VERY SLOW ROTATION ABOUT A CARBON-CARBON SINGLE BOND IN *o*-TOLYL-1,1'-DIADAMANTYLCARBINOL AND RELATED COMPOUNDS

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Abstract—Previous work on the ap and sp rotamers of a-tolyldi-t-butycarbinol (1a and 2a) has been extended to 1-adamantyl derivatives which are found to have abnormally high barriers to the $ap \rightarrow sp$ rotation. A semiquantitative explanation of the activation enthalpies for this conformational change is proposed. Rotameric ap and sp a-tolyl-1-adamantyl-t-butylcarbinols (1b and 2b) and a-tolyl-1,1'-diadamantylcarbinols (1c and 2c) are synthesised by the addition of a-tolyl-lithium to 1-adamantyl-t-butylketone and 1,1'-diadamantylketone, respectively. In both cases the major product is the less stable ap isomer. The rotation rates of 1b and 1c in dodecane correspond to activation energies of 33.9 and 39.1 kcal mol⁻¹, respectively, even higher than that for 1a, 29.8 kcal mol⁻¹. Steric energies are calculated by molecular mechanics for model structures corresponding to the ap and sp isomers and to two points on the rotation pathway, giving extrapolated theoretical activation enthalpies in qualitative agreement with the experimental data. The enhanced steric effect of the 1-Ad group can be attributed to three factors: restricted rotation of the methylene groups as opposed to the methyl groups in t-Bu: increase in bond angle strain due to the terminal cyclohexane ring; increase in non-bonding interactions by buttressing effects of the terminal cyclohexane methine and methylene hydrogens.

Stable rotamers (atropisomers, conformational isomers) can be isolated provided that the barrier to rotation about the relevant bond is sufficiently high and that the system possesses an asymmetric element which allows differentiation of the conformations.¹ The scope of research in this area is limited by the requirement that both of these conditions be satisfied, but in the last 12 years a number of rotamer pairs have been investigated, starting with bridged structures, such as fluorene² and triptycene³ derivatives. Triarylmethanes⁴ have also been studied and, more recently, the aryldi-*t*-butylcarbinols,⁵ 1a and 2a.

Whereas restricted rotation is usually followed by dynamic NMR,⁶ the rotamers obtained in this last case are so stable and so well differentiated that they can be analysed by glc. We now wish to report that replacement of the *t*-butyl groups by 1-adamantyl raises the activation energy for rotation about the sp^2-sp^3 carbon-carbon bond to the unprecedentedly high value of 39 kcal mol⁻¹.

Previously it was found that the introduction of the 2-methyl group⁵ raises the rotational barrier of phenyldit-butylcarbinol⁷ from about 20 to 29 kcal mol⁴. Elsewhere the presence of bulky substituents has been observed to slow the rate of rotation about C-C single bonds^{7a.8} but rarely has any attempt been made to interpret substituent effects upon rotational barriers quantitatively. The unexpectedly large steric effect of the 1-Ad group clearly called for an explanation and, insofar as the symmetry of the t-Bu and 1-Ad groups facilitates calculation, we felt that this was an appropriate startingpoint for a computer-assisted interpretation of the rotation rates. For various reasons a number of drastic simplifications have been made but, nevertheless, the results are in qualitative agreement with the experimental observations.

RESULTS AND DISCUSSION

We have developed a new synthesis of 1,1'-diadamantylketone, previously prepared by Wierniga *et al.* from 1-adamantylcarbonitrile.⁹ Recent success with the Barbier-type synthesis of 1-adamantyl derivatives *via* as yet unidentified organo-lithium species¹⁰ suggested that an easier route was conceivable. Addition of organo-lithium or organo-magnesium compounds to esters usually results in tertiary alcohols but, since tri-(1-adamantyl)carbinol is likely to be inaccessible, we reasoned that the reaction could well stop at the required ketone. Reaction of 1-bromoadamantane and the methyl ester of 1-adamantylcarboxylic acid with lithium in THF confirmed this prediction, giving 1,1'-diadamantylketone in 57% yield.

Rotation kinetics

Addition of o-tolyl-lithium to the ketone gave the expected o-tolyldi-(1-adamantyl) carbinols, 1c and 2a, in good yield. The product obtained was predominantly (92%) the less stable, anti-periplanar (ap) isomer, 1c, as indicated by the characteristic NMR and IR spectra. Glc analysis of pure lc, albeit at the rather high temperature required for such an involatile compound (ca. 215°), revealed no peak corresponding to the synperiplanar (sp) isomer, 2c. This contrasts with the behaviour of the corresponding *o*-tolyldi-*t*-butylcarbinol, 1a, where some rotation occurs even at the lowest practicable glc column temperature, about 100°. Study of the rotation kinetics in dodecane (Table 1) revealed that the reaction is indeed very slow with an energy barrier, ΔG^* of some 39.1 kcal mol⁻¹ at 200°. This is almost 10 kcal mol⁻¹ higher than that for 1a (29.8 kcal mol⁻¹)⁵ and about 6 kcal mol⁻¹ greater than that for the rotation of 1-methyl 9-(2-methyl-1-naphtyl)fluorene, the slowest





R ₁ = R ₂	= <u>t</u> -butyl (<u>la</u>)	$R_2 = 1 - ad$ $R_1 = tert$	amantyl (1b) -butyl	$R_1 = R_2 = 1$ -adamantyl (<u>lc</u>)			
т°с	k (s ⁻¹)	T°C	k (s ⁻¹)	т°с	k (s ⁻¹)		
80	1.26 × 10 ⁻⁵	145	3.27×10^{-5}	205	1.31×10^{-5}		
95	5.64×10^{-5}	165	1.75×10^{-4}	225	6.75×10^{-5}		
112	2.75×10^{-4}	185	7.89×10^{-4}	245	2.90×10^{-4}		
130	1.26×10^{-3}	205	3.00×10^{-3}	265	1.26×10^{-3}		
۵H	25.9		29.1		37.5		
۵s۴	-8.2		-10.1		-3.3		
^G [≠] 200	0°C 29.8		33.9		39.1		

Table 1. Rate constants for the rotation of o-tolyldialkylcarbinols in dodecane (ΔH^* and ΔG^* in kcal mol⁻¹, ΔS^* in e.u.)

previously reported.^{2d} Not unexpectedly, a barrier of about 34 kcal/mol, intermediate between those of 1a and 1c, was found for the o-tolyl-1-adamantyl-t-butylcarbinol, 1b, synthesised from the corresponding ketone.

Steric effects: Molecular Mechanics (MM)

Manifestly the rotation rates depend on the different steric requirements of the t-Bu and 1-Ad groups although, according to Taft's steric parameters,¹¹ these groups have rather similar spatial demands. However, it is becoming increasingly evident that the effective size of a group depends upon the constraints imposed by its environment. The current tendency is therefore to adopt a global approach to the interpretation of steric phenomena through empirical force field (molecular mechanics) calculations of strain energies.¹² This approach has been applied successfully to the treatment of solvolvtic and other reactivities in reactions controlled by steric factors, including several cases involving rotation about carbon-carbon single bonds.¹³ The method which has been the most used for rotation is the pointby-point mapping technique wherein energies are calculated for a series of conformations characterized by the value of the twist or dihedral angle about the relevant bond.

In studies on the reactivity of alcohols,¹⁴ the usual practice has been to replace the OH group by H or by Me and to perform calculations on the resulting methanes or ethanes. Though the second model has been used for the interpretation of oxidation rates,¹⁵ our experience with solvolysis suggests that the trisubstituted methanes are a more suitable approximation to congested tertiary alcohols.^{10c,16,17} This model has therefore been adopted in the calculations we shall describe. The modified Boyd-Allinger force field for benzenoid hydrocarbons was used.¹³

We first examined the relative stabilities of the rotamers (Table 2). Replacing t-Bu by 1-Ad increases the steric energy by an amount which is very close to the intrinsic difference¹⁸ between the two groups, about 2.9 kcal mol⁻¹. This is tantamount to saying that steric effects on the ground state energies are additive. Examined more closely, however, the calculations suggest that the differences between the steric energies of the rotamers *diminish* on going from 1a/2a to 1c/2c, while the rotation barriers *increase* in this order. This is the contrary of what would be expected on the basis of Leffler's rate-equilibrium relationship.²⁰ Clearly the difference in the activation energies from 1a to 1c lies in an enhancement of the steric energy of the transition state as t-Bu is replaced by 1-Ad.

	STRUC	TURE			CONFORMATIONS						
R ₁	R ₂	x	Z	N°	<u>A</u> (ap)	<u>B</u>	<u>c</u>	D(sp)	Inter- section		
<u>t</u> -Bu	<u>t</u> -Bu	н	н	I	11.3	31.5	31.5	11.3	38.8		
<u>t</u> -Bu	<u>t</u> -Bu	н	Me	II	19.2 ^a	45.0	45.5	13.0 ^a	56.6		
<u>t</u> -Bu	<u>t</u> ~Bu	Me	Me	III	43.9 ^a	54.1	55.2	36.8 ^a	60.0		
<u>t</u> -Bu	l~Ad	н	Me	IV	21.8	51.7	54.1	16.1	65.4		
l-Ad	<u>t</u> ~Bu	н	Me	v	21.8	56.9	51.1	16.1	66.2		
1-Ad	l∼Ad	н	Me	VI	24.4	65.8	61.1	19.0	76.9		

Table 2. Steric energies of aryldialkylmethanes (kcal mol⁻¹)

^a See ref.19.





P

Q



₽

Ortho-tolyl rotation

Understanding of the following descriptions of the geometrical changes associated with rotation will be facilitated by reference to the Schema, wherein atoms (1) to (16) are common to all three structures; the numbering system is arbitrary.



The rotation of *ap* o-tolyldialkylcarbinols can be considered as proceeding in three steps, each of about 60°: starting with the 2-methyl group roughly midway between the two t-butyl groups, **A**, rotation about the C(3)–C(8) bond first leads to a configuration **B** in which the C(2)–C(3) bond eclipses C(8)–C(9); subsequently the bond C(3)–C(4) eclipses C(8)–C(10), C; thereafter the reaction pathway leads downhill to the stable *sp* isomer, **D**. The transition state for this process must lie between **B** and C,²¹ but attempts to locate it by point-by-point mapping were unsatisfactory.²² Useful qualitative information about substituent effects upon the rotational barriers can, however, be obtained by comparing steric energies and geometries of **B** and **C** with those of the initial conformation **A**.

The calculated steric energies merit certain comments. It is satisfying to observe that the steric energy change on going from A to B or C increases in the order expected, from 1a to 1b to 1c. Barring abrupt changes in the energy profile between B and C, the differences between A and the hypothetical transition state should follow the same order (Fig. 1).

In the figure we have plotted steric energies against the reaction coordinate expressed as the rotation of the *o*-tolyl group relative to the plane which bissects the angle R_1 -C- R_2 in the *ap* conformation. Lines through A and B and C and D are projected to intersect at values of 56.6, 65.4 (66.2 if $R_1 = 1$ -Ad and $R_2 = t$ -Bu) and 76.9 kcal mol⁻¹, considered to be representative of the transition state for reaction of 1a, 1b and 1c, respectively. Taken with the energies of the *ap* conformer, A, these give "theoretical activation energies" of 37.4, 43.6 (44.4) and 52.5 kcal mol⁻¹, which are greater than the experimental activation enthalpies²² by factors of 1.44, 1.50 (1.52) and 1.40, respectively. The results of the MM calculations can therefore be said to be in qualitative agreement with the experimental data.²⁴

The fact that the calculated values are greater than those observed is to be expected insofar as we have replaced the OH group by the smaller H atom. It is



Fig. 1. Plot of steric energy against rotation angle for aryldialkylmethanes. (Roman numerals correspond to N° identifying structures in Table 2).

known that the replacement of an apparently unimportant group by a smaller one increases the rotational barrier.^{1,2a,25} The steric effect of this substituent upon the ground state energy is believed to be higher than that upon the transition state. Calculations on o-tolyldi-*t*butylethane (Table 2) appear to confirm this hypothesis. The effect of replacing H by Me upon the energy of A is indeed much greater than that upon **B** or **C**. Consequently the theoretical activation energy is only 0.62 of the experimental value.

Molecular distortion

As we have noted elsewhere,^{5b} the geometry of the trisubstituted methane differs in some respects from the crystallographic structure of the *sp* alcohol. Nevertheless, indications regarding the geometrical *changes* involved in the rotation process can be ascertained by comparing structures A to D sequentially. Table 3 gives pertinent data regarding the most important bond length, bond angle and dihedral angle changes for the di-t-butyl derivative. Rotation is accompanied by considerable elongation of all the bonds to the central tertiary carbon atom but the angle subtended by the *t*-butyl groups to this carbon is compressed. Bond angles to the aromatic ring and those of the ring itself are also very distorted in both B and C as compared to the rotamers.

Structural differences

Conformation **B** is a suitable point on the reaction coordinate for discussion of the features which distinguish t-Bu from 1-Ad and which allow us to understand qualitatively why there is so much disparity between their steric effects upon rotation rates. Certain features are common to all three structures investigated. One hydrogen at C(1) is generally almost coplanar with carbons (1) to (9) and interacts strongly with two (1-Ad) or four (t-Bu) hydrogens at atoms C(11) and C(12). Non-bonded repulsions between hydrogens at C(13) and C(16) also make a significant contribution to the steric energy. The structural deformations which we have mentioned in connection with rotation in the di-t-butyl derivative are found to be rather similar in the compounds bearing one or two 1-adamantyl groups (Table 4).

Small progressive deviations from normality can, however, be detected in certain of the bond angles and bond lengths, especially those concerned with the aromatic ring and the central tertiary carbon, C(8). These

	Terti	ary carbon	5					
	Во	nd lengths	a	Bond angles	a Di	hedral a	ngles ^a	
Conf.	3.8	8.9	8.10	9.8.10	2.3.8	.9.	2.3.8.10	
Ă	1.527	1.572	1.578	127.0	74.3		-86.3	
B	1.571	1.572	1.594	113.7	0.0)	-133.5	
<u>c</u>	1.569	1,585	1.580	109.0	-50.7		t180.0	
D	1.535	1.572	1.569	125.1	-103.7	,	106.7	
	Benze	noid carbo	ns					
	In	iternal bon	d angles				Exter	nai
Conf.	3.2.7	2.7.6	5.6.7	4.5.6	3.4.5	2.3.4	1.2.3	2.3.8
A	119.7	122.6	118.3	119.1	123.7	116.5	125.4	124.3
В	119.3	125.2	116.6	118.1	127.7	113.1	132.0	133.3
с	120.5	123.9	117.0	118.8	126.5	113.3	126.4	127.6
D	119.1	122.2	119.0	119.1	122.8	117.9	122.8	124.7

Table 3. Sequential variations in geometry of conformation $A \rightarrow D$ for o-tolyldi-t-butylmethane

^a Bond lengths, bond angles and dihedral angles are identified by numbers corresponding to the atoms concerned; thus, a.b. indicates the C(a)-C(b) bond length. Dihedral angle a.b.c.d is positive if clockwise rotation of bond c.d about the axis b.c eclipses it with bond a.b.

Table 4. Principal internal coordinates of the eclipsed conformation, B for the rotation of ap isomers, 1a-1c

		<u>Tertia</u>	ry carbon	8						
		Bond lengths ^a				Bond angle	es ^a D	Dihedral angles ^a		
R	R2	3.8	8.9	8.10		9.8.10	2.3.8	.9 2.	2.3.8.10	
tBu	<u>t</u> Bu	1.571	1.572	1.594		113.7	0.	o -	133.5	
tBu	l-Ad	1.577	1.579	1.605		112.5	0.	0 -	131.2	
I-Ad	I-Ad	1.583	1.596	1,620		113.2	0.	0 -	130.0	
		Benzen	oid carbo	<u>ns</u>	-			Fata	rnal	
R	R.	3.2.7	2.7.6	5.6.7	4.5.6	3.4.5	2.3.4.	1.2.3.	2.3.8	
tBu	<u>t</u> Bu	119.3	125.2	116.6	118.1	127.7	113.1	132.0	133.3	
<u>t</u> Bu	I-Ad	119.7	125.5	116.2	117.9	128.8	112.0	132.3	133.7	
1-Ad	l-Ad	120.4	125.7	115.6	117.6	130.1	110.5	132.4	136.5	

^a See Footnote, Table 3.

reflect the increased steric energy of the more congested transition states. The difference between t-Bu and 1-Ad would appear to lie essentially in the rigidity conferred upon the latter by the terminal cyclohexane ring. This manifests itself in various ways. Firstly, it increases the energetic price of any deformation of the molecular geometry in the vicinity of the tertiary carbons (9) and (10); secondly, whereas *t*-butyl group methyls can rotate in order to reduce interactions, rotation of the corresponding adamantyl group methylenes strains the constituent cyclohexane rings. This is particularly evident near C(1): the quasi-eclipsed methyl hydrogen is equidistant at about 2.14 Å from three adamantyl methylene hydrogens, at C(11), C(12) and C(26), and the corresponding cyclohexane ring is flattened by an average of 9° per dihedral angle. Furthermore, the presence of the terminal cyclohexane rings with their complement of methine and methylene hydrogens introduces what can be described as "buttressing effects". Whenever hydrogen atoms at C(11) to (16) are under pressure they are forced into proximity with the neighboring bridgehead hydrogens which are, in turn, brought closer to the adjacent methylene hydrogens. The sum total of the non-bonded steric energies therefore increases markedly compared to that of the *t*-butyl derivatives.

CONCLUSION

The approach which we have used to interpret the results of our study on slow rotation in *o*-tolyldi-alkylcarbinols comprises two major simplifications: instead of using Allinger's force field for oxa-compounds we adopt a well-tried hydrocarbon substitute force field; because it is difficult to freeze dihedral angles in highly congested systems we reduce the energy profile to 4 points and assume it to have the same general form as that found by Mannschreck for *iso*-propyl compounds. Consequently, the extrapolated activation enthalpies cannot be expected to reproduce the experimental data. Nevertheless, the calculations do express correctly the order and the relative magnitudes of the rotation barriers. Therefore some confidence can be placed in the resultant qualitative description of the different steric effects of the 1-Ad and t-Bu substituents. While a more rigorous molecular mechanical treatment could eventually provide better numerical agreement between experiment and theory, it is not likely that this image of the 1-adamantyl group as a rigid substituent will be radically modified.

EXPERIMENTAL

Synthesis of 1,1'-diadamantylketone

To the methyl ester of 1-adamantyl-carboxylic acid (11.0 g; 57 mmol) and finely-chopped lithium (0.91 g; 130 mmol) in tetrahydrofuran (200 mL), magnetically stirred under argon at room temp, was added during 5 min a soln of 1-bromoadamantane (13.3 g; 62 mmol) in THF (50 mL). The temperature was not allowed to rise above 35°. After 2 hr the residual lithium was filtered off, the reaction mixture poured into water, and the organic products extracted into hexane. After drying and evaporation of the solvent, the mixture was spatiated by column chromatography on alumina. 1,1'-diadamantane was followed by the ketone (9.6 g; 57% yield): mp, after recrystallisation from hexane. 189.5° (it⁹ 186.6–187.0°).

Synthesis of alcohols

Alcohols were synthesised by addition of the appropriate ketone (33 mmol) in ether (10 mL) to an excess of lithium-free o-tolyl-lithium (100 mmol in 40 mL ether) under argon at room temp. Isomers were separated from the crude reaction mixture (ap/sp:92:8) on alumina and were recrystallised from hexane. Larger amounts of the sp isomers were obtained by rotation of the ap isomer for 10-15 half-lives.

Rotation kinetics

Rotation rate constants were determined in dodecane as described previously.^{5a} Glc analyses were carried out on short 1% SE30 or 10% Carbowax 20M columns.

Though it is impossible, for reasons of space (the print-out for each diadamantyl derivative occupies about 3000 (lines), to give the results of the calculations in detail, we shall outline how they are analysed. The print-out includes an "itemized steric energy analysis" in which the steric energy contributions of all types associated with each atom taken separately are listed and summed. By this means particularly strained atoms are readily identified. The second step is to examine the separate contributions of these atoms in order to determine which interactions or distortions make the most important contributions to the steric energy. This procedure, in particular, allows us to identify the atoms which suffer severe non-bonded interactions with the most strained atoms and which relay the distortions to the peripheral atoms, themselves not highly perturbed. The final stage consists in comparing one conformation with another or one structure with another in order to detect the contributions which change significantly. In this way features common to all structures are eliminated; what remains are the factors responsible for the observed steric effects upon reactivity.

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Cpd	Yield	Analy	ysis mp(°C		VOH(cm ^{-'})	NMR (prom relative to TMS) (DMSO)						
		Calc.	Found		(CC1 ₄)	<u>t</u> -Bu	Ad	Ad	Me	он	3H	ortho-H
<u>1b</u>	50 %	C 84.56	84.78	107.5	3612, 3647	1.22	1.64	۱ <i>.</i> 93	2.68	4.35	7.13	8.07
		H 10.32	10.24									
<u>2b</u>	5 Z	C 84.56	84.61	108	3639	1.16	1.66	1.97	2.66	3.87	7.17	7.62
		H 10.32	10.23									
<u>lc</u>	81 %	C 86.10	85.90	195	3605, 3644	-	1.68	1.98	2.77	4.29	7.22	8.16
		H 9.81	9.62									
<u>2c</u>	6 %	C 86.10	85.87	180	3635	-	1.65	1.96	2.61	3.73	7.15	7.60
		H 9.81	10.02									

(1977).

Table 5. Yields, analyses and physical data on new alcohols

Steric energy calculations

All calculations were performed on an IBM 370 computer of the Centre National de la Recherche Scientifique using the Andose-Mislow program BIGSTRN (QCPE, University of Indiana, Bloomington, Indiana 47401).

Energies of the sp and ap rotameric methanes or ethanes were calculated without any geometric constraint. For conformations **B** and C, energies were calculated in the same way except that the carbon of the 2-methyl group, the benzenoid carbons, C(2)-C(7), C(8) and either C(9) or C(10) were constrained to remain in a given plane. This is achieved by setting one cartesian coordinate to zero for all 9 carbons concerned. The aromatic ring is therefore not allowed to buckle but can distort in the plane. In calculations on trimesitylmethane¹³, all independent movement of the aromatic carbons was was prohibited; this further constraint would greatly increase the transition state energies and did not seem to be justified in the present case since, moreover, it is known that the ring is an irregular hexagon in the sp isomer.^{5b}

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- ¹⁷It also considerably reduces the time required for calculation.
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- ¹⁹Normally, in Allinger's force field the centre of electron density is not taken to coincide with the nuclear position for hydrogen atoms but is offset by 8% of the C-H bond length. In a previous publication on rotamers^{5b} steric energies were calculated without this offset. The new values for *ap* or *sp* methanes and ethanes are about 1 and 4 kcal mol⁻¹ lower, respectively, but the steric energy differences between the *ap* and *sp* rotamers are hardly altered. No changes in the geometry of the carbon skeleton exceeding 0.003 A in bond length or 0.6° in bond angle were found. The conclusions of the previous works^{5b,16} are not therefore affected by this revision.
- ²⁰J. E. Leffler and E. Grunwald, Rates and Equilibria in Organic Reactions, pp. 163-4. Wiley, New York (1963).
- ²¹Semi-empirical energy calculations on $\alpha, \alpha, 2$ -6-tetrasubstituted toluenes show that the C_α-H bond is perpendicular to the plane of the ring in the transition state for rotation about the sp^2-sp^3 bond.^{13d,e,k,l} Nevertheless, it has been frequently assumed that for aryldialkylcarbinols⁷ and substituted toluenes^{8b} the rotation transition state involves eclipsing of the larger group at the sp^3 carbon and the ring. There is no evidence in support of this hypothesis. An analogous assumption has been made concerning rotation in highly congested ethylenes.^{8a,c}
- ²²In BIGSTRN the only device for blocking dihedral angles at values other than 0° tends to be unreliable for highly distorted structures.
- ²³The steric energies correspond to a hypothetical motionless state at 0° but, since we are comparing different conformations of a same molecule, corrections for zero-point energy, heat content and entropy are unnecessary.
- ²⁴Comparable data for phenyldi-*t*-butylcarbinol are not available. ΔG^{*} values for the 3,4,5-trimethoxy derivative range from 18.7 to 20.4 kcal mol⁻¹ at 25°C, depending on the solvent,^{7a} and 21.4 kcal mol⁻¹ at 142°C in DMSO.^{7b} Activation entropies vary widely in the first study and are probably unreliable. Assuming that the 4-OMe group lowers ΔG^{*} by about 0.8 kcal mol⁻¹ and that ΔS^{*} is the same as in our study (-9 e.u.)^{5b} we calculate that ΔH^{*} is roughly 18.1 kcal mol⁻¹ for this compound. Consequently, the extrapolated MM data overestimate this value by a factor of 1.52 in fair agreement with calculations on the *o*-tolyl derivatives.
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