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Conformational Analysis of 5-Substituted 1,3-Dioxanes. 6. Study of the Attractive *Gauche* Effect in O-C-C-O Segments.[1]

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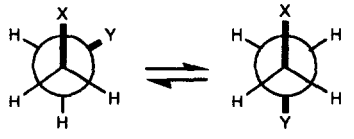
Abstract

The positions of equilibrium, established by acid catalysis, between diastereomeric *cis*- and *trans*-5-methoxy- (**2**), 5-methanesulfonyloxy- (**3**), 5-*p*-(methylphenyl)sulfonyloxy- (**4**), and 5-(*p*-nitrophenyl)sulfonyloxy-2-phenyl-1,3-dioxanes (**5**) are reported. Quantitation of the O-C-C-O attractive *gauche* effects in these compounds revealed substantial *gauche* effects in **3-5**; i.e., when the substituent at C(5) is tosylate, nosylate, and mesylate. No significant attractive *gauche* effect was observed for the 5-methoxy derivative. Good correlations between the magnitude of the attractive *gauche* effect and the positive character of the antiperiplanar hydrogens (H-4,6ax) in the *cis* diastereomers, as well as between the nucleofugicity of the 5-substituents and the energies for the unoccupied orbitals of lowest energy (E_{LUMO}) in the corresponding dioxanes, appear to support a hyperconjugative $\sigma_{C\text{-}H} \rightarrow \sigma^*_{C\text{-}OR}$ interpretation of the attractive *gauche* effect.

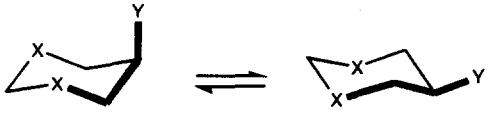
Introduction

Conformational equilibria in 1,2-disubstituted ethanes involve, as shown in eqs 1 and 2, *gauche* ⇌ *anti* interconversion of the 1,4-heterobutane segments present in the molecules.



(1)

gauche *anti*



(2)

gauche *anti*

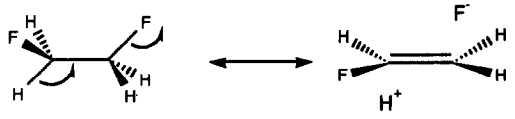
Repulsive steric and polar interactions usually make the *gauche* conformation significantly less stable relative to the *anti* one. There are, however, cases in which the *gauche* conformation is favored more (or the *anti* less) than calculated by consideration of steric and polar interactions. These cases have been treated in terms of a special "attractive *gauche* effect".[2-4]

The origin of the *gauche* attractive effect has been discussed by several authors. Wolfe has proposed a rationalization based on Allen's dissection of the total energy in a system into attractive and repulsive components.[5,6] The attractive component of E is V_{ne}, the nuclear-electron attraction, and the repulsive component is (V_{nn} + V_{ee} + T), where V_{nn} is the nuclear-nuclear repulsion, V_{ee} is electron-electron repulsion, and T is the kinetic energy of the electrons (eq 3).

$$E = (T + V_{nn} + V_{ee}) + (V_{ne}) \qquad (3)$$

It is argued that for small and electronegative substituents (e.g., F, O, CN) in a *gauche* arrangement, nuclear-electron attraction is more important than nuclear-nuclear and electron-electron repulsion.

The attractive *gauche* effect can also be interpreted as a hyperconjugative effect, in particular, bond-antibond orbital interactions.[7-10] Thus in the *gauche* conformation of 1,2-difluoroethane, the C-H bonds serve as donors to the antiperiplanar C-F bonds (acceptors) (eq 4).



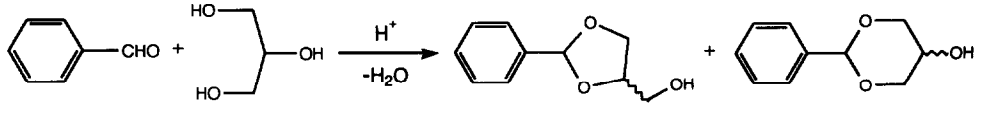
(4)

The present paper describes the preparation, and chemical equilibration of a series of 5-O-substituted 1,3-dioxanes. Evaluation of the attractive *gauche* effect in these compounds incorporating the O-C-C-O segment, and interpretation of the results with consideration of spectroscopic and quantum mechanical observations, was aimed at distinguishing between the above mentioned mechanisms.

Results and Discussion

A. Syntheses of the Diastereomeric *cis*- and *trans*-2-Phenyl-5-(*O*)-substituted-1,3-dioxanes.

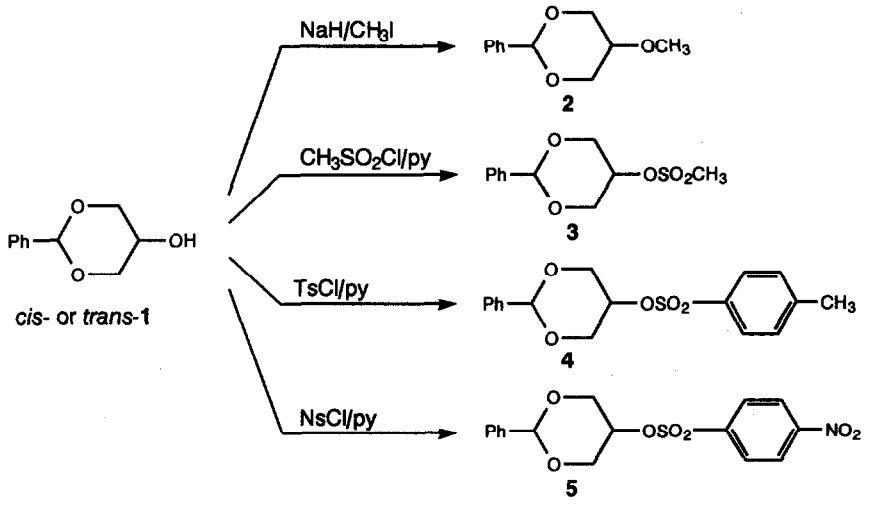
Condensation of benzaldehyde and glycerol, according to the described procedure,[11] afforded a 47:30:23 mixture of 5-membered dioxolanes, *cis*-2-phenyl-5-hydroxy-1,3-dioxane (*cis*-**1**), and *trans*-**1**, respectively (Scheme 1). Upon continued exposure to acid, this ratio changed to 22:34:44; i.e., thermodynamic control favors the 6-membered rings.



cis- and *trans*-**1**

Scheme 1

The diastereomeric carbinols 1 were separated by flash chromatography, and then converted to the corresponding methyl ethers by alkylation with sodium hydride/methyl iodide[12] (Scheme 2). In addition, *cis*- and *trans*-1 were treated with methylsulfonyl, *para*-toluensulfonyl, and *para*-(nitrophenyl)sulfonyl chloride (in solvent pyridine) to yield the desired mesylate, tosylate, and nosylate derivatives[13,14] (Scheme 2). Tables 1 and 2 contain the ^{1}H and ^{13}C chemical shifts in 1-5.



Scheme 2

Table 1. ^{1}H NMR Chemical Shifts (δ) for 1-5 at 270 MHz, at 27° C in $CDCl_3$.

	H(2)	H(4,6ax)	H(4,6ec)	H(5)	H(Ar-C2)	CH_3	H(Ar-C5)
cis-1	5.60	4.15	4.15	3.62	7.4-7.7		
trans-1	5.28	3.35	4.10	3.68	7.2-7.6		
cis-2	5.57	4.03	4.37	3.15	7.3-7.7	3.45	
trans-2	5.45	3.60	4.45	3.60	7.3-7.6	3.45	
cis-3	5.60	4.24	4.48	4.75	7.3-7.6	3.15	
trans-3	5.46	3.83	4.47	4.86	7.3-7.5	3.07	
cis-4	5.55	4.11	4.29	4.55	7.3-7.6	2.50	7.3-8.0
trans-4	5.45	3.75	4.30	4.65	7.3-7.7	2.50	7.4-8.0
cis-5	5.56	4.20	4.20	4.68	7.3-7.5		8.2-8.5
trans-5	5.42	3.80	4.29	4.71	7.3-7.5		8.1-8.4

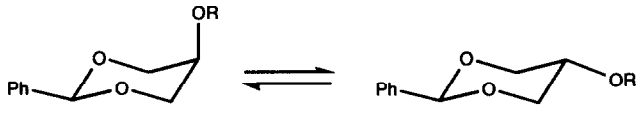
Table 2. ^{13}C NMR Chemical Shifts (δ) for **1-5** at 22.49 MHz, at 27° C in $CDCl_3$.

	C(2)	C(4,6)	C(5)	C*i*	C*o*	C*m*	C*p*	C*i'*	C*o'*	C*m'*	C*p'*	CH_3
cis-**1**	101.40	72.06	63.74	137.85	125.80	128.05	128.83					
trans-**1**	100.79	71.37	60.79	137.16	125.97	128.18	128.96					
cis-**2**	101.15	68.43	56.34	138.17	126.07	128.03	128.72					72.12
trans-**2**	100.92	69.59	56.85	137.55	125.84	127.92	128.62					69.37
cis-**3**	101.05	69.09	71.42	137.30	125.92	128.25	129.12					38.97
trans-**3**	101.26	68.65	67.77	136.72	126.09	128.36	129.27					38.18
cis-**4**	100.89	68.82	72.34	137.35	125.92	128.03	128.95	144.88	127.49	129.82	133.61	21.42
trans-**4**	101.14	68.53	68.10	136.68	125.96	127.85	128.29	145.46	129.15	130.07	132.68	21.62
cis-**5**	99.48	67.52	73.48	136.32	126.95	127.87	128.03	141.09	124.84	123.58	149.54	
trans-**5**	101.27	68.28	69.36	136.42	125.97	128.30	129.22	141.63	129.22	124.62	151.00	

B. Conformational Analyses of 2-5.

Equilibration (*cis* ⇌ *trans*) of diastereomeric dioxanes **2-5** was readily performed by means of BF_3.[15] The corresponding free energy differences are summarized in Table 3, which includes, for comparison purposes, the conformational preference of the methoxy, mesylate, tosylate, and nosylate substituents in cyclohexane.

Table 3. Conformational Equilibria (kcal/mol), and Magnitude of the Attractive *Gauche* Effect, in 5-Substituted 1,3-Dioxanes **2-5**.



X	ΔG° exptl	ΔG° cyclohexane[a]	ΔG° steric	$\Delta\Delta G^\circ$[b] (*gauche* effect)
OMe	-0.24 (±0.03)	-0.55	-0.29	0.05
OTs	-0.01 (±0.03)	-0.52	-0.26	0.25
ONs	+0.34 (±0.03)	c	-0.26	0.60
OMs	+0.48 (±0.04)	-0.56	-0.26	0.74

[a] Refs 16 and 17. [b] $\Delta\Delta G^\circ = \Delta G^\circ$exptl - ΔG°steric. [c] Not known.

Quantitation of the attractive *gauche* effect in **2-5** is not straight forward owing to the different steric requirements of a substituent at C(5) in 1,3-dioxane and in cyclohexane. For example, the usual equatorial preference of substituents in cyclohexane is largely due to the repulsive steric interactions with the axial hydrogens of the 3- and 5-positions; such interaction is absent in the analogous

5-substituted 1,3-dioxane, and therefore the magnitude of the attractive *gauche* effect tends to be overestimated.

Following a similar approach to that developed by Franck for the quantitation of anomeric effects,[18,19] we suggest the incorporation of a correction factor for the steric effect of an axial substituent at C(5) in the heterocycle, that can be approximated by comparison of *A*-values for substituents incapable of displaying an attractive *gauche* effect *versus* the conformational preferences of these groups in the heterocycle.

In this fashion, a correction factor α is applied (eq 5), and the magnitude of the *gauche* effect is then calculated according to equation 6.

$$\Delta G^{\circ}_{\text{steric}} = \alpha \cdot \Delta G^{\circ}_{\text{cyclohexane}} \qquad (5)$$

$$\textit{Gauche}\ \text{effect} = \Delta\Delta G^{\circ} = \Delta G^{\circ}_{\text{heterocycle}} - \Delta G^{\circ}_{\text{steric}} \qquad (6)$$

For example, the accepted *A*-value of 1.74 kcal/mol for a methyl group in cyclohexane diminishes, by a factor of 0.52, to 0.9 kcal/mol when at C(5) in 1,3-dioxane.[15] In the case of **2**, substracting the observed equatorial preference of -0.24 kcal/mol from the interpolated $\Delta G^{\circ}_{\text{steric}}$ for a 5-methoxy group [(0.55 x 0.52) - 0.24], indicates a rather small attractive *gauche* effect of 0.05 kcal/mol.[20] By contrast, substantial attractive *gauche* effects are derived for the tosylate, nosylate and mesylate substituents (Table 3).

C. Interpretation of the Results

We first sought for a relationship between the attractive *gauche* effect ($\Delta\Delta G^{\circ}$) and the nucleofugicity[23] of the 5-substituent. An interesting observation (Table 4) is that methoxy, a very poor nucleofuge, gives rise indeed to a very small attractive *gauche* effect. On the other hand, the tosylate, mesylate and nosylate groups are all good nucleofuges and present substantial effects (Table 4). Importantly, a good correlation was found between the nucleofugicity for each substituent and the energy of the lowest unoccupied orbital for the corresponding dioxanes, as determined from CNDO/2 calculations.[25a] (Table 4).

Table 4 Nucleofugicity[23] of the Sulfonate Groups in **3-5**, and Attractive *Gauche* Effect ($\Delta\Delta G^{\circ}$).

Cmpd.	Leaving Group	k_{rel}[a]	E_{LUMO} (a.u.)	$\Delta\Delta G^{\circ}$ (kcal/mol)
2	**-OCH_3**	~0	0.229	0.05
4	**-$OSO_2C_6H_4$-*p*-CH_3**	0.70	0.057	0.25
3	**-OSO_2CH_3**	1.00	0.048	0.74
5	**-$OSO_2C_6H_4$-*p*-NO_2**	13.00	0.007	0.60

[a] Ref 26.

It must be noted, however, that the mesylate group presents a stronger attractive *gauche* effect than the nosylate substituent, despite the fact that the latter is a much better leaving group. This result hints to the participation of a second stabilizing interaction for axial mesylate, but not for axial tosylate or nosylate. In this regard, AM1 calculations[25b] indicate that the lowest-energy conformer of *cis*-**3** presents a mesyl-outside [τ C(4)-C(5)-O(7)-S = 59.04°], methyl-up [τ C(5)-O(7)-S-CH_3 = 170°] conformation (Figure 1). The results of the AM1 study also indicate substantial positive charge at H(4,6-eq) (net charge +0.14 e^-) and substantial negative charge at the sulfonyl oxygens (net charge -0.97 e^-), so that we speculate the existence of an attractive electrostatic interaction between these atoms (Figure 1). According to this interpretation, delocalization of the electron density into the aromatic rings of the tosylate and nosylate analogues causes the magnitude of such interaction to dwindle in *cis*-**4** and *cis*-**5**.

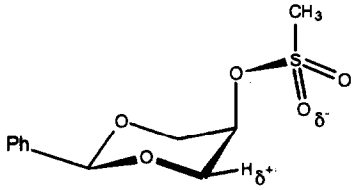


Figure 1. Attractive electrostatic interation in *cis*-**3**.

Much better correlations were found between $\Delta\Delta G^\circ$ and the charge present at H(4,6ax), or the proton NMR chemical shifts for the same hydrogens in **2-5** (Figures 2 and 3). Charges were estimated from CNDO/2 calculations, and the chemical shifts were, of course, extracted from the experimental NMR spectra (270 MHz, all in solvent $CDCl_3$).

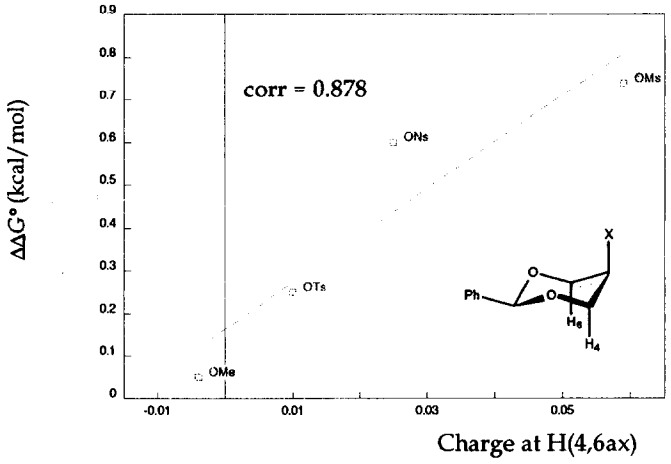


Figure 2. $\Delta\Delta G^\circ$ vs charge in axial H(4,6), as evaluated by CNDO/2 calculations.

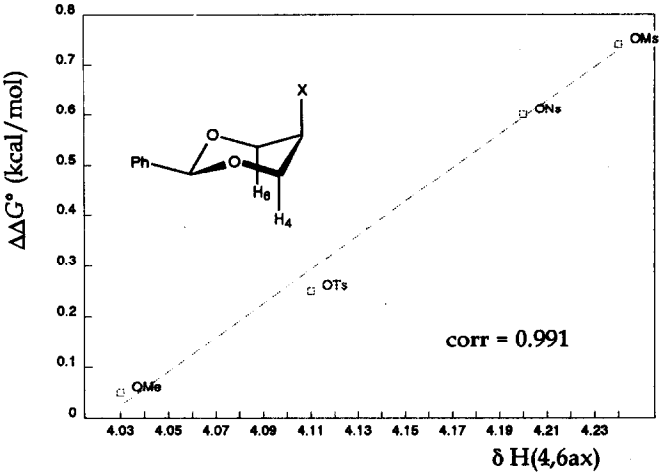
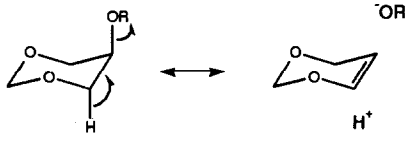


Figure 3. $\Delta\Delta G^{\circ}$ in dioxanes **2-5** *vs* ^{1}H NMR chemical shifts for H(4,6ax) in the *cis* isomer.

The above results, in particular the excellent correlation between the magnitude of the attractive *gauche* effect and the chemical shifts for the antiperiplanar hydrogens in *cis*-**2-5**, appear to support the hyperconjugative ($\sigma_{C\text{-}H} \rightarrow \sigma^{*}_{C\text{-}OR}$) mechanism[7-9] as responsible for the stabilization of the axial isomer; i.e., the attractive *gauche* effect (eq 7).



(7)

D. Summary

The conformational preferences of the methoxy, tosylate, nosylate and mesylate substituents in 5-substituted 1,3-dioxanes were evaluated by chemical equilibration of the appropriate diastereomeric models.

Quantitation of the O-C-C-O attractive *gauche* effects in these systems was carried out by consideration of the relative steric requirements of the -OR substituents in cyclohexane and the heterocycle. Substantial attractive *gauche* effects were found for **3-5**; i. e., when the substituent at C(5) is tosylate, nosylate and mesylate. No significant *gauche* effect was observed for the -OR equal methoxy.

Good correlations between the magnitude of the attractive *gauche* effect and the charge at the antiperiplanar hydrogens H(4,6ax) in the *cis* isomers (*gauche* models), as well as between the nucleofugicity of the 5-substituents and the energies for the empty orbitals of lowest energy (E_{LUMO}), could support the hyperconjugative ($\sigma_{C\text{-}H} \rightarrow \sigma^{*}_{C\text{-}OR}$) mechanism as an explanation of the attractive *gauche* effect.

Experimental Section

General Information. Melting points were obtained in a Mel Temp apparatus with an open capillary tube.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Proton NMR spectra were recorded on Varian EM-390 (90 MHz) and JEOL GSX270 (270 MHz) spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX-90Q (22.49 MHz) instrument, operated in pulse Fourier transform mode and locked on solvent deuterium.

Theoretical calculations were carried out with PCMODEL[27] and Allinger's MM2/77 program[28] in order to minimize the molecular structures, and CNDO/2[25] in the final studies.

***cis*- and *trans*-2-Phenyl-5-hydroxy-1,3-dioxane (*cis*- and *trans*-1).** These compounds were prepared by condensation of glycerol (8.93 g, 0.098 mol) and benzaldehyde (10.44 g, 0.098 mol) according to a published procedure.[29] The crude product (15.56 g) consisted of a mixture of 1,3-dioxolanes and 1,3-dioxanes. This mixture was separated by flash chromatography (hexane/ethyl acetate, 1:1) to afford 3.1 g (17.2 % yield) of *trans*-1 as a colorless oil, and 4.1 g (23.1 % yield) of *cis*-1 as white crystals, mp 84-84.5°C (lit.[29] mp 84°C). ^1H NMR spectrum in Table 1. ^{13}C NMR spectrum in Table 2.

***cis*- and *trans*-2-Phenyl-5-methoxy-1,3-dioxane (*cis*- and *trans*-2).** These compounds were prepared as described in the literature.[29] Carbinol *cis*-1 (6.45 g, 0.036 mol) was treated with 1.03 g (0.043 mol) of sodium hydride and 0.502 g (0.042 mol) of methyl iodide to afford 6.80 g (96.4 % yield) of crystalline *cis*-2, mp 47-48°C (lit.[30] mp 50°C). ^1H and ^{13}C NMR spectra in Tables 1 and 2, respectively.

Similarly, *trans*-1 was converted to *trans*-2 in 95 % yield. This compound is a colorless oil whose ^1H and ^{13}C NMR spectra are described in Tables 1 and 2, respectively.

***cis*- and *trans*-2-Phenyl-5-methanesulfonyloxy-1,3-dioxane (*cis*- and *trans*-3).** These compounds were synthesized according to the published procedure.[31] *cis*-2-Phenyl-5-hydroxy-1,3-dioxane (0.925 g, 5.1 mmol) was treated with 0.584 (5.1 mmol) of methanesulfonyl chloride to afford 1.259 g (95.5 % yield) of *cis*-3, mp 134-135°C (lit.[31] mp 134-135°C). ^1H and ^{13}C NMR spectra in Tables 1 and 2, respectively.

In similar fashion, *trans*-1 was converted to *trans*-3 in 96 % yield, mp 106-107°C (lit.[31] mp 106-107°C). ^1H and ^{13}C NMR spectra in Tables 1 and 2, respectively.

***cis*- and *trans*-2-Phenyl-5-(p-methylphenyl)sulfonyloxy-1,3-dioxanes (*cis*- and *trans*-4).** According to the general procedure of Fieser and Fieser,[13] one gram (5.6 mmol) of *cis*-1 was treated with 1.16 g (6.1 mmol) of tosyl chloride to furnish 2.0 g (98 % yield) of *cis*-4, mp 122-123°C (lit.[32] mp 127-128°C). ^1H and ^{13}C NMR spectra in Tables 1 and 2, respectively.

Similarly, *trans*-1 was converted to *trans*-4 in 98 % yield, mp 94-95°C (lit.[32] mp 95-96°C). ^1H and ^{13}C NMR spectra in Tables 1 and 2, respectively.

***cis*-and *trans*-2-Phenyl-5-(p-nitrophenyl)sulfonyloxy-1,3-dioxanes (*cis*- and *trans*-5).** The common procedure[13] was modified as follows. In a dry 50 mL round-bottom flask provided with magnetic stirrer, 0.4 g (2.2 mmol) of *cis*-1, 20 mL of benzene and 0.18 g (2.2 mmol) of pyridine were placed. (*p*-Nitrophenyl)sulfonyl chloride (0.49 g, 2.2 mmol) was added dropwise with stirring, and the reaction mixture was stirred at ambient temperature for 2 hours, and then left standing for 24 h at 5°C. The reaction mixture was washed with water and extracted with methylene choride. The usual workup procedure afforded 0.75 g (92 % yield) of *cis*-5, mp 144-145°C. The *trans* isomer, *trans*-5, was obtained in similar fashion, mp 114-116°C. ^{1}H and ^{13}C NMR spectra in Tables 1 and 2, respectively. The purity of these compounds was estimated as ≥ 97%.

Equilibrations and Analysis. Equilibrium was approached from both sides; boron trifluoride etherate was the catalyst: *ca.* 50 mg of the dioxane was placed in a 20 mL ampoule and dissolved in 10 mL of chloroform before the addition of two to three drops of the catalyst. The ampule was sealed and submerged in a constant-temperature bath (Brinkmann, RM6 LAUDA) until equilibrium was reached. Quenching was effected by pouring the equilibrating solution into aqueous sodium bicarbonate. The dioxanes were then extracted with chloroform, dried, and evaporated, and the progress of the equilibration was conveniently monitored by ^{1}H NMR spectroscopy.

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[20] In contrast, both 1,2-dimethoxyethane[21] and poly(ethylene glycol)[22] are predominantly in the *gauche* conformation about the C-C bond. (We suspect entropy effects are responsible for this contrasting behavior).

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