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Internal Rotation in the Singly Bonded Dimers of Substituted C_{60}. A Molecular Lever

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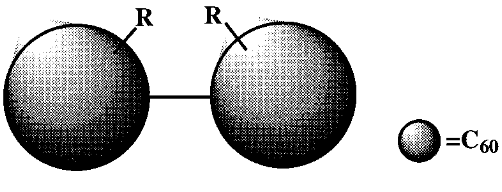
The rotation about the intercage bond of singly bonded C_{60} dimers $RC_{60}C_{60}R$ (R = H, Me, and *t*-Bu attached at ortho or para positions from pivot carbon atoms) obtained by the dimerization of $RC_{60}^{\bullet}$ radicals, has been studied by molecular mechanics. The predicted rotational barriers are high, ranging from 15 kcal/mol for the least hindered *p,p′*-$(HC_{60})_2$ to the almost forbidding values for those carrying *tert*-butyl groups. Contrary to the general notion, rotamers with R groups approached close to each other like the gauche form are predicted to be consistently *more* stable than those with maximally separated Rs (trans), by as much as 10 kcal/mol in the case of R = *tert*-butyl. The reasons for the unexpected stability of the gauche-like conformation as opposed to the trans-like conformation in these fullerene dimers have been analyzed in detail and interpreted in terms of a lever effect peculiar to the dumbbell shape of the molecule.

Introduction

Buckminsterfullerene (C_{60})[1] is known to dimerize into various forms.[2−5] The C_{60} dimers are particularly interesting as the potential precursors of giant C_{120} fullerenes[6] and also as the simplest model of the pearl-necklace-type C_{60} polymers.[7] While none of these have been fully characterized, the singly bonded, dumbbell-shaped dimers of the general formula $RC_{60}C_{60}R$ (**1**, R = H, halo, alkyl) are relatively well studied.[2] Dimers **1** are formed by the recombination of $RC_{60}^{\bullet}$ radicals, which in turn can be prepared *in situ* by addition of $R^{\bullet}$ to C_{60}.[2a] Substituents R are considered to be attached at ortho or para positions relative to the intercage bond, based on the ESR spectra of monomeric species $RC_{60}^{\bullet}$ showing the unpaired electron being localized within the six-membered ring that carries the R group.[2a]



1

Dimers **1** provide profoundly interesting targets for the studies of internal rotation and rotational isomerism. A C−C single bond carrying such large cage fragments at both ends is a novelty.[8] With substituents close to the rotating bond, we may expect severe steric interactions and high barriers for the rotation of pivot bond. Indeed, we found that the familiar rule of thumb in the confor-

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§ On leave of absence from the Nitto Denko Corporation, 1992−1993.

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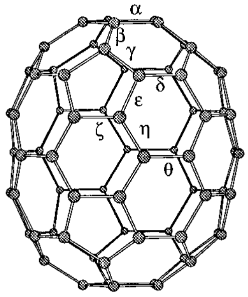
mational analysis favoring an anti conformation over syn or gauche does not hold any longer in **1**.

Computational Method and Nomenclature

Molecular mechanics force field MM3(89)[9] was used throughout this work. Geometry optimization was carried out without symmetry constraint until total energy remained unchanged within 0.01 kcal/mol during successive iterative cycles. Torsional energy surfaces were drawn by applying the bond driver technique. Discontinuity often appeared in the torsional energy surface and led to the overestimation of rotational barrier heights. This problem has been addressed.[10]

MM3 is known to well reproduce the experimentally determined structure of C$_{60}$.[11] Recently Scuseria[12] reported that the structures of C$_{28}$ to C$_{120}$ fullerenes obtained by this force field were similar to those obtained by STO-3G calculations. As an additional test, we compared the lengths of eight unique C−C bonds in C$_{70}$ (**2**) calculated by various theoretical methods with those determined by X-ray analyses at low temperatures (Table 1):[13−15] MM3 performed well in reproducing the subtle variation among α to θ bonds[16] for its simple scheme.



2

The performance of MM3 regarding energy is difficult to evaluate, but circumstantial evidence is favorable: MM3 is the only computational method that correctly reproduces the measured heats of formation of C$_{60}$ and C$_{70}$ (Table 2), and the relative MM3 energies of C$_{76}$, C$_{78}$, and C$_{84}$ isomers are consistent with the results of separation work.[17] We use here MM3 energies with due care.[18] Computations have been carried out on Hewlett-Packard-Apollo DN10000 and 9000/750 and Titan 2-800 workstations.

Table 1. Experimental and Calculated Lengths of Eight Types of Bonds (α to θ) in C$_{70}$ (2). Standard Deviations of Experimental Errors Are Given in Parentheses

	expt		calcd				
bond[a]	X1[b]	X2[c]	LDA[d]	DZP[e]	AM1[f]	PM3[g]	MM3
α	1.453(3)	1.434(8)	1.448	1.451	1.464	1.457	1.452
β	1.387(4)	1.377(10)	1.393	1.375	1.387	1.386	1.392
γ	1.445(3)	1.443(9)	1.444	1.446	1.460	1.453	1.447
δ	1.387(3)	1.369(10)	1.386	1.361	1.375	1.374	1.381
ϵ	1.447(2)	1.442(7)	1.442	1.457	1.467	1.463	1.459
ζ	1.426(3)	1.394(11)	1.434	1.415	1.434	1.426	1.421
η	1.414(2)	1.418(7)	1.415	1.407	1.414	1.412	1.416
θ	1.462(4)	1.457(12)	1.467	1.475	1.465	1.463	1.466
corr.	0.003[h]	0.003[h]	0.002[i]	0.002[h]	0.002[i]	0.002[i]	
SD[j]			0.004$_6$	0.011$_8$	0.009$_4$	0.007$_8$	0.005$_4$
SD[k]			0.012$_9$	0.011$_9$	0.013$_5$	0.011$_3$	0.008$_4$

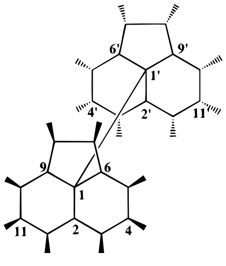
[a] See structure drawing **2**. [b] Reference 13. [c] Reference 14. [d] Local density functional theory: Andreoni, W.; Gygi, F.; Parrinello, M. *Chem. Phys. Lett.* **1992**, *189*, 241. [e] HF using double-ζ basis of Huzinaga with polarization: Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *180*, 451. [f] Piqueras, M. C.; Crespo, R.; Tomas, F. *J. Mol. Struct. (Theochem)*, in press. [g] New parameters set for AM1: Stewart, J. J. P.; Coolidge, M. B. *J. Comput. Chem.* **1991**, *12*, 1157. [h] Correction term to be added to bond lengths in order to convert X-ray values taken at 100 K into r_g values (MM3 standard): Allinger, N. L.; Zhou, X. F.; Bergsma, J. *J. Mol. Struct. (Theochem)* **1994**, *118*, 69. [i] Allinger's suggestion temporarily extended to these methods. [j] Standard deviation of differences in the corrected, computed bond lengths from the X-ray values (X1). [k] Standard deviation of differences in the corrected, computed bond lengths from the X-ray values (X2).

Table 2. Comparison of Observed and Calculated Standard Heats of Formation ΔH_f°(g) of C$_{60}$ and C$_{70}$ (kcal/mol)

		calcd			
	obsd	MM3[a]	AM1[b]	PM3[c]	6-31G*//STO-3G[d]
C$_{60}$	609.6(36)[e]	573.4[f]	972.8	811.7	672
C$_{70}$	675.5(21)[e]	639.5	1071.5	884.2	

[a] This work. [b] (a) Rudzinski, J. M.; Slanina, Z.; Togasi, M.; Ōsawa, E. *Thermochim. Acta* **1988**, *125*, 155. (b) Harada, M.; Ōsawa, S.; Ōsawa, E.; Jemmis, E. D. *Chem. Lett.* **1994**, 1037. (c) Ōsawa, S.; Harada, M.; Ōsawa, E.; Kiran, B.; Jemmis, E. D. *Fullerene Sci. Technol.* **1995**, *3*, 225. [c] Stewart, J. J. P.; Coolidge, M. B. *J. Comput. Chem.* **1991**, *12*, 1157. [d] Schulman, J. M.; Disch, R. L. *J. Chem. Soc., Chem. Commun.* **1991**, 441. [e] Beckhaus, H.-D.; Verevkin, S.; Rüchardt, C.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Mohn, H.; Müller, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 996. Numbers in parentheses are experimental errors inferred from Beckhaus' paper (footnote e) in the last two digits. [f] Diederich (ref 17) reports a marginally higher value.

Scheme 1



Since we consider below only those dimers which carry Rs at either ortho or para positions from the pivot carbon atoms,[2a] places of substitution are limited to the cage carbon atoms 2, 4, 6, 9, 11, 2′, 4′, 6′, 9′, and 11′ (see Scheme 1 for the numbering). Among a large number of these combinations, only

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(9) (a) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. (b) Lii, J.-H.; Allinger, N. L. *Ibid.* **1989**, *111*, 8566, 8576. (c) Allinger, N. L.; Li, F.; Yan, L., Tai, J. C. *J. Comput. Chem.* **1990**, *11*, 868. Program MM3 is obtained from Technical Utilization Corporation, 235 Glen Village Court, Powell, OH 43065, through licence agreements.

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(12) Murry, R. L.; Colt, J. R.; Scuseria, G. E. *J. Phys. Chem.* **1993**, *97*, 4954.

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(14) van Smaalen, S.; Petricek, V.; de Boer, J. L.; Dusek, M.; Verheijen, M. A.; Meijer, G. *Chem. Phys. Lett.* **1994**, *223*, 323.

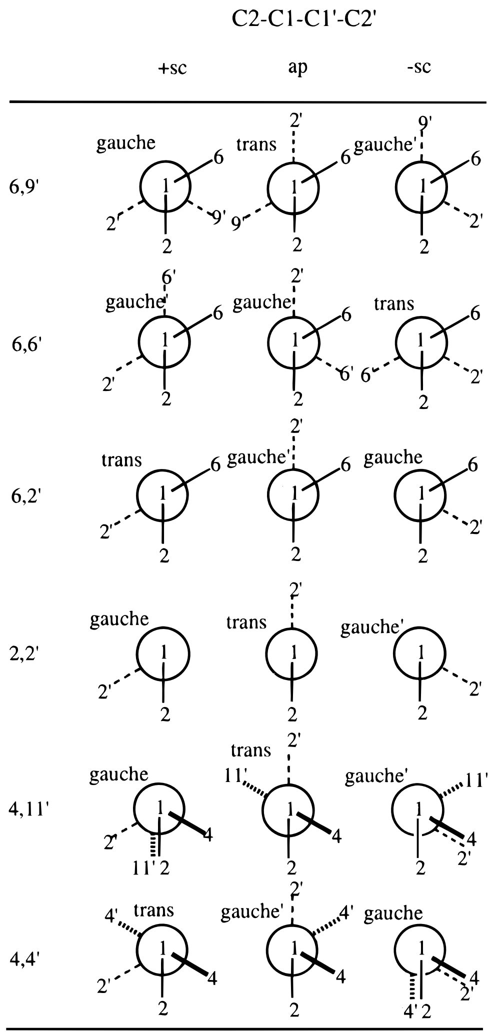
(15) For previous experimental determinations of these bond lengths, see the following. (a) Electron diffraction of thin film: McKenzie, D. R.; Davis, C. A.; Cockayne, D. J. H.; Muller, D. A.; Vassallo, A. M. *Nature* **1992**, *355*, 622. (b) X-ray analysis of Ir adduct: Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 8953. (c) X-ray analysis of bis-Ir adduct: Balch, A. L.; Lee, J. W.; Olmstead, M. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1356. (d) X-ray analysis of S$_8$ adduct at room temperature: Roth, G.; Adelman, P. *J. Phys. I Fr.* **1992**, *2*, 1541.

(16) Some of the variations observed in these bond lengths can be qualitatively interpreted by analogy with C$_{60}$. Bonds connecting two five-membered rings (β and δ, 1.39 Å) are distinctly shorter than those on the five-membered ring (α, γ, and ϵ, 1.45 Å). Bond η (1.41 Å) is unique for **2** in that it is exocyclic to only one pentagonal ring, hence significantly longer than β and δ, while θ, another new bond type is the longest of all (1.46 Å). For a new interpretation based on the bond alternation patterns, see ref 17.

(17) Yoshida, M.; Fujita, M.; Ōsawa, E. *J. Chem. Soc., Faraday Trans.*, submitted for publication.

(18) Large scale calculations of fullerenes with electron correlation: (a) Strout, D. L.; Murry, R. L.; Xu, C.; Eckhoff, W. C.; Odom, G. K.; Scuseria, G. E. *Chem. Phys. Lett.* **1993**, *214*, 576. (b) Cioslowski, J. *Chem. Phys. Lett.* **1993**, *216*, 389.

Scheme 2



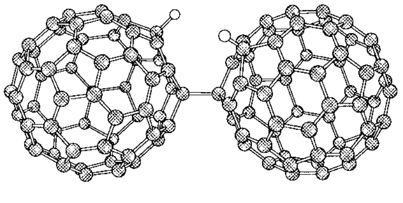
six positional isomers, 6,9′, 6,6′, 6,2′, 2,2′ (both Rs are in ortho positions), 4,11′, and 4,4′ (both para), were considered, and the mixed dimers were excluded.[19] Three rotamer types, sc, ap, and −sc, that arise during rotation about the C1−C1′ bond of $(RC_{60})_2$ are illustrated in Scheme 2. These Klyne−Prelog notations refer to the C2−C1−C1′−C2′ dihedral system. Spatial relationship between the two substituents across the pivot bond is designated here as trans, gauche, and gauche′, even though the relation is not of the vicinal 1,4-type but of the 1,6- and 1,10-types. In order to avoid confusion, Klyne−Prelog notation is adhered to whenever a 1,4-relation is mentioned.

Results

$(HC_{60})_2$. Computed torsional energy curves are given in Figure 1a.[20] It will be immediately clear that the internal rotation is highly hindered even in the dihydro C_{60} dimers. Let us start by comparing energy minima. The increasing order of steric energies averaged over the rotamers among the six positional isomers studied is $4,4' \cong 4,11' \ll 6,6' < 6,9' \ll 6,2' < 2,2'$, indicating that para dimers are distinctly more stable than ortho dimers. From Figure 1a alone, we can readily predict that the right side of the recombination−dissociation equilibrium

$$2(HC_{60}^{\bullet}) \rightleftharpoons (HC_{60})_2$$

will be dominated by the para dimers. Among the energy minima, the gauche rotamer of para-4,4′-dihydro dimer **3** is the global energy minimum. The reason for the unexpected preference of the gauche over the trans rotamer will be discussed later in this paper.



3 (C_2)

In the ortho dimers of $(HC_{60})_2$, syn barriers that occur between gauche and gauche′ rotamers are very high (30−40 kcal/mol, Figure 1a) compared to the known barrier of 2.9 kcal/mol for a pair of vicinal protons to pass in ethane.[21] For this reason, the partial rotation +sc ⇌ ap ⇌ −sc must be the prevailing torsional process in the ortho dimers.

In the para dimers, 4,4′ and 4,11′, the attached hydrogen atoms do not seem to feel each other even in the syn barriers as their torsional potential curves produce a simple sigmoid of constant amplitude. Nevertheless, the calculated barrier heights (15 kcal/mol) are 50% higher than those of similarly substituted hexamethylethane (8−10 kcal/mol).[22] This increase arises partly from the *almost simultaneous* eclipsing[23] of six atoms attached to the rotating bond, unlike open systems wherein the passing of the barrier is believed to involve delayed moves of substituents so that the eclipsing occurs only one at a time.[24] A relatively small "backing" angle allowed at the pivot C_{60} carbon atoms can be considered to be another reason.

$(MeC_{60})_2$. While the order of average steric energies is similar to that for $(HC_{60})_2$, namely $4,4' \cong 4,11' \ll 6,6' \cong 6,9' \ll 6,2' \ll 2,2'$, Figure 1b reveals that the ortho dimers of $(MeC_{60})_2$ are much less stable than the para dimers, in contrast to $(HC_{60})_2$.[25] Hence the ortho dimers are unlikely to exist in the dissociation−recombination equilibrium of $(MeC_{60})_2$. Even in the para dimers, the syn conformation does not exist any more, as seen from the discontinuity at the −sc form of the 4,4′ isomer and the sp of the 4,11′ in the torsional energy curves (Figure 1b). Hence only the partial rotation +sc ⇌ ap ⇌ −sc should be taking place, involving barriers of ca. 15 kcal/mol. The global minimum conformer is again a gauche rotamer of 4,4′ isomer **4**.

(t-$BuC_{60})_2$. Because of the bulkiness of the *tert*-butyl group, ortho dimers were excluded from consideration from the outset, and only the para dimers, 4,4′ and 4,11′, were studied. Before discussing their unusual rotational aspects, we illustrate the remarkable structural deformations in the central portions of gauche and trans energy minima of 4,11′ isomer (**5** and **6**), arising from the high

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[19] This assumption is reasonable when R substituents are large, because the equilibrium is shifted to the homogeneous dimer. However, mixed dimers may be significantly populated for dimers carrying small Rs.

[20] Numerical details are deposited in supporting information.

[21] Wilson, E. B. *Chem. Soc. Rev.* **1972**, *1*, 293.

[22] (a) Anderson, J. E.; Pearson, H. *J. Am. Chem. Soc.* **1975**, *97*, 764. (b) Bushweller, C. H.; Anderson, W. G.; Goldberg, M. J.; Gabriel, M. W.; Gilliom, L. R.; Mislow, K. *J. Org. Chem.* **1980**, *45*, 3880.

[23] The local symmetry is not exactly C_{3h} due to the 5/6/6 ring fusion at the carbon atoms.

[24] (a) Hounshell, W. D.; Dougherty, D. A.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 3149. (b) Ōsawa, E.; Shirahama, H.; Matsumoto, T. *J. Am. Chem. Soc.* **1979**, *101*, 4824.

[25] Note that the scale of abscissa is different in (a) and (b).

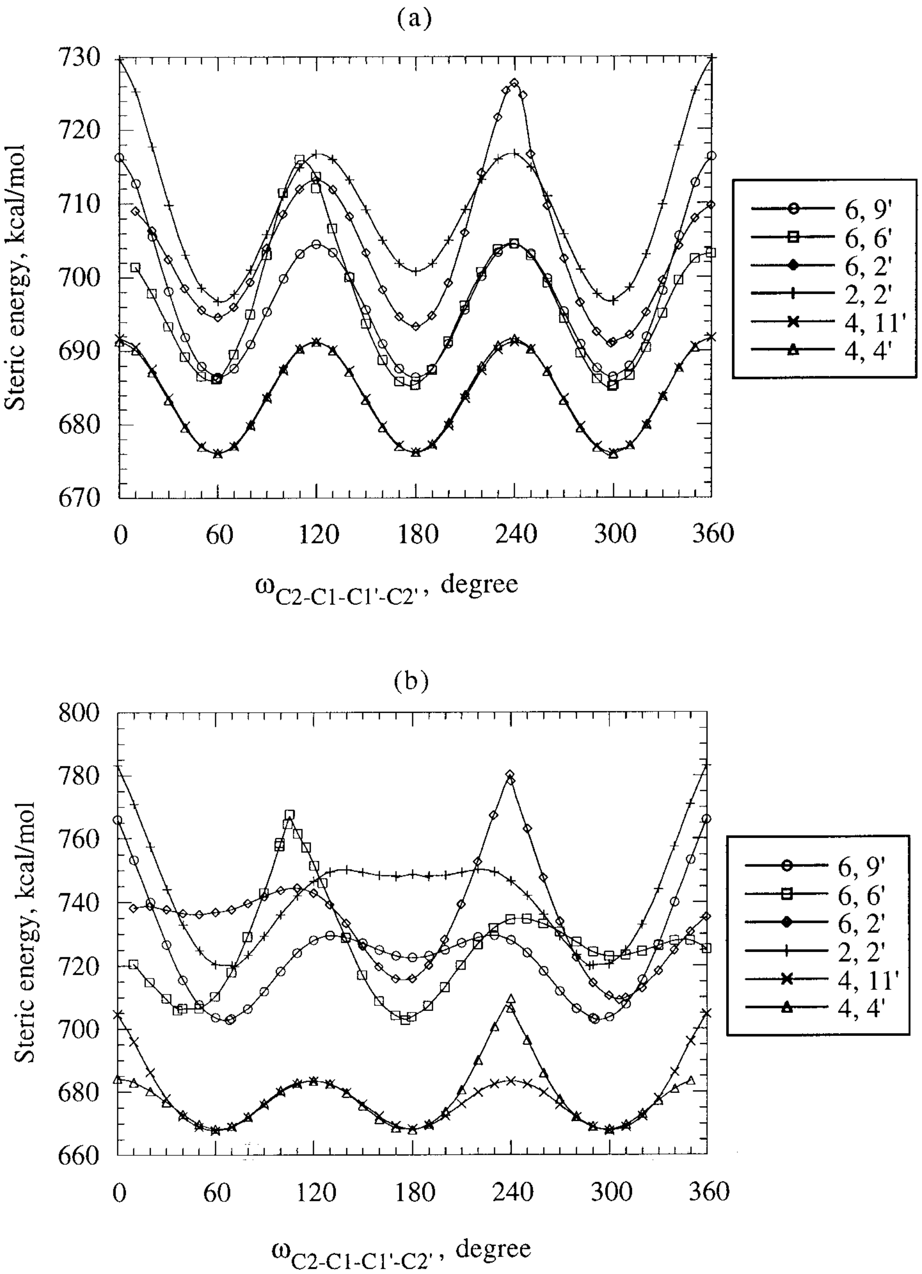
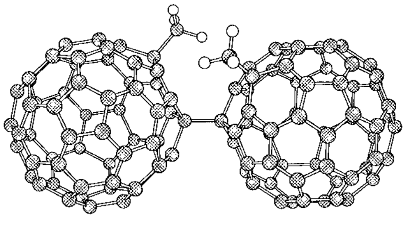


Figure 1. Energy profiles of rotation about the pivot bond in singly bonded C_{60} dimers, (a) $(H\text{-}C_{60})_2$ and (b) $(Me\text{-}C_{60})_2$. See Schemes 1 and 2 to identify the relative disposition of substituents at energy minima. Note that the discontinuity seen in the -sc rotamer of the 4,4′ positional isomer represents a highly crowded sp barrier, as do the sharp rises in the curves of 6,6′ isomer at −sc and of 6,2′ isomer at +sc.

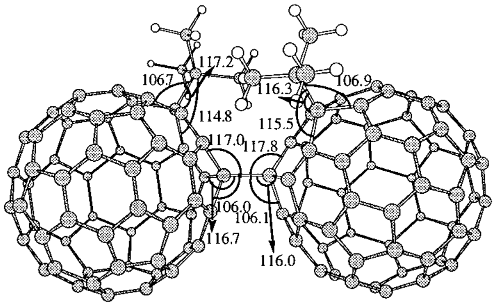


4 (C_2)

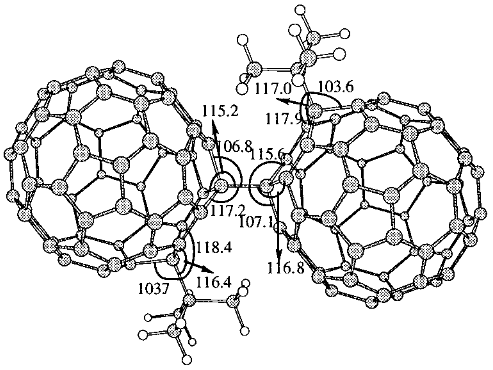
crowding. In addition to the greatly deformed valence angles at the pivot carbon atoms, we note that the vector containing the intercage pivot bond does not pass through the center of the cage, as can be seen from these structural drawings. The "off-axis" deviation is also evident in the substituent−C_{60} bond, which bends away from the facing C_{60} cage. These bending deformations increase during the rotational process and play an essential role in the rotational behavior of $(t\text{-}BuC_{60})_2$ as mentioned below.

There are three bonds that can rotate, an intercage pivot bond and two t-BuC_{60} bonds. Rather than rotating all three bonds, we covered only the interesting portions of the torsional energy surface by applying the two-bond driver option[10] to the intercage bond and one of the t-BuC_{60} bonds while leaving the other *tert*-butyl group free in a staggered position. The most unusual feature in the partial energy surfaces thus obtained (Figure 2) is the destabilization of the trans form (in the center) relative to the gauche forms (both sides).

The global minimum is a gauche′ rotamer of the 4,4′ isomer **7**, the position of which on the energy surface is indicated by a solid arrow in Figure 2b. The gauche conformers of the 4,11′ isomer (**5** and its mirror image) have almost the same steric energies as **7**.[20] In view of the large computed energetic advantage (10 kcal/mol)

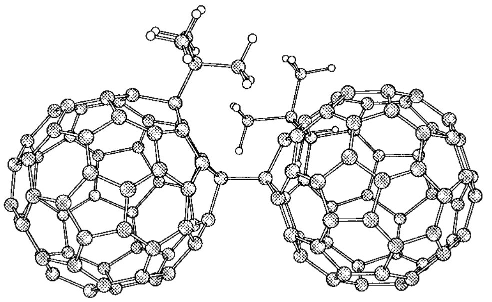


5 (C_2)



6 (C_i)

relative to the trans form, these gauche forms are expected to populate exclusively in the dimerization equilibrium. Since they are located at the bottom of deep energy wells of at least 20 kcal/mol in height, they will be atropisomers, if isolated.



7 (C_2)

Discussion

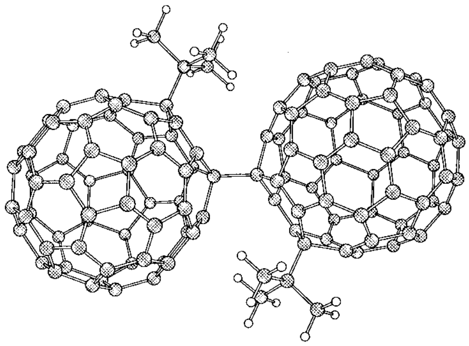
The unusual results on the barrier heights reported above for the internal rotation in $(RC_{60})_2$ should depend at least partly on the validity of the length of pivot bond optimized with MM3. Various theoretical calculations have given contradictory results:[26] the values calculated by molecular mechanics may not be totally reliable because of the possibility of strong orbital interaction through bond, whereas molecular orbital methods agree in that the intercage bonds of C_{60} dimers are of normal length,[3a,8] except for a tight-binding theory which predicts a rather long bond of 1.64 Å.[27] Experimental verification is awaited.

Table 3. Computed Energy Difference (MM3, kcal/mol) between the Substituent-Approached (Gauche or Gauche′) and -Separated (Trans) Rotamers of $(RC_{60})_2$.[a] Gauche Is More Stable Than Trans

R	R, R[a]	
	4,11′	4,4′
H	0.09	0.17, −0.13
Me	0.45	0.26, 0.18
t-Bu	10.18	9.85, 7.72

[a] See Schemes 1 and 2 for nomenclature and numbering of positions.

The most notable outcome of this work is the surprising reversal of the stability order between the substituent-approached, gauche rotamer and the substituent-separated, trans rotamer. The trend is consistent among all the substituents studied in this work (Table 3). We had initially anticipated the usual order, trans below gauche, even for the $(t\text{-BuC}_{60})_2$, which also appears to have been implied by Morton and his group[2a] when they presented the drawing of a trans rotamer of 4,11′ isomer **8** in their paper based on molecular modeling. Actually, **8** might appear as the best conformation according to common sense alone.[28] The unexpected reversal in the well-recognized order of conformational preference merits further clarification. We describe below the results of our analysis in some detail.



8 (C_i)

In Figure 3 the total steric energy (relative to the global minimum) of the 4,4′ and 4,11′ isomers of $(t\text{-BuC}_{60})_2$ is decomposed into nine component terms.[29] This figure shows that the two major contributors to the destabilization of trans rotamer (the central minimum) are the "other vdw" (long-range van der Waals interactions excluding those between vicinal atom pairs) and the "bending" terms. The former accounts for about one-half

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[26] (a) Ōsawa, S.; Ōsawa, E. In *Science and Technology of Fullerene Materials*, Vol. 359, MRS Symposium Proceedings Series; Materials Research Society: Pittsburg, 1995; pp 145−156. (b) Ōsawa, S.; Ōsawa, E. *Fullerene Sci. Technol.*, in press.

[27] Xu, C. H.; Scuseria, G. E. *Phys. Rev. Lett.* **1995**, *74*, 274.

[28] **8** is doubly wrong. Common sense would tell, in predicting a stable conformation of $(t\text{-Bu-C}_{60})_2$, (1) to remove the bulky groups as far apart as possible and (2) to reduce the nonbonded repulsion between the *tert*-butyl group and the adjacent C_{60} cage by increasing their separation as much as possible. The distance between a methyl group of the *tert*-butyl group and the cage surface is larger when the *t*-Bu-C_{60} bond is in the eclipsed conformation like **8** than in the staggered conformation like **6**. According to our calculations, however, **8** corresponds to an energy maximum! Its location on the torsional energy surface is indicated in Figure 2a with a white arrow. At this point, the other *tert*-butyl group is staggered relative to the vicinal $C_{sp^3}{-}C_{sp^2}$ bonds on the cage surface; hence this point does not exactly correspond to **8**. When the two *t*-Bu/C_{60} bonds are rotated in separate two-bond drive runs while keeping the trans pivot conformation, this point became a sharp hilltop. The torsional energy surface is shown in Figure 6 of the supporting information.

[29] The total steric energy curves correspond to the front end of the torsional energy surfaces shown in Figure 2. Namely, both *tert*-butyl groups are in a staggered conformation.

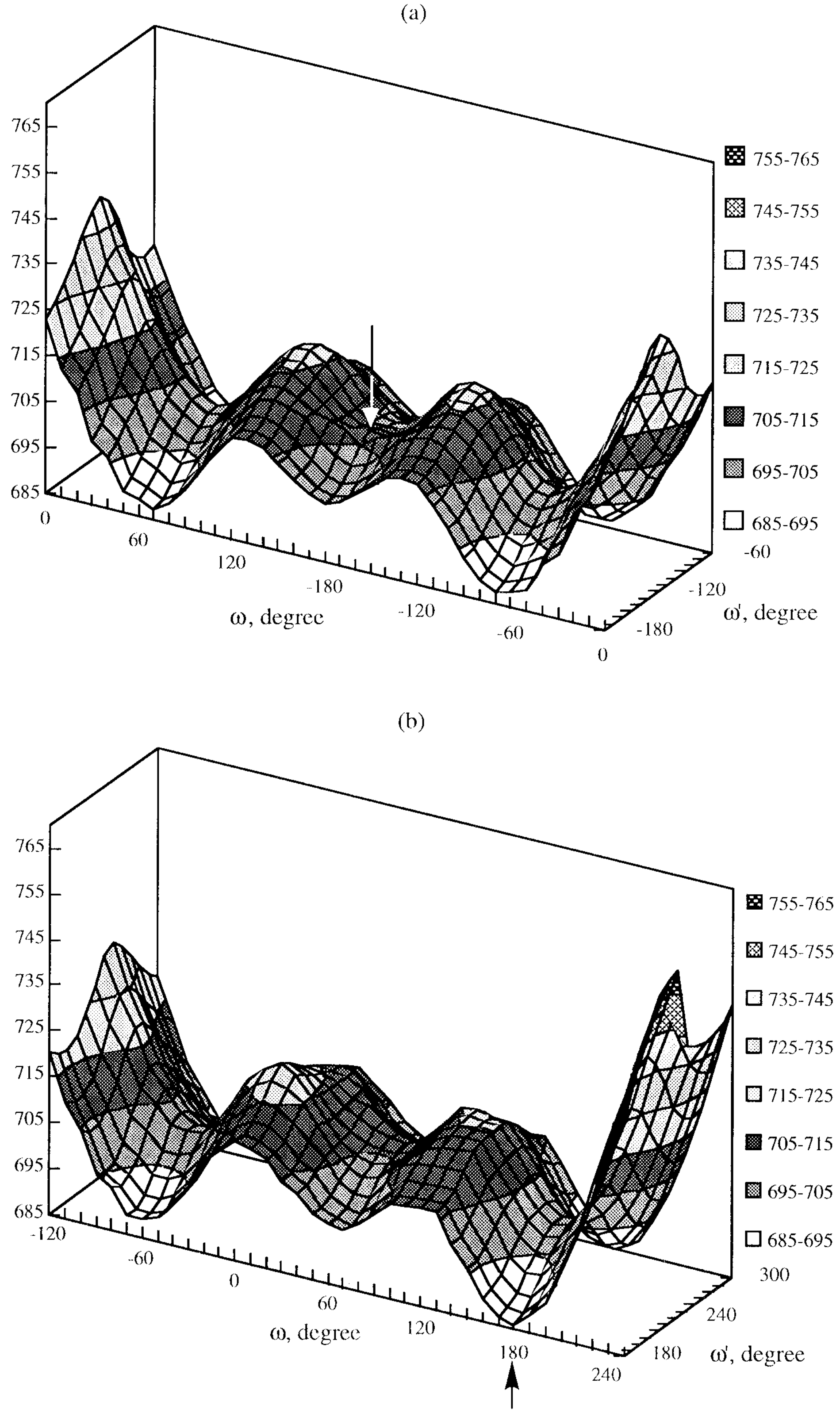

Figure 2. Torsional energy surfaces of para dimers of $(t\text{-BuC}_{60})_2$ obtained by simultaneous rotation of the pivot bond and one of the t-BuC$_{60}$ bonds. Dihedral angles are defined by C2−C1−C1′−C2′ for ω and by Me−C$_q$−C4−C3 for ω' (see Scheme 1 for the numbering). (a) 4,11′ isomer: white arrow indicates the location of conformation **8**. Three minima along the front cross section correspond, from left to right, to **5** (gauche), **6** (trans), and a rotamer enantiomeric to **5** (gauche′), respectively. (b) 4,4′ isomer: solid arrow indicates the location of global energy minimum **7**. C2−C1−C1′−C2′ dihedral angle axis is phase-shifted so that gauche, trans, and gauche′ conformers appear in this order from left to right for ease of comparison with (a).

of the trans-gauche energy difference and was further decomposed in Figure 4 into two main types, one acting between the two *tert*-butyl groups, *t*-Bu/*t*-Bu, and the other working between a *tert*-butyl group and the C$_{60}$ cage, *t*-Bu/C$_{60}$, both across the pivot bond. To our surprise, the *t*-Bu/*t*-Bu interactions in the gauche rotamers are not repulsive but weakly *attractive* as indicated by two small dips at these rotamers.[30] The repulsive *t*-Bu/C$_{60}$ interaction is by far the stronger cause of the trans-gauche energy difference.

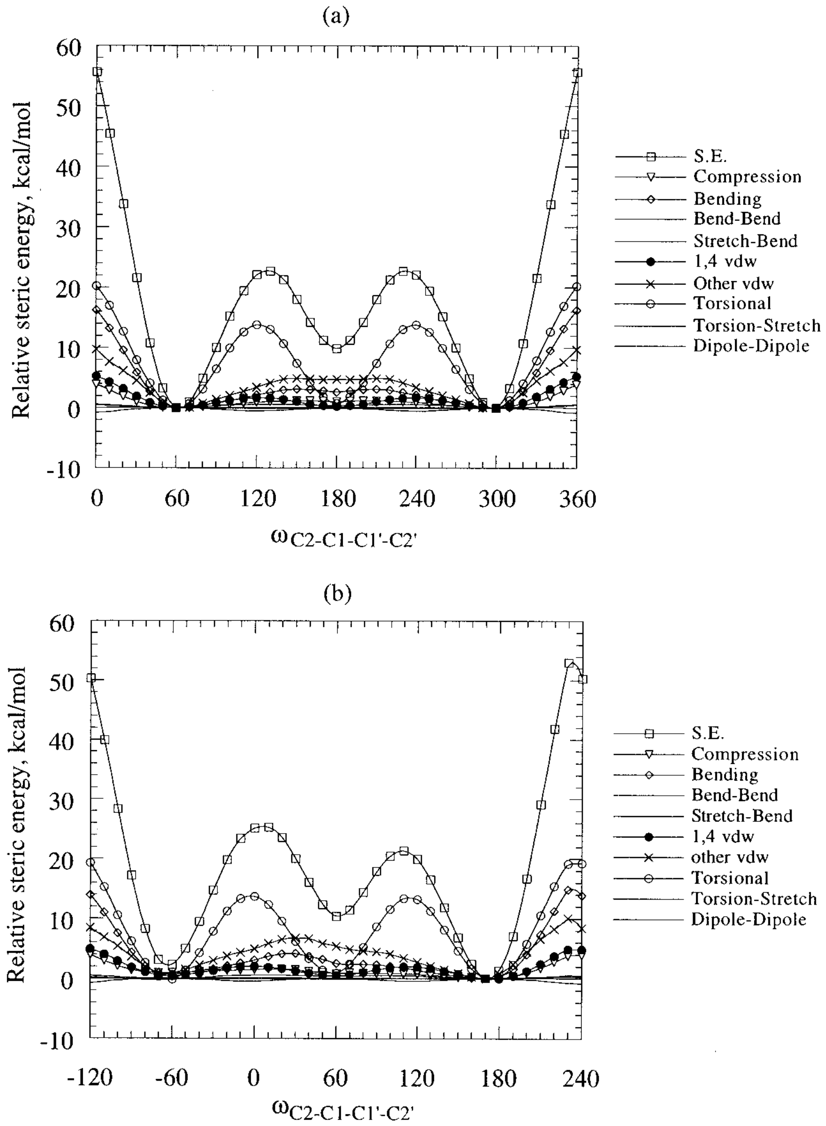

Figure 3. Decomposition of the total MM3 steric energy into component terms during the rotation of pivot bond in two positional isomers, (a) 4,11′ and (b) 4,4′, of (t-Bu-C_{60})$_2$. Abbreviations: total = total steric energy; bend = valence angle bending energy; other vdw = van der Waals interaction energy between more remote atom pairs than 1,4-type; torsion = torsional energy. Only the important components are marked on the curves for clarity, while unmarked curves correspond to bond stretch−compression, dipole−dipole interaction, and 1,4-van der Waals interaction energies. In (b), the phase of C2−C1−C1′−C2′ dihedral angle axis is shifted as in Figure 2.

The second largest cause of the trans-destabilization, the bending term, is similarly dissected into major components as shown in Figure 5.[31] The dominant roles of pivot "C_{piv}" and substituent-bearing "C_{sub}" atoms (two upper curves) were actually anticipated from their greatly deformed valence angles as shown in the drawings **5** and **6**. Figure 5 demonstrates interesting variations in the valence angles during the rotation of the intercage bond. The 3-fold pattern of C_{piv} curve originates from the torsional potential: strained at the eclipsed conformation but relaxed at the staggered. The C_{sub} curve follows the pattern of the long-range van der Waals interaction of the t-Bu/C_{60} type mentioned above. Consequently, deformations at C_{sub} atoms becomes more pronounced in the trans rotamer than those at C_{piv} atoms.

Clearly, the two major sources of the trans-destabilization are the repulsive t-Bu/C_{60} interaction and the valence angle deformation at the *tert*-butyl-bearing C_{60} carbon atoms. The complex phenomenon as analyzed above may be understood by invoking a lever effect. As the pivot bond rotates toward trans rotamer, bending deformations as mentioned above combine to *reinforce* congestion on both sides of molecule by the lever mechanism (**9**). When the *tert*-butyl group attached to the left C_{60} cage of this illustration is pressed by the right C_{60} cage to bend itself backward (to left) and simultaneously push down the left cage, these movements worsen its contact with the *tert*-butyl group on the lower right, which eventually pushes up the right C_{60} cage to nullify all the strain-relieving adjustments around the left *tert*-butyl group. Thus, considerable strain will remain unreleaved in the trans rotamer. One of the methyl hydrogen atoms in **6** has been pressed to within 2.3 Å of a C_{60} carbon atom,

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(30) Examples are known on the stabilization of an apparently congested situation by van der Waals attraction: (a) Ōsawa, E. In *Advances in Molecular Structure Research*, Vol. 2; Hargittai, I., Hargittai, M., Eds.; JAP Press: Connecticut, in press. (b) Tsuzuki, S.; Schäfer, L.; Goto, H.; Jemmis, E. D.; Hosoya, H.; Tanabe, K.; Ōsawa, E. *J. Am. Chem. Soc.* **1991**, *113*, 4665. (c) Cao, M.; Schäfer, L. *J. Mol. Struct. (Theochem)* **1993**, *284*, 235.

(31) As judged by the MM3 valence angles, the approximate C_3 symmetry of methyl and *tert*-butyl groups is not grossly disturbed even by such a strong interaction with the C_{60} cage.

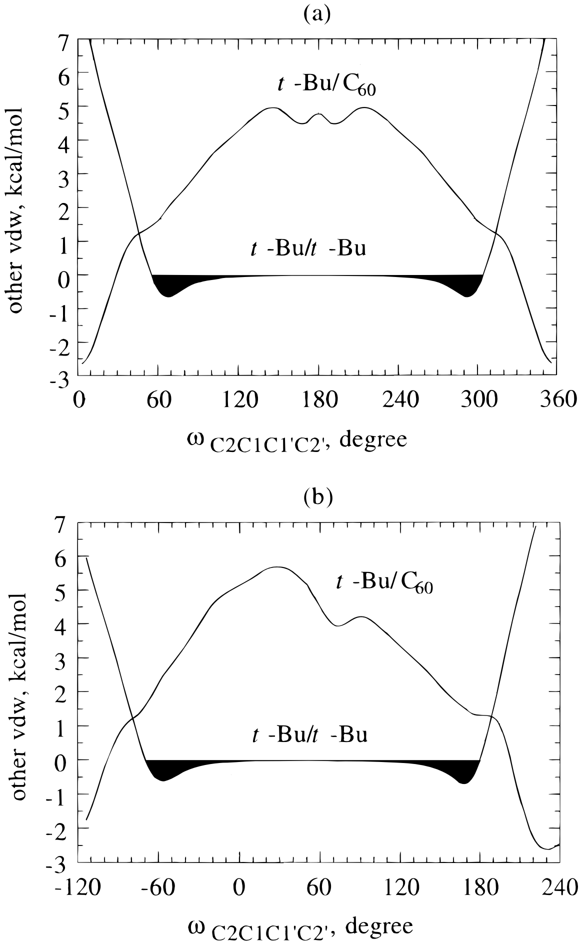
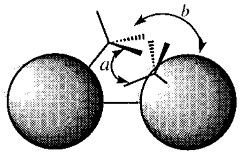
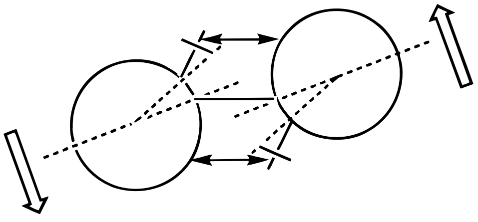


Figure 4. Decomposition of long-range van der Waals interaction energies of (a) 4,11′ and (b) 4,4′ isomers of (t-Bu-C_{60})$_2$ into those between substituents (t-Bu/t-Bu, *a* in the inset) and between the nonbonded *tert*-butyl group and C_{60} cage (t-Bu/C_{60}, *b*). Note that the phase of C2−C1−C1′−C2′ rotation angle is shifted in (b) for ease of comparison.



producing 1.7 kcal/mol of repulsion in this pair alone according to MM3.



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In contrast, similar swing of C_{60} cages around the pivot bond in the course of rotation toward a gauche rotamer produces an effect opposite from that of trans rotamer, namely, in this case the bending deformations on both sides of molecule work cooperatively to *diminish* intramolecular repulsive interactions (**10**).

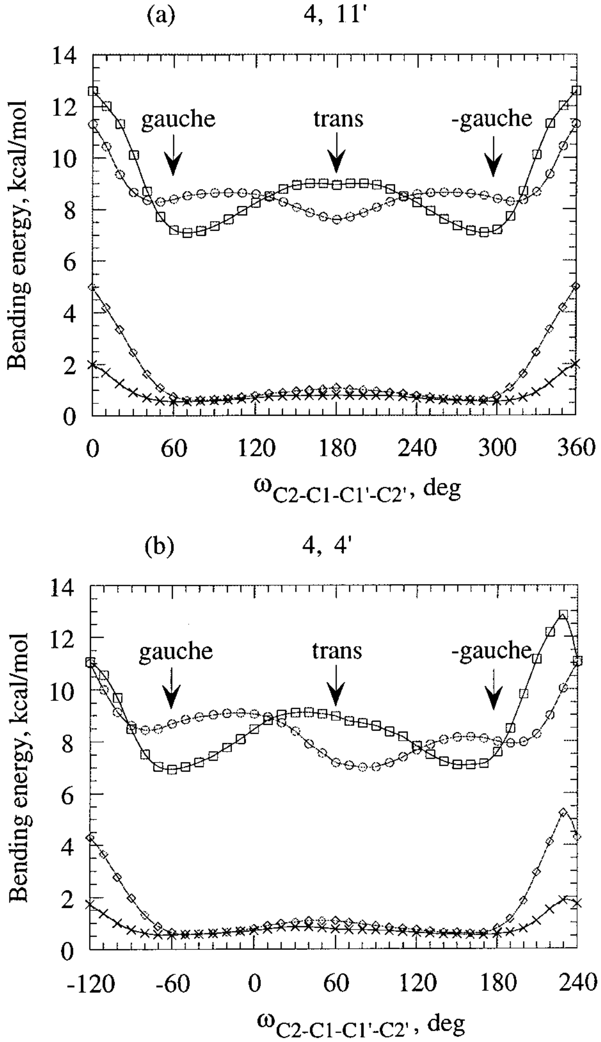
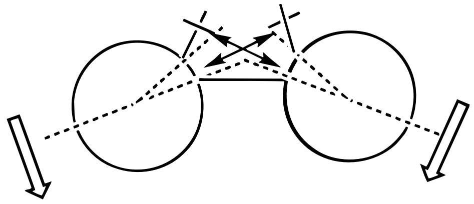


Figure 5. Decomposition of bending energy curves of (a) 4,11′ and (b) 4,4′ isomers of (t-Bu-C_{60})$_2$ into major components as the function of rotation angle at the pivot bond. Each point in the curves marked with C_{piv} (○), C_{sub} (□), C_q (◇), and C_{Me} (×) corresponds to the summation of bending energies involving the pivot carbon atom, the sp^3 carbon atom carrying the *tert*-butyl group, quaternary carbon atom of *tert*-butyl group, and methyl carbons, respectively, as the central atom at certain pivot dihedral angles.



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The lever effect is not restricted to the conformations near energy minima, as seen from another feature that characterizes the internal rotation of the (t-BuC_{60})$_2$ molecule: ac barriers that appear during the rotation of gauche or gauche′ to trans rotamer are unusually high (21−24 kcal/mol) compared to the H- and methyl-substituted C_{60} dimers (Figure 3). The torsional energy component contributes about 15 kcal/mol, which corresponds to the simultaneous eclipsing barrier mentioned above. The remainder consists of the same sources which destabilize the trans relative to the gauche form, namely, the long-range nonbonded repulsion and angle bending strain that accompanies the large repulsive interaction between the *tert*-butyl group and its facing C_{60} cage are the two dominant causes. Actually, the lever effect starts to work as soon as the dihedral angle between the *tert*-butyl groups exceeds a right angle.

The lever effect is not restricted to the *tert*-butyl-bearing C_{60} dimers, either. The destabilization of trans relative to gauche rotamer appears in the ortho dimers of H- and methyl-substituted cases as well (Figure 1 and Table 3), wherein trans rotamers are always less stable than the corresponding gauche rotamers, especially so in $(MeC_{60})_2$ (Figure 1b). A close look at the curve of the sterically most demanding 2,2′ isomer of $(MeC_{60})_2$ reveals that the trans rotamer is actually a small energy maximum! Even when R = H, the trans form of the ortho 2,2′ isomer is 4 kcal/mol less stable than the gauche rotamers (Figure 1a). Hence we may conclude that the lever effect is ubiquitous in dumbbell-shaped C_{60} dimers carrying ortho or para substituents.[32]

Finally, the rotation of *tert*-butyl groups in $(t\text{-}BuC_{60})_2$ is worth a special note. Activation enthalpy for the internal rotation of t-BuC_{60} bond in the monomeric $t\text{-}BuC_{60}^{\bullet}$ radical is reported to be 7.3 kcal/mol.[2d] In the case of its dimer, however, the two-bond driver calculations of the two C_q-C_q *tert*-butyl bonds with the pivot bond fixed at the trans form give much higher barrier heights of 16−17 kcal/mol.[20] The remarkable increase in the barrier height arises from the large friction between the *tert*-butyl group and the facing C_{60} cage of the dimer, which does not exist in the monomeric species. The congestion produced by squeezing a *tert*-butyl group into the small space around the pivot bond of a C_{60} dimer could well be one of the highest among the known organic molecules.

Conclusions

Two unusual rotational characteristics about the intercage bond are predicted for the singly bonded dimers of buckminsterfullerene derivatives $(RC_{60})_2$, R = H, Me, *t*-Bu: the high rotational barrier heights of at least 15 kcal/mol or more and the preference of gauche to trans rotamer. The former can be interpreted by almost simultaneous eclipsing in the rotational transition state, while the latter was explained by invoking a lever mechanism. The lever effect appears most remarkably when R = *t*-Bu.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, No. 05233107, from the Ministry of Education, Science and Culture.

Supporting Information Available: Table 4 lists numerical data for Figures 1 and 2: MM3-conformational energies and populations for energy minima, rotational barrier heights, weighted average steric energies for positional isomers, and Cl−Cl′ bond lengths for all the stationary points. Figures 6a and 6b are the torsional energy surfaces of $(t\text{-}BuC_{60})_2$ with regard to the rotation of two C_q-C_q *tert*-butyl bonds in the trans rotamers of the (a) 4,11′ isomer and (b) 4,4′ isomer, respectively (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[32] We learned from Andrew Podosenin and Stephen R. Wilson, New York University, that they have also observed the same destabilization of trans rotamers compared to the gauche rotamers in 4,4′- and 4,11-$(RC_{60})_2$, R = *i*-Pr, CCl_3, and CBr_3, as we have found here.