Ab Initio Conformational Analysis of 1,4-Dioxane

Darren M. Chapman and Ronald E. Hester*

Department of Chemistry, University of York, Heslington, York YO1 5DD, England

Received: September 24, 1996; In Final Form: February 21, 1997⊗

The inversion of 1,4-dioxane has been studied by using *ab initio* molecular orbital theory at the HF/6-31G* and BLYP/6-31G* levels. A total of 10 stationary points were characterized as energy minima or transition states. Vibrational frequencies were calculated for the chair and two twist-boat conformations. The chair conformation is the lowest in energy, followed by the two twist-boats. The transition state connecting the chair and the twist-boats is a half-chair structure, in which four atoms in the ring are planar. Thermochemical analysis of the chair, twist-boats, and the half-chair structures yields a value of the free energy of activation to ring inversion that is in good agreement with experiment.

Introduction

The conformational analysis of cyclohexane has been extensively studied and is well understood. It has played a major role in understanding the conformational analysis of saturated carbon compounds in general. At room temperature, cyclohexane exists almost entirely as the chair conformer. The other stable conformer, the twist-boat, was first observed in 1975 by Squillacote *et al.*[1] when cyclohexane vapour at 800 °C was deposited into an argon matrix at 40 K, thus trapping the equilibrium mixture which contained approximately 30% twist-boat. Warming the matrix to above 70 K decreased the intensity of the twist-boat infrared absorption bands. By measuring their rate of decay at different temperatures, the free energy of activation $\Delta G^{\ddagger}_{\mathrm{tb}}$ for the twist-boat to chair transformation was calculated as 22.0 ± 0.2 kJ mol^{-1}. This study was followed by a more detailed investigation of the twist-boat bands by Offenbach *et al.*[2] in 1981, which included normal-coordinate calculations for the chair, twist-boat, and boat conformations. More recently, a gas phase ^{1}H NMR study of cyclohexane by Ross and True[3] has yielded thermodynamic parameters for the overall chair-to-chair inversion process.

There have been a number of recent theoretical studies on the conformational analysis of cyclohexane.[4−8] The results are convincing in that the calculated $\Delta G^{\ddagger}$ of inversion compares well with the experimental data. The proposed mechanism of inversion is

$$\text{chair} \rightarrow [\text{half-chair}] \rightarrow \text{twist-boat} \rightarrow [\text{boat}] \rightarrow \ldots \rightarrow \text{twist-boat} \rightarrow [\text{half-chair}] \rightarrow \text{chair}$$

with the $\Delta G^{\ddagger}_{\mathrm{c}}$ of inversion being associated with the step chair → [half-chair]. For cyclohexane, this barrier is in the range of 40−45 kJ mol^{-1}.

There has been comparatively little work reported on 1,4-dioxane and, to our knowledge, no *ab initio* study of its various conformers. Electron diffraction shows the molecule to have a chair conformation that is slightly more puckered than cyclohexane.[9] The ring inversion barrier was finally measured in 1971 by two groups. Jensen *et al.*[10] observed the changes in the ^{13}C NMR satellite spectra of a 100 MHz ^{1}H spectrum, while Anet *et al.*[11] measured the ^{1}H NMR spectrum of hexadeuterio-1,4-dioxane at low temperature. Both groups calculated $\Delta G^{\ddagger}_{\mathrm{c}}$ for ring inversion to be 40.6 kJ mol^{-1}.

A theoretical study of 1,4-dioxane by Pickett and Strauss[12] evaluated the energies of all significant conformations using a potential function derived from vibrational and geometrical data. They calculated the $\Delta G^{\ddagger}_{\mathrm{c}}$ for chair → twist-boat to be 42.2 kJ mol^{-1}.

One interesting feature of 1,4-dioxane not present in cyclohexane are two possible forms of the twist-boat, boat, half-chair, and sofa structures. This arises from the fact that the two oxygens can occupy two different positions. For example, in the boat conformer, either two oxygen atoms can be at the apex or two carbon atoms.

Methods

The geometries, energies, and IR and Raman spectra of several conformers of 1,4-dioxane were calculated using *ab initio* molecular orbital theory.

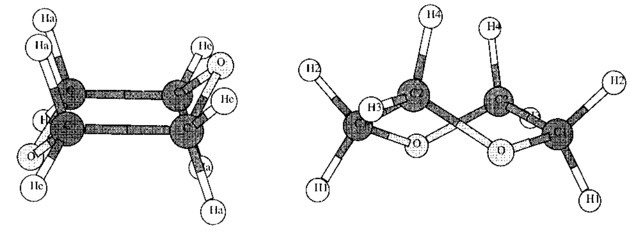
On the basis of previous work on cyclohexane, 10 different conformers were studied. These are the chair, two twist-boats, two boats, two half-chairs, two sofas, and a planar structure (see Figures 1a−h). The half-chairs have four coplanar atoms, while the sofas have five coplanar atoms. These conformers were studied because the calculations on cyclohexane indicated that they are important intermediates along the inversion pathway.

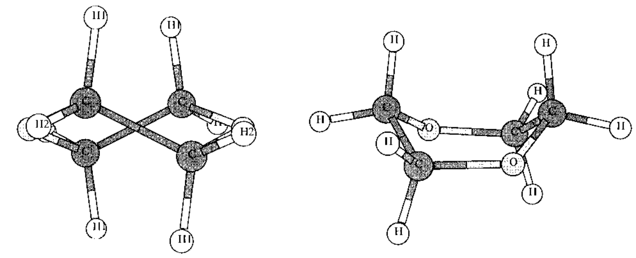
The geometries of all the conformers were initially optimized using Hartree−Fock (HF) theory with the 6-31G* basis set.[13] The gradient techniques in the CADPAC 6.0[14] package were used for this purpose. Full use of symmetry was made wherever possible. For saddle point geometries, a constrained optimization was performed using the appropriate point group. This ensured that the optimization did not lead to a local minimum geometry.

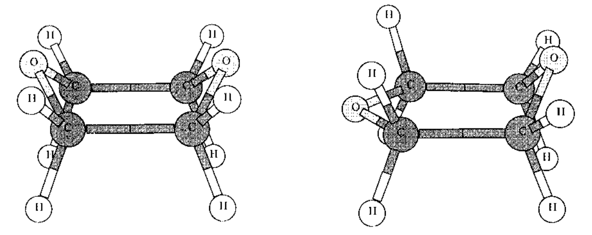
The HF/6-31G* optimized structures were used as the starting point for a density functional theory BLYP[17]/6-31G* geometry optimization, using the HIGH grid option in CADPAC. The HF/6-31G* optimized structures also were used for a single point MP2/6-31G* energy calculation for comparison with the HF and BLYP energies. Because of a high computational overhead, it was not considered to be justified for this essentially mechanistic study to optimize the geometries at the MP2/6-31G* level.

⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S1089-5639(96)02932-5 CCC: $14.00


(a) chair (b) 2,5 twist-boat


(c) 1,4 twist-boat (d) 2,5 boat


(e) 1,4 boat (f) 1,4 sofa

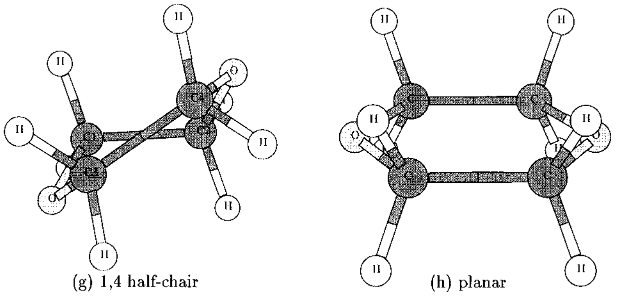

(g) 1,4 half-chair (h) planar

Figure 1. Eight conformations for 1,4-dioxane in order of increasing energy.

The vibrational wavenumbers and IR and Raman spectra were calculated for all the conformers at the HF/6-31G* level. In order to perform the vibrational analysis, the force constant matrices in Cartesian coordinates were transformed to the corresponding matrices in symmetry coordinates.[15] The symmetry coordinates were simply the appropriate combinations of internal coordinates as defined by the symmetry group. Vibrational analysis was then performed using the usual Schachtschneider FG matrix programs.[16] Vibrational wavenumbers were calculated for only the chair and two twist-boats at the BLYP/6-31G* level.

Finally, the thermochemical data for the chair, 1,4 half-chair, and 2,5 twist-boat conformers of dioxane at 298.15 and 100 K were calculated at the HF/6-31G* level using Gaussian 94.[18] For comparison, a thermochemical analysis on the chair, half-chair and twist-boat conformers of cyclohexane was also performed. All wavenumbers used in the thermochemical analysis were scaled by a factor of 0.896, derived from the comparison with experimental data (see below).

Results and Discussion

Optimized Geometries and Energies. The lowest energy structure, as expected, was found to be the chair form of C_{2h} symmetry. Energies for the other structures relative to the chair structure are given in Table 1. For all structures other than those corresponding to energy minima, one or more imaginary frequencies, n_{ivibs}, occurs in the vibrational mode analysis. The deviations between the HF and BLYP sets of energies given in Table 1 are seen to be small. The MP2 values all are larger but the relative ordering is identical apart from the two twist-boat forms (see below).

TABLE 1: Conformation Energetics (in kJ mol^{-1}) for 1,4-Dioxane

conformer	ΔE(HF)	ΔE(BLYP)	ΔE(MP2)[a]	n_{ivibs}
chair (C_{2h})	0.0	0.0	0.0	0
2,5 twist-boat (C_2)	+28.5	+29.1	+31.2	0
1,4 twist-boat (D_2)	+27.7	+30.1	+31.2	0
2,5 boat (C_2)	+29.5	+30.8	+33.4	1
1,4 boat (C_{2v})	+36.7	+34.4	+40.2	1
2,5 half-chair (C_1)	+41.4	+39.0	+47.4	1
1,4 sofa (C_s)	+43.1	+41.7	+49.3	1
1,4 half-chair (C_2)	+46.1	+45.2	+53.6	1
2,5 sofa (C_1)	+46.4	+45.4	+53.7	1
planar (D_{2h})	+103.0	+99.1	+121.0	3

[a] MP2 energies calculated at HF optimized geometry.

TABLE 2: HF/6-31G* and Experimental Parameters[a] for the Chair, 1,4 Twist-Boat, and 2,5 Twist-Boat Conformers of 1,4 Dioxane

parameter	theoretical value	exptl value	parameter	theoretical value	exptl value
		Chair			
CC	1.54	1.523	COC	110.3	112.4
CO	1.44	1.423	CCH$_e$	111.3	
CH$_e$	1.10	1.112	CCH$_a$	109.6	
CH$_a$	1.11	1.112	OCCO	57.5	57.0
CCO	110.6	109.2	CCOC	−57.3	−57.0
		1,4 Twist-Boat			
CC	1.52		COC	115.1	
CO	1.41		CCH$_1$	109.7	
CH$_1$	1.09		CCH$_2$	110.3	
CH$_2$	1.08		OCCO	60.0	
CCO	111.5		CCOC	−28.0	
		2,5 Twist-Boat			
OC$_1$	1.45		OC$_2$C$_1$	110.1	
OC$_2$	1.43		OCCO	−37.3	
CC	1.55		CCOC$_1$	63.4	
OCH$_1$	105.5		C$_2$OCC	−25.3	
OCH$_2$	110.4		COCH$_1$	−145.7	
OCH$_3$	106.5		COCH$_2$	97.6	
OCH$_4$	110.0		COCH$_3$	176.7	
COC	111.7		COCH$_4$	−59.9	
OC$_1$C$_2$	110.9				

[a] Bond lengths in angstroms and interbond and torsional angles in degrees. Experimental values taken from ref 8.

The geometric parameters for the chair and twist-boat conformers are given in Table 2. Only the structure of the chair form has been determined experimentally, and the experimental values[9] from gas phase electron diffraction are also given in Table 2.

There are two other energy minima structures. These are the 2,5 twist-boat and the 1,4 twist-boat. The HF/6-31G* calculation predicted the 1,4 twist-boat to be the more stable of the two. However, this order was reversed using density functional theory (DFT) at the BLYP/6-31G* level, with the 2,5 twist-boat being the more stable. We may conclude that these two structures have closely similar energies since the small differences between them are similar to the uncertainties expected in the values themselves. The single-point MP2/6-31G* energy calculations served to confirm this (see Table 1).

TABLE 3: Scaled HF, BLYP, and Experimental Wavenumbers and HF IR and Raman Intensities for the Chair Conformer of 1,4-Dioxane

wavenumber/cm^{-1}						
HF	BLYP	exptl[a]	IR intensity (HF)	Raman intensity (HF)	sym	potential energy distribution[b] (HF)
2944	2992	2970	0.0	85.3	a_g	$97\nu\ (\mathrm{CH_e})$
2943	2990	2970	43.7	0.0	b_u	$87\nu\ (\mathrm{CH_e}) + 12\nu\ (\mathrm{CH_a})$
2941	2987	2968	0.0	54.4	b_g	$89\nu\ (\mathrm{CH_e}) + 11\nu\ (\mathrm{CH_a})$
2940	2986	2968	61.8	0.0	a_u	$97\nu\ (\mathrm{CH_e})$
2865	2888	2863	86.6	0.0	b_u	$88\nu\ (\mathrm{CH_a}) + 12\nu\ (\mathrm{CH_e})$
2860	2880	2863	0.0	100.0	a_g	$98\nu\ (\mathrm{CH_a})$
2857	2872	2856	0.0	6.8	b_g	$89\nu\ (\mathrm{CH_a}) + 11\nu\ (\mathrm{CH_e})$
2851	2866	2856	19.6	0.0	a_u	$97\nu\ (\mathrm{CH_a})$
1491	1472	1459	0.0	2.6	a_g	$73\delta\ (\mathrm{HCH}) + 11\delta\ (\mathrm{OCH_a})$
1484	1464	1457	2.4	0.0	b_u	$72\delta\ (\mathrm{HCH}) + 12\delta\ (\mathrm{OCH_e}) + 11\delta\ (\mathrm{OCH_a})$
1476	1453	1449	0.2	0.0	a_u	$75\delta\ (\mathrm{HCH})$
1470	1451	1444	0.0	11.7	b_g	$79\delta\ (\mathrm{HCH})$
1424	1386	1397	0.0	1.3	a_g	$32\delta\ (\mathrm{CCH_a}) + 22\delta\ (\mathrm{OCH_a}) + 16\delta\ (\mathrm{OCH_e}) + 15\nu\ (\mathrm{CC})$
1403	1376	1378	5.7	0.0	b_u	$37\delta\ (\mathrm{CCH_e}) + 27\delta\ (\mathrm{OCH_e}) + 14\delta\ (\mathrm{OCH_a}) + 12\delta\ (\mathrm{CCH_a})$
1386	1355	1369	22.1	0.0	a_u	$36\delta\ (\mathrm{OCH_a}) + 35\delta\ (\mathrm{CCH_a}) + 14\delta\ (\mathrm{OCH_e})$
1347	1321	1335	0.0	1.7	b_g	$34\delta\ (\mathrm{CCH_e}) + 27\delta\ (\mathrm{OCH_e}) + 25\delta\ (\mathrm{OCH_a}) + 12\delta\ (\mathrm{CCH_a})$
1306	1285	1305	0.0	9.2	a_g	$46\delta\ (\mathrm{OCH_e}) + 22\delta\ (\mathrm{OCH_a}) + 11\delta\ (\mathrm{CCH_a}) + 11\delta\ (\mathrm{CCH_e})$
1298	1277	1291	7.5	0.0	b_u	$50\delta\ (\mathrm{OCH_a}) + 32\delta\ (\mathrm{OCH_e})$
1264	1238	1256	36.5	0.0	a_u	$39\delta\ (\mathrm{OCH_e}) + 26\delta\ (\mathrm{CCH_e}) + 12\nu\ (\mathrm{OC}) + 11\delta\ (\mathrm{CCH_a})$
1220	1198	1217	0.0	4.3	b_g	$47\delta\ (\mathrm{OCH_a}) + 32\delta\ (\mathrm{OCH_e}) + 11\delta\ (\mathrm{CCH_a})$
1163	1112	1136	100.0	0.0	a_u	$70\nu\ (\mathrm{OC}) + 15\nu\ (\mathrm{CC})$
1155	1077	1128	0.0	1.7	b_g	$82\nu\ (\mathrm{OC})$
1139	1065	1110	0.0	1.5	a_g	$26\delta\ (\mathrm{CCH_e}) + 25\delta\ (\mathrm{CCH_a}) + 20\delta\ (\mathrm{OCH_a})$
1097	1063	1086	2.8	0.0	a_u	$31\delta\ (\mathrm{OCH_a}) + 23\delta\ (\mathrm{OCH_e}) + 16\delta\ (\mathrm{CCH_a}) + 12\delta\ (\mathrm{CCH_e})$
1042	1029	1052	6.5	0.0	b_u	$28\delta\ (\mathrm{OCC}) + 28\delta\ (\mathrm{CCH_e}) + 16\delta\ (\mathrm{CCH_a}) + 11\delta\ (\mathrm{OCH_e})$
1006	964	1015	0.0	6.6	a_g	$45\nu\ (\mathrm{OC}) + 41\nu\ (\mathrm{CC})$
890	858	889	40.6	0.0	b_u	$59\nu\ (\mathrm{OC}) + 19\delta\ (\mathrm{COC}) + 11\delta\ (\mathrm{CCH_e})$
874	837	881	12.5	0.0	a_u	$47\nu\ (\mathrm{CC}) + 26\delta\ (\mathrm{CCH_e}) + 12\nu\ (\mathrm{OC})$
852	833	853	0.0	1.1	b_g	$31\delta\ (\mathrm{CCH_a}) + 27\delta\ (\mathrm{CCH_e}) + 23\nu\ (\mathrm{OC}) + 16\delta\ (\mathrm{OCH_e})$
832	811	837	0.0	6.2	a_g	$53\nu\ (\mathrm{OC}) + 35\nu\ (\mathrm{CC})$
600	594	610	8.9	0.0	b_u	$35\delta\ (\mathrm{OCC}) + 32\delta\ (\mathrm{CCH_a}) + 12\delta\ (\mathrm{COC}) + 10\delta\ (\mathrm{CCH_e})$
478	471	490	0.0	1.0	b_g	$54\delta\ (\mathrm{OCC}) + 28\delta\ (\mathrm{CCH_a})$
420	429	435	0.0	0.1	a_g	$47\delta\ (\mathrm{COC}) + 12\delta\ (\mathrm{CCH_e}) + 10\tau\ (\mathrm{OCCO})$
397	407	424	0.0	0.1	a_g	$48\tau\ (\mathrm{COCC}) + 23\tau\ (\mathrm{OCCO}) + 11\delta\ (\mathrm{CCH_e})$
258	266	288	12.3	0.0	b_u	$69\tau\ (\mathrm{COCC}) + 22\delta\ (\mathrm{COC})$
237	242	274	0.6	0.0	a_u	$55\tau\ (\mathrm{OCCO}) + 22\tau\ (\mathrm{COCC}) + 16\delta\ (\mathrm{OCC})$

[a]Experimental values taken from ref 18. [b] Key: ν indicates bond stretching, δ interbond angle deformation, and τ torsional angle deformation.

The boat structures are not energy minima structures, but are transition states, as indicated by the occurrence of an imaginary frequency in the vibrational analysis. Surprisingly, the 2,5 boat is the lower energy conformer of the two. However, vibrational analysis of the 2,5 twist-boat indicates that less displacement is required to achieve the 2,5 boat than the 1,4 boat.

One point worth noting about the other conformations is that the 1,4 sofa is more stable than the 1,4 half-chair, even though the sofa is more constrained than the half-chair. The most likely explanation for this is that an arrangement in which the oxygen atoms are coplanar in a ring is unstable due to the repulsions between electron lone pairs.

The energy and the number of imaginary vibrations for the planar structure indicate that this is not a transition state, but simply a very high-energy structure.

Vibrational Analysis. The vibrational spectrum of the chair conformation is the only one which has been measured experimentally.[19] The theoretically calculated wavenumbers for the chair conformer were therefore scaled linearly to the experimental values using least-squares fitting. The linear scaling factors and the standard deviations were found to be 0.896 and 20 cm^{-1}, respectively, at the HF/6-31G* level of theory and 0.990 and 24 cm^{-1}, respectively, at the BLYP/6-31G* level.

We note that density functional theory using the BLYP functional gives better unscaled wavenumbers than does Hartree−Fock theory, *i.e.*, scale factor closer to unity. However, the scaled Hartree−Fock wavenumbers are slightly better than the DFT wavenumbers, *i.e.*, smaller standard deviation. Because of this, the scaled Hartree−Fock force constant matrices were used for the vibrational analysis.

The scaled HF/6-31G* vibrational wavenumbers and IR and Raman intensities for the chair and the two twist-boat conformers of 1,4-dioxane are given in Tables 3−5. Also given are the HF/6-31G* potential energy distribution components greater than 10%. Tables 3−5 also contain the scaled BLYP/6-31G* wavenumbers for comparison purposes.

Chair. The chair conformation has a center of inversion, and there is a mutual exclusion between IR and Raman bands. The 36 fundamental vibrations can be divided into 10 a_g (Raman active), 9 a_u (infrared active), 8 b_g (Raman active), and 9 b_u (infrared active) modes.

The vibrations in the region 2950−2850 cm^{-1} are all CH stretches, those in the region 1500−1470 cm^{-1} are HCH scissoring. HCH wagging and rocking modes occur in the region 1450−1040 cm^{-1}, while the region 1000−230 cm^{-1} contains mainly ring deformations and torsions.

The lowest wavenumber vibrations are particularly interesting. The vibration at 237 cm^{-1} corresponds to conversion of the chair to the 1,4 half-chair, and the vibration at 397 cm^{-1} corresponds to conversion to the planar structure.

Twist-Boat. The 2,5 twist-boat has C_2 symmetry, and its 36 fundamental vibrations can be divided into 19 of a-type symmetry, and 17 of b-type symmetry. There is no center of inversion and all vibrations are both IR and Raman active. The vibrations can be classified into groups in approximately the

TABLE 4: Scaled HF and BLYP Wavenumbers and HF IR and Raman Intensities for the 1,4 Twist-Boat Conformer of 1,4-Dioxane

wavenumber/cm-1		IR	Raman		
HF	BLYP	intensity (HF)	intensity (HF)	sym	potential energy distribution[a] (HF)
2915	2967	31.8	36.6	b$_2$	78ν (CH$_2$) + 21ν (CH$_1$)
2915	2964	0.0	82.4	a	97ν (CH$_2$)
2911	2963	64.7	2.4	b$_1$	96ν (CH$_2$)
2910	2961	19.3	7.9	b$_3$	87ν (CH$_2$) + 13ν (CH$_1$)
2857	2893	72.1	8.4	b$_2$	79ν (CH$_1$) + 21ν (CH$_2$)
2854	2887	0.0	100.0	a	98ν (CH$_1$)
2851	2883	1.2	1.8	b$_3$	88ν (CH$_1$) + 12ν (CH$_2$)
2840	2867	18.2	0.1	b$_1$	97ν (CH$_1$)
1500	1493	0.0	1.9	a	30δ (HCH) + 14τ (H$_1$COC) + 11τ (H$_1$CCH$_1$) + 11τ (H$_2$COC)
1489	1485	0.4	2.1	b$_2$	33δ (HCH) + 27τ (H$_1$CCH$_2$)
1483	1477	0.6	1.8	b$_1$	33δ (HCH) + 14τ (H$_1$COC)
1482	1475	0.7	8.6	b$_3$	27τ (H$_1$CCH$_2$) + 27δ (HCH)
1419	1384	0.0	0.4	a	24δ (CCH$_1$) + 20ν (CC) + 12ν (CO) + 11δ (OCH$_2$)
1394	1377	3.9	0.3	b$_3$	36δ (CCH$_2$) + 15δ (OCH$_2$) + 11δ (OCH$_1$)
1383	1364	15.0	1.8	b$_1$	39δ (CCH$_1$) + 13δ (OCH$_2$) + 12ν (CC) + 11δ (OCH$_1$)
1340	1326	0.0	2.2	b$_2$	31δ (CCH$_2$) + 21δ (OCH$_1$) + 16δ (OCH$_2$) + 13δ (CCH$_1$)
1276	1267	0.0	4.6	a	27δ (OCH$_2$) + 15δ (CCH$_1$) + 13δ (CCH$_2$)
1256	1235	38.4	2.2	b$_1$	31δ (OCH$_2$) + 21ν (CO) + 17δ (CCH$_2$) + 12δ (CCH$_1$)
1242	1232	0.7	3.4	b$_3$	36δ (OCH$_1$) + 21δ (OCH$_2$) + 15τ (H$_1$CCO)
1219	1193	7.7	0.0	b$_2$	22δ (OCH$_1$) + 20δ (OCH$_2$) + 18ν (CO) + 16δ (CCH$_2$)
1170	1101	100.0	2.2	b$_1$	66ν (CO) + 14ν (CC)
1160	1090	12.5	0.7	b$_2$	75ν (CO)
1112	1078	0.0	1.1	a	14τ (H$_1$COC) + 14τ (H$_2$COC) + 11δ (CCH$_1$)
1093	1059	2.8	0.0	b$_1$	15δ (CCH$_1$) + 11τ (H$_1$CCH$_2$) + 11δ (OCH$_2$) + 10τ (H$_2$CCH$_2$)
1043	1035	1.9	1.9	b$_3$	23δ (CCH$_2$) + 16δ (CCO) + 14δ (COC)
1003	970	0.0	4.5	a	49ν (CO) + 36ν (CC)
877	844	37.0	0.0	b$_3$	68ν (CO) + 22δ (COC)
859	833	15.7	0.5	b$_1$	50ν (CC) + 15ν (CO) + 14δ (CCH$_2$)
854	826	1.9	1.0	b$_2$	28ν (CO) + 29δ (CCH$_1$) + 17δ (CCH$_2$)
814	790	0.0	5.4	a	57ν (CO) + 27ν (CC)
579	575	1.0	0.2	b$_3$	24τ (H$_2$COC) + 18δ (COC) + 14δ (CCO) + 13δ (CCH$_1$)
485	475	2.0	0.7	b$_2$	65δ (CCO) + 15δ (CCH$_1$)
440	446	0.0	0.1	a	37δ (COC) + 18δ (CCO) + 15ν (CC)
274	267	0.0	0.1	a	16τ (H1CCO) + 15τ (H1COC) + 10τ (OCCO) + 10τ (H$_1$CCH$_1$)
262	264	0.9	0.0	b$_1$	27τ (H1COC) + 15τ (H2COC) + 11τ (CCOC) + 11τ (H$_2$CCO)
91	44	9.8	0.0	b$_2$	37τ (H$_1$COC) + 36τ (H$_2$COC) + 25τ (CCOC)

[a] Key: ν indicates bond stretching, δ interbond angle deformation, and τ torsional angle deformation.

same way as for the chair form, *e.g.*, those in the region 2950−2850 cm^{-1} are all CH stretches. Again the lowest wavenumber vibrations are the most interesting from a conformational point of view. The vibration at 89 cm^{-1} corresponds to conversion to the boat forms. Both boat forms are obtainable *via* this vibration, but less displacement is required to achieve the 2,5 boat form than the 1,4 boat form.

The 1,4 twist-boat has D_2 symmetry, and its 36 fundamental vibrations can be divided into 10 of a-type symmetry, 9 of b$_1$-type symmetry, 9 of b$_2$-type symmetry, and 8 of b$_3$-type symmetry. Once again, the vibrations can be classified into the same groups as for the chair form. Two different half-chair conformers are obtained *via* the vibration at 262 cm^{-1}; vibration one way leads to the two oxygen atoms and carbon atoms 3 and 4 being planar, and vibration the other way leads to the two oxygen atoms and carbons 1 and 2 being planar (see Figure 1g). The lowest vibration at 91 cm^{-1} corresponds to conversion to the 2,5 boat.

Conformational Analysis. We propose two mechanisms for dioxane inversion:

chair → [1,4 half-chair] → 1,4 twist-boat →
[1,4 half-chair] → chair

and

chair → [1,4 half-chair] → 1,4 twist-boat →
[2,5 boat] → ... → 1,4 twist-boat → [1,4 half-chair] → chair

This proposal is based on the vibrational analysis and by comparison with the established mechanism of inversion for cyclohexane.

Excitation to the 1,4 half-chair is *via* the lowest wavenumber vibration of the chair form. It is the simplicity of the mechanism of activation to this form that leads us to the conclusion that the 1,4 half-chair forms the barrier to inversion, rather than the lower energy 2,5 half-chair conformation. The 1,4 half-chair can then relax to either the 1,4 twist-boat structure or back to the chair form. If there is enough energy in the system, then this transformation can continue all the way through the 1,4 twist-boat to the other 1,4 half-chair. Otherwise, the molecule may become trapped in the 1,4 twist-boat conformation until enough energy is available to overcome the energy barrier. The two 1,4 twist-boat forms are connected to the 2,5 boat conformer *via* the lowest vibration at 91 cm^{-1}. The calculated values for ΔG, ΔH, and ΔS for several transformations of cyclohexane and 1,4-dioxane are given in Table 6 for comparison.

If we assume that the inversion of both cyclohexane and dioxane is *via* a half-chair transition state, then the calculated $\Delta G^{\ddagger}_{\mathrm{c}}$ of activation to ring inversion is +43.75 and +41.72 kJ mol^{-1}, respectively. The HF calculated $\Delta G^{\ddagger}_{\mathrm{c}}$ for dioxane is in good agreement with the reported experimental[10,11] value of 40.6 kJ mol^{-1} and gives further evidence that the 1,4 half-chair is the transition state, rather than the 2,5 half-chair. The HF calculated $\Delta G^{\ddagger}_{\mathrm{c}}$ for cyclohexane is also in good agreement with experiment: the gas phase NMR value[3] is 43.7 kJ mol^{-1} and that from low temperature NMR studies[20] is 43.1 kJ mol^{-1}. A

TABLE 5: Scaled HF and BLYP Wavenumbers and HF IR and Raman Intensities for the 2,5 Twist-Boat Conformer of 1,4-Dioxane

wavenumber/cm^{-1}		IR	Raman		
HF	BLYP	intensity (HF)	intensity (HF)	sym	potential energy distribution[a] (HF)
2953	3000	34.5	72.1	a	$68\nu(\mathrm{CH_3}) + 26\nu(\mathrm{CH_1})$
2948	2997	70.6	15.2	b	$72\nu(\mathrm{CH_3}) + 24\nu(\mathrm{CH_1})$
2932	2976	3.2	24.9	b	$70\nu(\mathrm{CH_1}) + 26\nu(\mathrm{CH_3})$
2932	2974	35.2	26.1	a	$66\nu(\mathrm{CH_1}) + 28\nu(\mathrm{CH_3})$
2874	2882	82.7	100.0	a	$55\nu(\mathrm{CH_4}) + 38\nu(\mathrm{CH_2})$
2861	2866	100.0	10.3	b	$80\nu(\mathrm{CH_2}) + 13\nu(\mathrm{CH_4})$
2851	2860	5.6	20.2	a	$55\nu(\mathrm{CH_2}) + 41\nu(\mathrm{CH_4})$
2844	2856	21.0	9.6	b	$83\nu(\mathrm{CH_4}) + 15\nu(\mathrm{CH_2})$
1512	1493	1.3	1.4	a	$59\delta(\mathrm{HC_2H}) + 17\delta(\mathrm{HC_1H})$
1494	1481	1.3	0.7	b	$69\delta(\mathrm{HC_1H})$
1492	1477	0.6	6.2	b	$67\delta(\mathrm{HC_2H})$
1491	1471	0.1	9.4	a	$60\delta(\mathrm{HC_1H}) + 18\delta(\mathrm{HC_2H})$
1419	1391	2.1	1.1	a	$18\delta(\mathrm{OCH_1}) + 14\delta(\mathrm{CCH_1}) + 14\nu(\mathrm{CC}) + 11\delta(\mathrm{CCH_4})$
1412	1377	8.1	0.4	b	$18\delta(\mathrm{CCH_2}) + 14\delta(\mathrm{CCH_3}) + 11\delta(\mathrm{OCH_2}) + 11\delta(\mathrm{OCH_3})$
1386	1350	19.4	2.0	b	$22\delta(\mathrm{OCH_4}) + 21\delta(\mathrm{OCH_1}) + 17\delta(\mathrm{CCH_4}) + 14\delta(\mathrm{CCH_1})$
1351	1325	0.0	1.2	a	$18\delta(\mathrm{OCH_4}) + 14\delta(\mathrm{CCH_2}) + 13\delta(\mathrm{CCH_4}) + 13\delta(\mathrm{CCH_3})$
1285	1262	4.3	1.9	a	$29\delta(\mathrm{OCH_3}) + 27\delta(\mathrm{OCH_4}) + 12\delta(\mathrm{CCH_4}) + 12\delta(\mathrm{CCH_3})$
1271	1243	38.6	3.4	b	$39\delta(\mathrm{OCH_3}) + 17\delta(\mathrm{CCH_3}) + 13\delta(\mathrm{OCH_4})$
1243	1214	1.7	4.1	a	$32\delta(\mathrm{OCH_2}) + 18\delta(\mathrm{CCH_2}) + 17\delta(\mathrm{OCH_1}) + 12\delta(\mathrm{CCH_1})$
1240	1212	34.0	4.6	b	$32\delta(\mathrm{OCH_2}) + 28\delta(\mathrm{OCH_1}) + 11\delta(\mathrm{CCH_2})$
1184	1147	99.4	1.2	b	$26\nu(\mathrm{OC_2}) + 13\delta(\mathrm{OCH_3}) + 13\delta(\mathrm{CCH_1}) + 13\delta(\mathrm{OCH_4})$
1173	1104	5.0	0.6	a	$42\nu(\mathrm{OC_1}) + 30\nu(\mathrm{OC_2})$
1155	1067	56.4	1.9	b	$16\delta(\mathrm{CCH_3}) + 14\delta(\mathrm{OCH_1}) + 13\delta(\mathrm{CCH_4}) + 12\nu(\mathrm{OC_1})$
1105	1058	1.7	0.3	a	$20\nu(\mathrm{OC_2}) + 18\delta(\mathrm{OCH_1})$
1013	965	10.8	6.7	a	$37\nu(\mathrm{CC}) + 24\nu(\mathrm{OC_1}) + 20\nu(\mathrm{OC_2})$
990	962	1.2	0.4	b	$16\nu(\mathrm{OC_2}) + 14\delta(\mathrm{OC_1C}) + 13\nu(\mathrm{OC_1}) + 13\delta(\mathrm{OC_2C})$
890	871	22.7	0.1	b	$44\nu(\mathrm{CC}) + 18\nu(\mathrm{OC_2}) + 17\delta(\mathrm{CCH_2})$
857	837	38.6	0.4	b	$29\nu(\mathrm{OC_1}) + 15\delta(\mathrm{CCH_3}) + 13\nu(\mathrm{OC_2})$
854	814	7.1	3.1	a	$19\nu(\mathrm{CC}) + 18\delta(\mathrm{CCH_1}) + 17\delta(\mathrm{CCH_2}) + 15\delta(\mathrm{CCH_4})$
837	809	5.1	5.5	a	$39\nu(\mathrm{OC_1}) + 25\nu(\mathrm{CC}) + 12\delta(\mathrm{CCH_3})$
649	636	14.2	0.1	b	$20\delta(\mathrm{CCH_4}) + 17\delta(\mathrm{CCH_1}) + 14\delta(\mathrm{COC}) + 13\delta(\mathrm{OC_1C})$
525	513	0.4	1.4	a	$29\delta(\mathrm{OC_2C}) + 22\delta(\mathrm{OC_1C}) + 12\delta(\mathrm{CCH_1}) + 11\delta(\mathrm{CCH_4})$
442	440	0.0	0.9	a	$49\delta(\mathrm{COC}) + 15\delta(\mathrm{OC_2C})$
304	308	6.3	0.0	a	$47\tau(\mathrm{C_1OCC}) + 14\delta(\mathrm{OC_2C}) + 14\tau(\mathrm{OCCO})$
237	239	5.3	0.0	b	$38\tau(\mathrm{C_1OCC}) + 24\tau(\mathrm{OCCO}) + 20\tau(\mathrm{C_2OCC})$
89	85	4.0	0.0	a	$46\tau(\mathrm{C_2OCC}) + 38\tau(\mathrm{OCCO}) + 11\tau(\mathrm{C_1OCC})$

[a] Key: ν indicates bond stretching, δ interbond angle deformation, and τ torsional angle deformation.

TABLE 6: ΔG, ΔH and ΔS for Selected Cyclohexane and 1,4-Dioxane Transformations Calculated at the HF/6-31G* Level[a]

transformation	ΔG	ΔH	ΔS	T
1,4-Dioxane				
chair → 1,4 twist-boat	+26.23	+27.41	+3.96	298.15
chair → 1,4 half-boat	+41.72	+43.91	+7.35	298.15
1,4 twist-boat → 1,4 half-chair	+16.81	+17.80	+9.90	100.00
Cyclohexane				
chair → twist-boat	+25.79	+28.89	+10.40	298.15
chair → half-chair	+43.75	+46.11	+7.92	298.15
twist-boat → half-chair	+18.15	+18.64	+4.90	100.00

[a] Units: ΔG and ΔH in kJ mol^{-1}, ΔS in J K^{-1} mol^{-1}, and temperature in K.

previously published calculation of this free energy of activation at the MP2 level[4] gave 44.1 kJ mol^{-1}. Our HF calculated activation enthalpy for cyclohexane ($\Delta H^{\ddagger}_{c} = 46.1$ kJ mol^{-1}) is somewhat lower than the value obtained from gas phase NMR studies[3] (50.4 kJ mol^{-1}), and here the previously published MP2 level calculations[4] are in better agreement with the gas phase value. The fact that our HF/6-31G* level $\Delta H^{\ddagger}_{c}$ value is closer to the experimental value from low-temperature NMR studies[20] (45.2 kJ mol^{-1}) is perhaps fortuitous, and it appears that less reliance can be placed on HF calculated $\Delta H^{\ddagger}_{c}$ values than for $\Delta G^{\ddagger}_{c}$ values for dioxane as well as for cyclohexane. It is the mechanism of inversion that is the main focus of interest in this paper, however, and accordingly we judge that our vibrational analysis obviates the need for further thermodynamic parameter calculations at the MP2 level.

Acknowledgment. We are grateful for financial support from the U.K. Engineering and Physical Sciences Research Council.

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