Application of Empirical Potential Energy Calculations to Organic Chemistry. Part 22.[1,2] Restricted Internal Rotation in Substituted 1,1′-Bipiperidines, 1-Cyclohexylpiperidines, and Related Molecules due to 1,5-Interactions across the Pivot Bond

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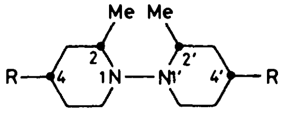
The reported high barriers (75—80 kJ mol^{-1}) for a conformational process of 2,2′-dimethyl-4,4′-dialkyl-1,1′-bipiperidines (**1**) do not originate from the claimed eclipsing conformation but are attributed to a staggered barrier appearing in the course of the rotation of N–N bond, wherein two sets of g^Pg^M arrangements in Me–C(2)–N(1)–N(1′)–C(6′) and C(6)–N(1)–N(1′)–C(2′)–Me units are inescapably locked into a strained S_2 symmetric disposition. This proposal is based on molecular mechanics calculations of model molecules including 1-(2-methylcyclohexyl)-2-methylpiperidine (**4**; $R^1 = R^2 =$ Me). Bond drive calculations of bicyclohexyls variously substituted at 2, 2′, 6, or 6′ positions also predict a number of examples wherein the rotation around the pivot bond should be restricted.

Experimental studies on restricted rotation about the single bond of organic molecules by the dynamic n.m.r. technique have mostly been confined to those for fully substituted atoms like the C–C bonds of perhalogenated or peralkylated ethanes.[3] The systematic dependence of the barrier height on the steric bulk of α-substituents has been noted,[3b] and careful selection of hindering groups led to the identification of a number of atropisomers.[3c] In these cases, simultaneous occurrence of three pairs of eclipsing interactions (1,4 type) is the source of the barrier. It is rather surprising that the possibilities of restricted rotation due to longer range interactions (1,5 and 1,6) have only been studied sporadically.[4] With such a powerful computational technique as molecular mechanics[5] now available as a new tool for stereochemical analysis, it is now feasible to study explicitly the effects of intramolecular long-range non-bonded interactions on molecular properties.[6] This paper describes a new and general cause of highly hindered rotation about single bonds between partially substituted atoms, wherein barriers arise from intensified g^Pg^M interactions (1,5 type).

Our study started from the unusually high N–N rotational barriers in *meso*-2,2′-dimethyl-4,4′-dialkylbipiperidines (**1**) reported recently by Ogawa *et al.*[7] Thus far, the determination of rotational barriers about the N–N bond in alkylhydrazines like (**1**), which are of considerable interest in relation to the *gauche*-effect,[3a,8,9] has been hampered by concomitant inversion at the nitrogen atom.[10] The nitrogen inversion took place also in Ogawa's system (**1**) when R = H to give an observed free energy of activation of 52.7 kJ mol^{-1} (Table 1). This process, called single passing inversion of the nitrogen atom [see equation (1) of ref. 2], involved chair–chair inversion of the piperidine ring where 2- and/or 2′-methyl is brought into the axial position of the inverting ring. Ring inversion (and hence nitrogen inversion as well) can be suppressed by introducing alkyl groups into the 4 and 4′ positions which destabilize the inverted ring by a 1,3-diaxial interaction with the 2- and 2′-methyl group. Actually, Ogawa observed a conformational process having higher activation energies (75—80 kJ mol^{-1}) with tetra-alkylbipiperidines (**1**; R = Me, Bu^t) and assigned the process to the single passing rotation around the N–N bond wherein a pair of N–C bonds is eclipsed [see equation (2) of ref. 2].[7] This is the first successful separation of N–N bond rotation from nitrogen inversion.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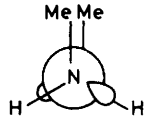
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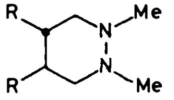
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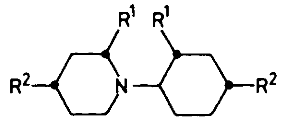
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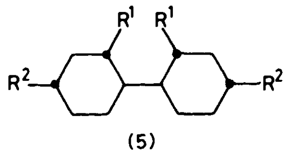
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Table 1. Experimental activation energies of single passing conformational processes in cyclic and acyclic tetra-alkylhydrazines (kJ mol^{-1})

	(1)				(3)				
	R	$\Delta G^{\ddagger}$	T/°C	Ref.	R	$\Delta G^{\ddagger}$	T/°C	$\Delta H^{\ddagger}$	Ref.
N inversion	H	52.7	−18 to −29	7*a*	$(CH_2)_4$	53.1[a]	2	56.9	12
N–N rotation	Me	74.0	62—72	7*a*	H	43.1[b]	−30	49.8	12
	Bu^t	79	80—105	7*b*					

[a] *ea*→*ee*. See S. F. Nelsen, *Acc. Chem. Res.*, 1978, **11**, 14, for notations. [b] Pertains to the ring inversion *ee*→*aa*. See text.

However, the observed barrier is simply too high to be considered as a reference height for the single passing N–N rotation. For example, the *ab-initio*-calculated corresponding barrier for *NN'*-dimethylhydrazine (**2**) is *ca.* 20 kJ mol^{-1} in enthalpy.[11] The ring inversion of a hexahydropyridazine derivative (**3**; R = H) (Table 1)[12] may be a better model for the single passing N–N rotation of tetra-alkylhydrazines, but the observed barrier in this case (43.1 kJ mol^{-1}) also is only 55% of Ogawa's barrier. It seemed likely that some large but not readily apparent steric effects are involved in the observed high barrier of (**1**), and we decided to simulate this process by the molecular mechanics method.[5]

Computational Technique.—Allinger's force field MM2[13] was used throughout this work. Although this force field has not been parameterized for the N–N function, and cannot handle hydrazines (**1**) as such, parameters for aliphatic amines have recently been implemented with the lone-pair electron treated as a quasi-atom.[14] Since the C–N bond has practically the same length as the N–N bond (both 1.44—1.46 Å),[15] substituted 1-cyclohexylpiperidine (**4**) should be a good model for the present purpose. Only the *meso*-forms were considered for (**4**).

In the coverage of the three-dimensional, two-parametric torsional energy surface of (**4**),[16] it is assumed that the non-chair deformation took place in the piperidine ring. However, the estimated chair–chair interconversion barrier of piperidine (59 kJ mol^{-1})[17] is slightly higher than the corresponding barrier of cyclohexane (50.6 ± 2.1 kJ mol^{-1}),[18] indicating that the piperidine ring is less flexible than cyclohexane. Hence, a slightly lower activation energy would have resulted if the cyclohexane ring of (**4**) was twisted. We further assume that the non-chair deformation involves movements of C(6) into the direction away from the approaching 2'-methyl group. Dihedral angles were driven at a constant interval of 15° using a highly automated driver subroutine.[16b] The whole calculation of 266 points for (**4**; $R^1 = R^2 = \text{Me}$) (Figure 1) consumed 110 min of CPU time on a HITAC M-200H system. The positions of major saddle points were located by thoroughly covering small areas around them. The original point data were then fitted to a smoothed surface using a spline function.[16b]

Results and Discussion

Torsional Energy Surfaces of 1-*Cyclohexylpiperidines* (**4**).—The results of one-bond driver calculations of 1-cyclohexylpiperidine (**4**; $R^1 = R^2 = \text{H}$) and its 2,2'-dimethyl derivative (**4**; $R^1 = \text{Me}$, $R^2 = \text{H}$) have been described in the preliminary communication.[2] More extensive portions of torsional energy surface are now covered using the two-bond driver technique[16] for 2,2',4,4'-tetramethylcyclohexylpiperidine (**4**; $R^1 = R^2 = \text{Me}$) as the model while driving the pivot bond as well as the N(1)–C(2) bond of piperidine ring simultaneously (Figure 1). The torsional energy curve (Figure 1) published previously[2] corresponds to the cross-section of the three-dimensional surface along the curve connecting the points A, (B), (C), and D.†

Conformations A and D, with the nitrogen lone pair and H(1') in a *gauche*-disposition, represent the two most stable points in Figure 1.‡ Rotation of the pivot bond [N(1)–C(1')] of A to more and more positive C(6)–N(1)–C(1')–C(2') dihedral angle

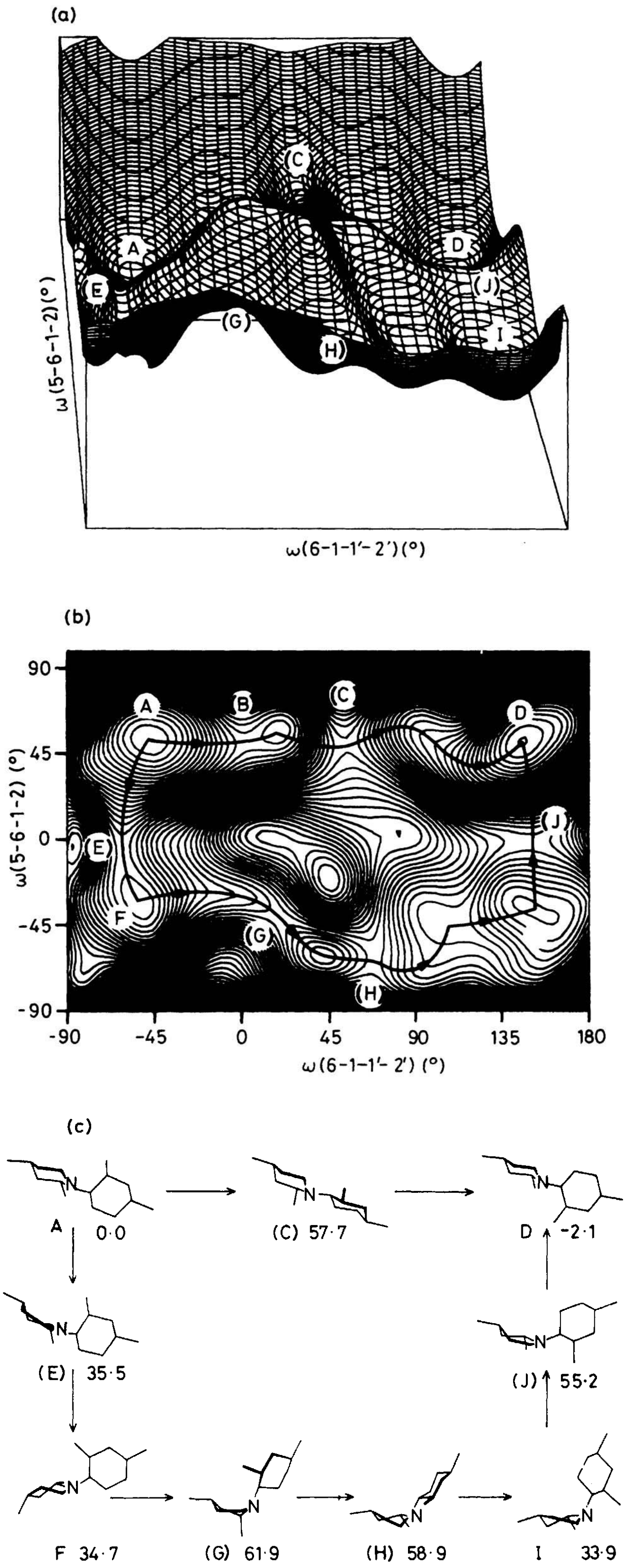

Figure 1. Two-parametric torsional energy surface of 1-(2,4-dimethylcyclohexyl)-2,4-dimethylpiperidine (**4**; $R^1 = R^2 = \text{Me}$) for the rotations about pivot and N(1)–C(6) bonds by MM2 two-bond driver calculations. Energies (kJ mol^{-1}) are relative to the *gauche* conformer A. (a) Perspective drawing. (b) Contour map with a line spacing of 2.1 kJ mol^{-1}. (c) Scheme of major stationary points

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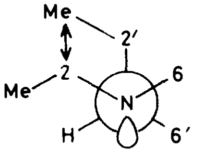
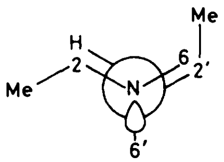
† Letters in parentheses denote saddle point conformations and those without parentheses energy minima.

‡ That these conformations exactly correspond to the two diastereoisomeric global-minima of (**1**) is an incidental result of the fact that the only one other staggered conformation (C) with the lone pair and H(1') in the *anti*-orientation happens to be a special, high-energy form as mentioned below.



A,(E),F



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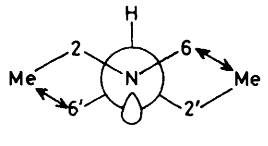

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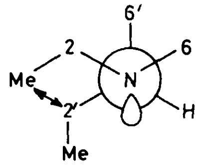
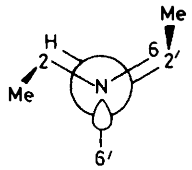


D, I,(J)



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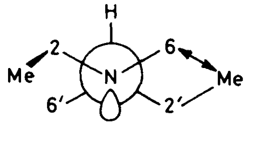
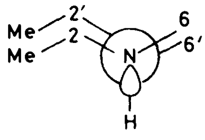


(H)



(K)

(to the right of Figure 1) leads to a saddle point (B), in which C(2′) and C(6) are eclipsed. This point corresponds to the single passing barrier and was considered the highest point in the torsional itinerary of (**1**).[7] Actually, (B) is just a weak saddle point leading to a much higher, well defined saddle point (C). This conformation was previously conceived as an energy minimum[7] because all bonds about the rotating bond are staggered, but is now found to be one of the highest points in Figure 1 and most probably corresponds to the barrier observed for (**1**). The calculated height of (C) relative to A (58 kJ mol^{-1}) is lower than the observed by 17 kJ mol^{-1}, but this difference can be rationalized if one recalls the tendency of MM2 to underestimate high C–C rotational barriers.[19,20] The presence of two methyl groups at C(2) and C(2′) is a necessary condition for the occurrence of this barrier, since it completely disappeared when 1-cyclohexylpiperidine (**4**; $R^1 = R^2 =$ H) was similarly driven.[2] Further drive of (**4**; $R^1 = R^2 =$ Me) leads to the global-minimum D and completes the conformational process, which is characterized by a sustained chair–chair conformation with almost constant N(1)–C(2) dihedral angles [Figure 1(c)].

The possibility of a non-chair pathway is indicated in Figure 1 as a trajectory involving (E), F, (G), (H), I, and (J). While there should be a large number of deformation modes for the piperidine and cyclohexane ring of (**4**), manipulation of a framework model indicates that the combined drive of N(1)–C(1′) and N(1)–C(2) bonds is most likely to be significant. As Figure 1 shows, pseudorotation along the non-chair piperidine ring brings the cyclohexane ring into the pseudoaxial position at several critical points. The saddle point (G) has two such substituents which make this conformation considerably less stable than (C).

Another possibility that must be considered is the double passing barrier involving two pairs of N–C bonds eclipsing practically simultaneously as in (K). However, the MM2-calculated energy of (K) exceeds 100 kJ mol^{-1} relative to A. Since this value is certainly underestimated,[20] this possibility was excluded.

It is now highly likely that the barrier (C) is the most important point in the conformational process of this molecule. Close inspection of this barrier suggests a pair of g^Pg^M arrangements involving Me–C(2)–N(1)–C(1′)–C(6′) and Me–C(2′)–C(1′)–N(1)–C(6), indicated by double arrows in the Newman projection, as the predominant sources of strain in (C). In general, when two *gauche*-units with opposite signs are present in adjoining bonds of alkanes, a strained, 'forbidden' conformation arises and is 'allowed' only at the corner of cycloalkanes.[21,*] In (C), a pair of such arrangements are generated simultaneously during the rotation of the pivot bond. A special situation here is that these double g^Pg^M arrangements are locked into an S_2 symmetry so effectively at the barrier that there is no way of relieving the strain, as in the *anti*-conformation of 2,3-dimethylbutane.[19a] The situation manifests itself in the unusual structural features of barrier (C) (see Figure 2 of ref. 2). It is pertinent to stress the effect of the pairwise appearance of g^Pg^M arrangements to raise the barrier height. A single g^Pg^M arrangement appears in A, D, F, (H), and (J), but strains in these cases are at least partly released by appropriate deformations. For example, the adjacent g^P [C(2)–N(1)–C(1′)–C(2′), 80.5°] and g^M [N(1)–C(1′)–C(2′)–Me, −56.9°] units in A avoid each other by twists and by increasing valence angles [C(1′)–C(2′)–Me, 115.6°].

Now that the source of barrier in the single passing rotation of (**1**) [and (**4**)] becomes clear, the nitrogen atom need not necessarily be present. We use hydrocarbon models, namely substituted bicyclohexyls (**5**), to study in more detail the effect of substituents on the height of the staggered barrier.

Torsional Energy Surface of Bicyclohexyls (**5**).—2,2′,4,4′-Tetramethylbicyclohexyl (**5**; $R^1 = R^2 =$ Me) gave essentially the same features for the two-parametric torsional energy surface as (**4**) (Figure 2), except that the saddle points have steric energies up to 17 kJ mol^{-1} lower than those of (**4**; $R^1 = R^2 =$ Me). This is a consequence of the longer natural length of the C–C compared with the N–C bond. The longer pathway through the twisted cyclohexane ring again involves a significantly higher barrier (G) than the barrier (C) of the shorter pathway. Other 2,2′-dimethylbicyclohexyls (Table 2) also behave essentially similarly to their nitrogen-containing counterparts. Therefore, we concentrate henceforth only on the barrier (C) of the short chair–chair pathway.

The introduction of bromide or methoxycarbonyl groups for R^1 of (**5**) (Table 2) is predicted to be ineffective in raising the height of the staggered barrier. Despite its apparent steric bulk, the ester group was found to rotate itself to place its plane at the least hindered angles.

2-Methylbicyclohexyl (**6**) shows a doublet barrier, both peaks being 25.1 kJ mol^{-1} in height, in the region of (C) according to one-bond driver calculations (Figure 3, solid line). The first barrier involves a close approach between methyl and equatorial H(6′). The g^Pg^M interaction in this simple molecule is considerably more intensified compared with acyclic cases like

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[*] According to MM2, enthalpies of the *aa*, g^Pg^P, and g^Pg^M conformers of n-pentane are −151.7, −144.8, and −138.3 kJ mol^{-1}, respectively. Since a high degree of freedom for deformation is available for the g^Pg^M conformer, the energy differences with other conformers are not large.

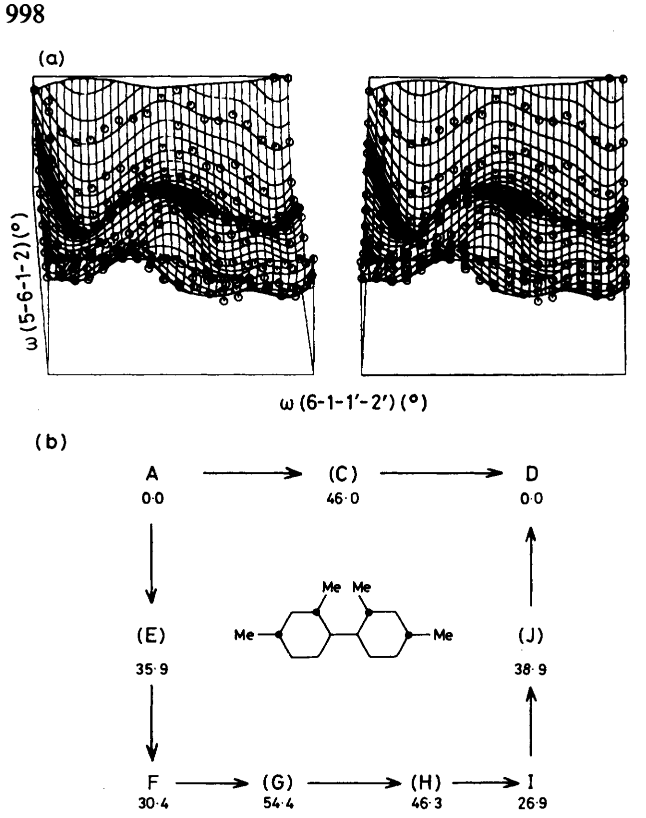

Figure 2. Two-parametric torsional energy surface of 2,2',4,4'-tetramethylbicyclohexyl (**5**; $R^1 = R^2 = Me$) for the rotations about pivot and C(1)–C(6) bonds by MM2 two-bond driver calculations. (a) Stereopair of perspective drawing with original data points as circles. (b) Scheme of major stationary points. Steric energies in kJ mol^{-1} are relative to the *gauche*-conformer (A)

Table 2. Barrier heights (kJ mol^{-1}) for rotation about pivot bond of substituted cyclohexylpiperidines (**4**) and bicylohexyls (**5**) by one- and two-bond driver calculations with MM2[a]

			Barriers (kJ mol^{-1})	
	R^1	R^2	A→(B)	A→(C)
(**4**)	H	H	21.3	*b*
	Me	H	27.2	58.2
	Me	Me	27.2[c]	57.7[c]
	Me	Bu^t	27.6[c]	59.4[c]
(**5**)	H	H	11.7	*b*
	Me	H	11.7	49.9
	Me	Me	20.9[c]	46.0[c]
	Me	Bu^t	20.9[c]	49.4[c]
	Br	Me	13.8[d]	40.2
	Br	Bu^t	16.7[d]	39.3
	CO_2Me	Me	17.1[d]	26.3

[a] For conformations A, B and C, see illustrations. [b] Conformation C is the energy minimum for this molecule. [c] Obtained by two-bond driver calculations. Other values are obtained by the one-bond driver method. [d] Shoulder.

the g^Pg^M conformer of n-pentane, because any attempt to escape the congestion in the g^Pg^M interaction will increase the *gauche* interaction in the C(6)–C(1)–C(1')–C(2') unit on the other side of the molecule. Nevertheless, the steric situation here is clearly not as severe as in (C) of (**4**; $R^1 = R^2 =$ alkyl), hence the barrier is quite low. The second barrier corresponds to a single passing barrier (B'), which is higher than (B) because 2-methyl and axial H(6') are close.

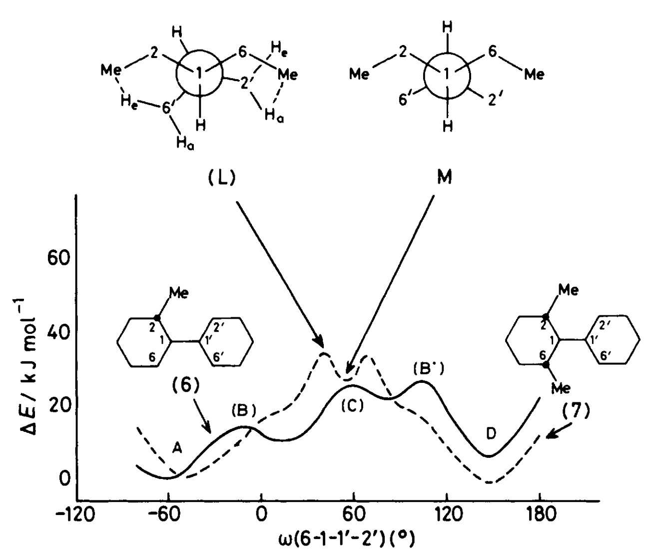

Figure 3. Torsional energy profiles of 2-methyl- (**6**) (solid line) and 2,6-dimethyl-bicyclohexyl (**7**) (dashed line) for rotation about the pivot bond by MM2 one-bond driver calculations. Energies are relative to the *gauche*-conformer A

2,6-Dimethylbicyclohexyl (**7**) is the first molecule studied in this work which has a plane of symmetry at (C). Hence the torsional energy curve (Figure 3, dotted line) is almost* symmetrical on both sides of a line of dihedral angle (6-1-1'-2') = 60°. The first maximum (L) is characterized by the close no-bond interactions: 2-Me–equatorial 6'-H and 6-Me–axial 2'-H. At the point M which corresponds to (C) of 2,2'-dimethyl-(**4**) and -(**5**), the equivalent pair of two g^Pg^M interactions are considerably relaxed by pushing C(2') and C(6') away from both methyls: the C(1)–C(1') length of 1.572 Å and C(1)–C(1')–C(2) [and C(1)–C(1')–C(6)] angle of 114.1° are both normal, and this point becomes an energy minimum. This observation leads us to recognize the importance of S_2 symmetry in (C) of (**4**; $R^1 = R^2 =$ alkyl) in raising its steric energy. The second maximum is enantiomorphic to the first.

It would be highly interesting to study systematically the effect of alkyl substituents in the 2, 2', 6, and 6' positions of bicyclohexyls. However, as the congestion is increased by the introduction of more and more alkyl groups, even the two-bond driver technique proved to be not enough to locate saddle points exactly. A more powerful computational technique to characterize saddle points is necessary.[5b] Until MM2 is equipped with such an option, we are deterred from further study. However, we conclude that certain possibilities exist for realizing atropisomerism regarding the rotation of partially substituted C–C bonds if long-distance no-bond interactions can be effectively accumulated across the rotating bond.

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* Not exactly, because of the artefact 'lag' problem inherent to the one-bond driver technique. See ref. 16*a*.

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