by the decrease in the energy from the electrostatic and non-bonded interactions (1.6 and 0.9 kJ/mol). This dissection of energy terms is of course force field dependent, but it is notable that the total torsion angle energy of the forms ^2E and $_2E$, containing eclipsed bonds around C(4)−C(5), is lower than that of ${}^5_4T$ and ${}^4_5T$, in which θ_0 is almost staggered. The calculated steric energy difference (ΔE = 1.5 kJ/mol) is somewhat larger than the experimental value of 0.5–0.6 kJ/mol[32,33]. Because $\Delta E < RT$ at 25°C, free pseudorotation occurs. The calculated ΔH_f° is close to the experimental value (−299.4 *vs.* −297.5 ± 0.8 kJ/mol[37]).

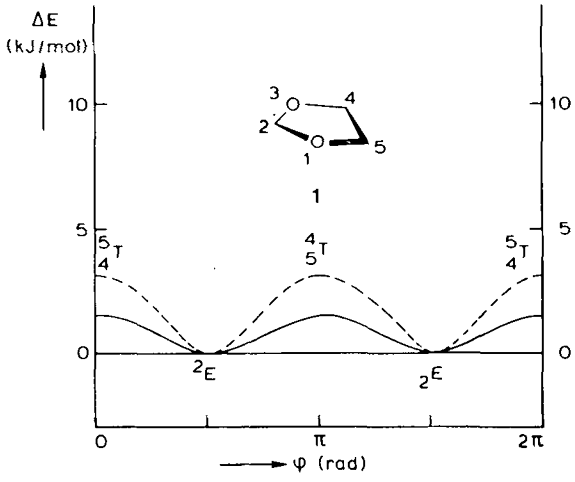

Fig. 3. Calculated energy profiles of the pseudorotation in 1,3-dioxolane **1** *(full line ε = 1.5, broken line ε = 80).*

Quantum-chemical calculations either give very flat conformations[38] (MINDO/3) or still larger pseudorotation barriers[27,28] ($\Delta E \geqslant 3.3$ kJ/mol). Contrary to our results, energy minima are predicted[28] for ${}^5_4T$ and ${}^4_5T$ and transition states for ${}^2E$ and ${}_2E$ using a 6–31$G*$ basis, but without complete optimization of the geometries. Microwave spectroscopy[33] of **1** indicates that both ${}^2E$ and ${}^5_4T$ are maxima on the pseudorotation path (with ${}^5_4T$ 0.1 kJ/mol higher in energy than ${}^2E$) and that the geometry of the minimum energy conformation is near ${}_1E$ and ${}^5_1T$. We conclude that both molecular mechanics and quantum-chemical calculations correctly show that the unsubstituted **1** is an almost free pseudorotor. Very minor changes in force-field parameters may influence the balance of the various energy terms and, in this way, the positions of minima and transition states on the pseudorotation paths, as calculated using the MM method. Regarding the calculated value of the barrier height and the efforts involved in its application, the MM method is to be preferred.

*4,5-Dimethyl-substituted 1,3-dioxolanes (**2** and **3**)*

Upon *cis*-4,5-dimethyl substitution of **1**, the C_s symmetry of ${}^2E$ and ${}_2E$ is preserved, whereas the C_2 symmetry of ${}^5_4T$ and ${}^4_5T$ is lost. As a result of the latter, ${}^2E$ and ${}_2E$ are non-equivalent in the case of **2**. The conformation of minimum energy is ${}_2E$ in which C(2) at the flap of the envelope points away from the *cis*-4,5-dimethyl groups (Fig. 4). At first sight, it seems unusual that the global minimum ${}_2E$ contains a pair of eclipsed methyl groups along C(4)–C(5). Pseudorotation into both directions, however, moves one of these methyl groups into a pseudo-axial position with a more strongly unfavourable interaction with the C(2)-methylene moiety. The two equivalent transition states, ${}^2_1T$ and ${}^2_3T$ (ΔE = 6.23 kJ/mol), enclose the relative minimum ${}^2E$ (ΔE = 6.20 kJ/mol). These conformations are very similar and ${}^2_1T$, ${}^2E$ and ${}^2_3T$ form a single transition state around $\varphi = 0.5\pi$. Because ΔE = 6.2 kJ/mol, pseudolibration occurs for **2**.

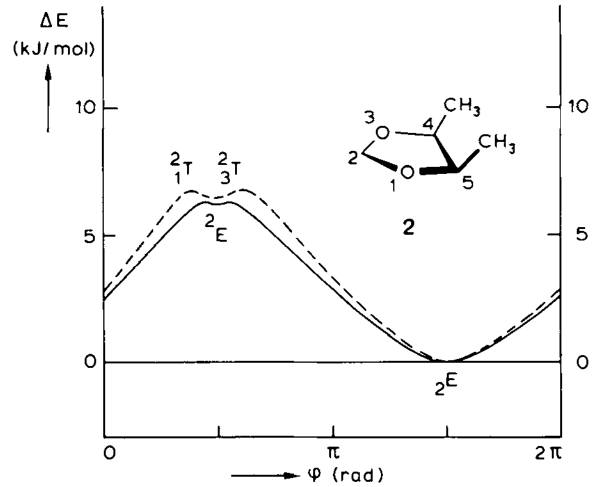

Fig. 4. Calculated energy profiles of the pseudorotation in cis-*(4*S*,5*R*)-dimethyl-1,3-dioxolane* **2** *(full line ε = 1.5, broken line ε = 80).*

Upon *trans*-4,5-dimethyl substitution of **1**, the C_s symmetry of ${}^2E$ and ${}_2E$ is lost, whereas the C_2 symmetry of ${}^5_4T$ and ${}^4_5T$ is conserved. In the case of **3**, ${}^2E$ and ${}_2E$ vanish as minima due to steric hindrance between C(2) at the flap of the envelope and either methyl group at C(4) or C(5) (Fig. 5). This unfavourable interaction is diminished by increasing θ_0 and two equivalent minima ${}^5E$ and ${}_4E$ are found (θ_0 = 37°). In these minima, both methyl substituents are in pseudo-equatorial positions, in contrast with the pseudo-axial positions in the relative minimum ${}^4_5T$. The two minima ${}^5E$ and ${}_4E$ are separated by a negligible barrier ${}^5_4T$ and the relative minimum ${}^4_5T$ is enclosed between two equivalent transition states ${}^4_3T$ and ${}^1_5T$. In a simplified description, the pseudorotation of **3** involves a single minimum around $\varphi = 0$ and a single transition state around $\varphi = 1.0\pi$ with ΔE = 7.2 kJ/mol (pseudolibration).

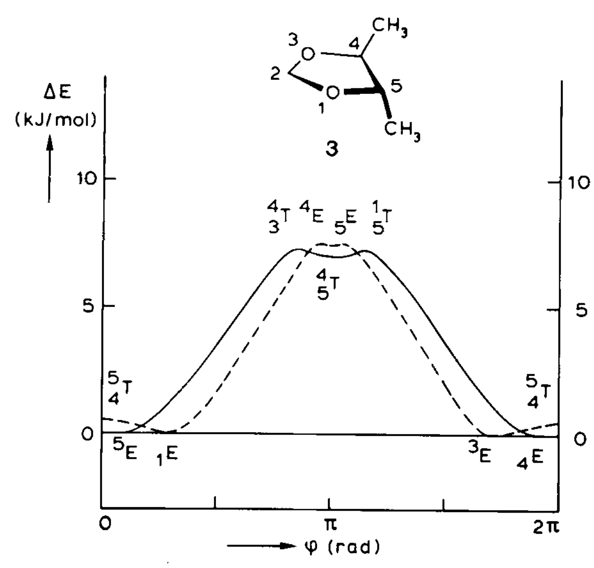

Fig. 5. Calculated energy profiles of the pseudorotation in trans-*(4*S*,5*S*)-dimethyl-1,3-dioxolane* **3** *(full line ε = 1.5, broken line ε = 80).*

For both **2** and **3**, it has been shown using ^{13}C NMR that the barriers to pseudorotation are low and that the methyl substituents are probably in an uncompressed environment[6,22c]. The calculated ΔH_f° of **3** is 4.4 kJ/mol smaller than that of **2**. This reflects the fact that only in **3** can both methyl groups occupy a pseudo-equatorial position in the minimum energy conformation.

Upon increasing ε from 1.5 to 80, the overall pictures for **1–3** as discussed above are retained (Figs. 3–5, broken lines). The optima at ε = 80 are close to those at ε = 1.5. The electrostatic interactions almost vanish at ε = 80, which results in small increases in the pseudorotational barriers, consistent with literature data[39].

*2,2-Dimethyl-substituted 1,3-dioxolanes (**4**, **5** and **6**)*

Upon 2,2-dimethyl substitution of **1–3**, the symmetry of the parent compounds is preserved, but the pseudorotation paths are affected drastically. In ${}^2E$ and ${}_2E$ of **4**, unfavourable interactions between one of the geminal methyl groups at C(2) and the transannular hydrogen atoms at C(4) or C(5) occur. As a result, contrary to **1**, the global minima of **4** are ${}^5_4T$ and ${}^4_5T$ ($\theta_0 = \pm 39°$) (Fig. 6). The relative minima ${}^2E$ and ${}_2E$ are enclosed by equivalent transition states ${}_1E$ and ${}_3E$ and by ${}^1E$ and ${}^3E$. The regions between ${}_1E$ and ${}_3E$ and between ${}^1E$ and ${}^3E$ can be seen as two transition states around $\varphi = 0.5\pi$ and $\varphi = 1.5\pi$, respectively. ΔE(1.5 kJ/mol) equals that of **1**, indicating free pseudorotation. The calculated ΔH_f° differs considerably from the value obtained from increments by *Stern* and *Dorer*[40] (– 387.2 *vs.* – 416.7 kJ/mol).

For **5**, the difference in conformational energy between ${}^2E$ and ${}_2E$ is enlarged, relative to that for **2**, due to the

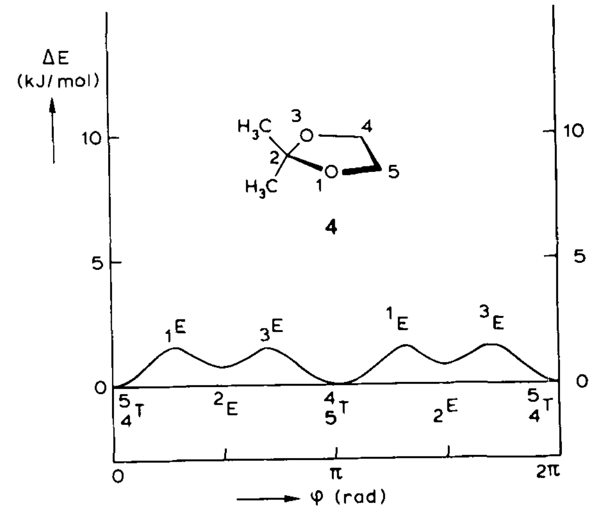

Fig. 6. Calculated energy profile of the pseudorotation in 2,2-dimethyl-1,3-dioxolane **4**.

increased steric hindrance in ^2E caused by the 2,2-dimethyl substitution (Fig. 7). The general picture of **2** is preserved, but the global minima $_5E$ and $_4E$ are close to those of **4**. The pseudorotation of **5** is characterized by a rather flat region between $\varphi = 1.1\pi$ and $\varphi = 1.9\pi$ and a transition region around $\varphi = 0.5\pi$ (ΔE = 10.9 kJ/mol).

Finally, for **6**, the pseudorotation is similar to that for **3**, although it is somewhat simplified due to the merging of the optima of **3** around $\varphi = 0$ into the single minimum ^5_4T (Fig. 8). The height of the broad barrier at $\varphi = 0.7\pi$–1.3π is enlarged (ΔE = 13.9 kJ/mol), due to steric hindrance between the geminal methyl groups at C(2) and the 4- and 5-methyl groups in the pseudo-axial position. In this case, the conformational energy of the planar form (ΔE = 15.4 kJ/mol) is close to this barrier. Therefore, considerable ring flattening can occur during the pseudorotation of **6**.

Both for **5** and **6**, 1,3-transannular non-bonded interactions have been demonstrated using ^{13}C NMR[41]. The difference between the calculated ΔH_f° values of **5** and **6** (5.7 kJ/mol) is somewhat larger than the difference between the corresponding values of **2** and **3**, in accord with the increased size of the groups at C(2).

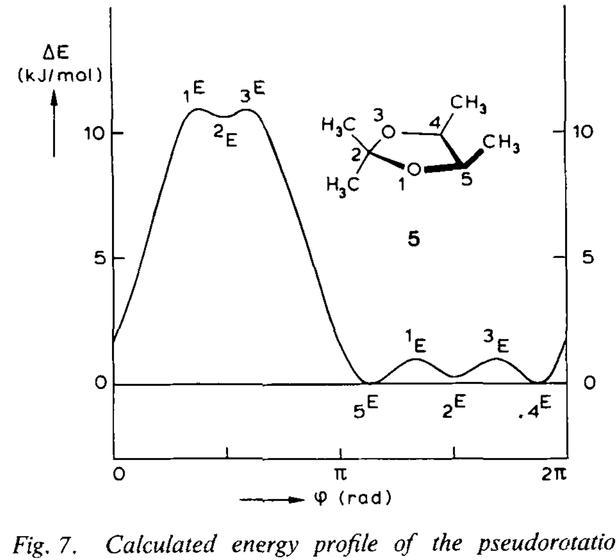

Fig. 7. Calculated energy profile of the pseudorotation in cis-*(2,2,4*S*,5*R*)-tetramethyl-1,3-dioxolane* **5**.

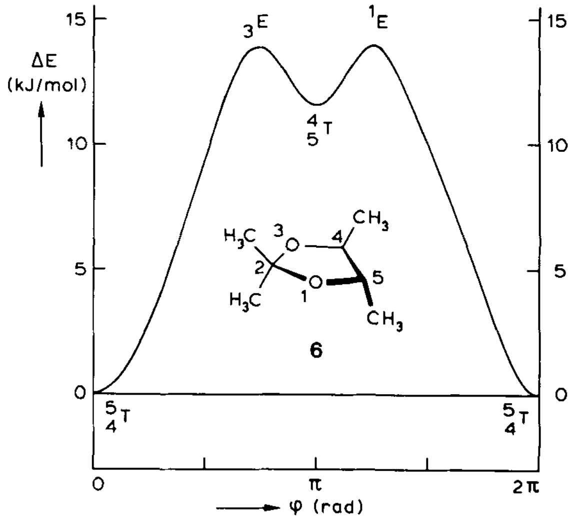

Fig. 8. Calculated energy profile of the pseudorotation in trans-*(2,2,4*S*,5*S*)-tetramethyl-1,3-dioxolane* **6**.

¹H NMR experiments

Differences between experimental and calculated values of $^3J(4,5)$ (Table I) are smaller than 0.8 Hz. This suggests that the energy profiles obtained by molecular mechanics are realistic. Table I also contains the minimum and maximum values of $^3J(4,5)$ at the appropriate phase angles φ. Only in the case of *trans* 4,5-disubstituted 1,3-dioxolanes **3** and **6** is the calculation of $^3J(4,5)$ rather sensitive for φ and the differences in $E(\varphi)$.

From the equilibration at 25°C, a value for $\Delta(\Delta G)_{\mathrm{expt}}$ of 3.8 kJ/mol is obtained, which is in agreement with experimental data for other substituted 1,3-dioxolanes[42] and borate monoesters[43]. We calculated $\Delta(\Delta H)$ = 2.5 kJ/mol for $\varepsilon = 1.5$ and for $\varepsilon = 80$ in aprotic media[44]. At $\varepsilon = 80$ in protic media, a correction should be made for specific solvation[45] and $\Delta(\Delta H)$ decreases to 1.3 kJ/mol. The calculated entropies are very similar for **M** and **R**, but that for **3** is about 8 J · mol^{-1} · °C^{-1} larger than that for **2**. Taking this into account brings $\Delta(\Delta G)_{\mathrm{calcd}}$ close to the experimental value.

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