Nature of Cyclobutane Bonds in the Neutral [2+2] Dimer of C₆₀

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Previous theoretical calculations have predicted normal bond lengths for the pivot cyclobutane bond (C1−C1′) and abnormally long lengths in the hinge bond (C1−C2) of the neutral [2+2] C_{60} dimer (**1**). This result did not agree with the theory that the orbital-interaction-through-bond of $\pi-\sigma-\pi$ type enhanced by strain should elongate the mediating σ bond. The orbital interaction through the pivot bond of **1** was indeed detected by the analysis of MO energy levels. Hence the present case offers the first definitive evidence against the bond elongation theory. Instead, we present a universal, parabola-like relation between the lengths (r) of the symmetrical C_q-C_q bond in **1**, and other head-to-head cage dimers, and the s-character in the σ orbital localized at the bond. The relation found here explains all the previously observed lengths of pivot bonds in the head-to-head cage dimers including **1**.

1. Introduction

Buckminsterfullerene, C_{60}, polymerizes under a variety of conditions,[1] but the structures of the products remain largely unknown. While the coalescence products may be too complex to seriously attempt any analysis,[2] the seemingly simple addition polymers have not been well characterized either. The [2+2] cycloaddition mode (**1**) has been well accepted for both the neutral dimers obtained by photoirradiation[3−5] and the polymers of alkali fullerites;[6,7] it has recently been proposed that the latter consist of singly bonded C_{60} units (see **11**).[5,8] We restrict our attention here only to the neutral dimers of C_{60}, which are most likely to have the structure **1**.
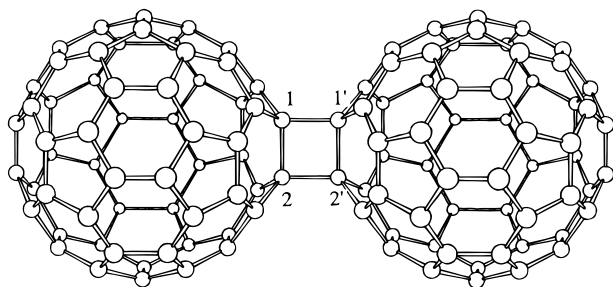
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The continued failure in the diffraction analysis of the neutral dimer of C_{60} has stimulated a number of computational investigations on the long-postulated [2+2] structure.[5,9−16] One particular structural aspect repeatedly reported in these theoretical papers attracted our curiosity: the pivot bond C1−C1′ is always predicted to be significantly longer than the hinge bond C1−C2 as long as the level of theory used was equal to or above the semiempirical method, as can be seen in Table 1. The values in this table may appear too long for a cyclobutane bond, but we should recall the fact that the standard bond length to be compared with those of **1** should be that of persubstituted
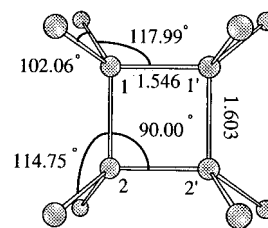
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TABLE 1: Observed and Computed Cyclobutane Bond Lengths (Å) of the [2+2] C_{60} Dimer (1)

pivot C1−C1′	hinge C1−C2	method[a]	ref
1.561	1.616	MNDO	5
1.575	1.585	3-21G LDA	5
1.594	1.606	3-21G B3LYP	5
1.575	1.594	3-21G HF	5
1.546	1.603	AM1	this work
1.560	1.620	*ab initio*	11, 13
1.64	1.612	TB	15
1.583	1.590	DF-TB	16

[a] TB = tight-binding MO. LDA = local density approximation of density functional (DF) theory. For other abbreviations, see ref 5.

octamethylcyclobutane, 1.571 Å (by AM1), rather than that of parent cyclobutane, 1.554(21) Å[17] or 1.543 Å (AM1).

We had anticipated a much longer pivot bond and a shorter hinge bond, as mentioned later, but first tried to explain the computed order by the existing theories on valence angles. As shown below (**1′**), each of the bridge carbon atoms (C1, C2, C1′, C2′, all equivalent) have a pair of small valence angles (90°, 102°) and four large angles (all 118°).[8] One could interpret the normal pivot bond length as follows: shrinkage due to large exocyclic valence angle (118°)[18] was compensated by elongation due to the stretch−bend interaction across the small endocyclic angle (90°). However, this interpretation does not explain the abnormal elongation of the hinge bond, which has also been observed in other cyclobutane-fused C_{60} derivatives.[19]

1′

According to the $\sigma-\pi-\sigma$ orbital-interaction-through-bond (OITB) effect,[20] the pivot bond could have been elongated to an unusually long distance, and this effect could have been enhanced by angle strain in the central bridge.[21] In contrast, the hinge bond is free from the OITB effect due to the adverse

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alignments of orbitals but may be mechanically compressed by clamping with the rigid C_{60} cages. We now face the fact that none of the existing theories of bond lengths can explain the enigmatic difference in the lengths of cyclobutane bonds of **1**.

We wish to present in this paper an interpretation for the computed bond lengths. The seemingly subtle problem is related with the perspective of using **1** as a precursor of C_{120} giant fullerenes,[22,23] which we will discuss in the last part of this paper.

2. Computational Methods

MOPAC version 6.01 by J. J. P. Stewart was obtained from the Japan Chemistry Program Exchange, 1-7-12 Nishinenishi, Tsuchiura-shi, Ibaraki-ken, 300, Japan (Fax 81-298-30-4162; Program No. P049). The AM1 Hamiltonian[24] in the program package was used for the HF/SCF MO calculations of **1** and other molecules. AM1 reproduces the observed structural parameters of C_{60}[25] and C_{70}[8] well, but grossly overestimates the heats of formation of fullerenes.[26] Therefore we used the AM1 energies only on a relative basis. Localized molecular orbitals were obtained from the canonical AM1 MOs by using a modified method of Von Niessen[27] packaged in MOPAC. Convergence criteria in the SCF cycle were 10^{-4} kcal/(mol·Å) for the energy threshold and 10^{-2} kcal/(mol·Å) for the energy gradient norm.

All computations have been carried out on Hewlett-Packard-Apollo DN10000, 9000/750 and Titan 2-800 workstations.

3. Results and Discussion

3.1. Effect of Orbital-Interaction-Through-Bond. The OITB of $\pi-\sigma-\pi$ type has been believed to weaken the mediating bond by mixing π^* antibonding character into it, especially when the bond is under strain.[21,28] To address the contradictory observations on the computed bond lengths of pivot bonds in **1**, we first checked if the OITB is really present in this molecule. According to the character table of point group D_{2h},[29] the OITB between C_{60} portions of **1** occurs only in four π MOs having symmetries B_{1u}, B_{3g}, A_g, and B_{2u}. Electron density contours of these high-energy occupied molecular orbitals (Figure 1) clearly demonstrate the operation of OITB: orbitals No. 240 (HOMO, B_{1u}) and No. 239 (the second HOMO, B_{3g}) are in-phase and out-of-phase combinations, respectively, of π MOs in the two separate C_{60} cages. The observed ordering is the reverse of the conventional *out-of-phase above in-phase* rule. The same situation applies to the other pair of orbitals, Nos. 232 (A_g) and 231 (B_{2u}). This analysis provides strong evidence for the operation of OITB.[30]

There can be two mechanisms that cause the reversal of energy levels. Let us take the former case, namely, the reversal of B_{3g} *vs* B_{1u} MO levels, as an example. One is the mixing of an antibonding orbital of B_{3g} symmetry with the high-lying bonding B_{3g} MO, which is illustrated on the right side of Scheme 1 (the bonding−antibonding interaction). In this mechanism, the antibonding contribution to the pivot bond will increase and the bond may be destabilized and elongated. The other is the mixing of a deeper lying bonding orbital of B_{1u} symmetry with the high-lying bonding orbital of symmetry B_{1u} symmetry, on the left side of Scheme 1 (bonding−bonding interaction). In the second mechanism, there will be no overall effect on the strength of the pivot bond. The computed results (Table 1) that the pivot bond is not elongated support the second mechanism rather than the first one, which anyway involves only a weak interaction between the well-separated energy levels.

This analysis presents a strong argument against the bond elongation theory by OITB.[21] So far the evidence supporting
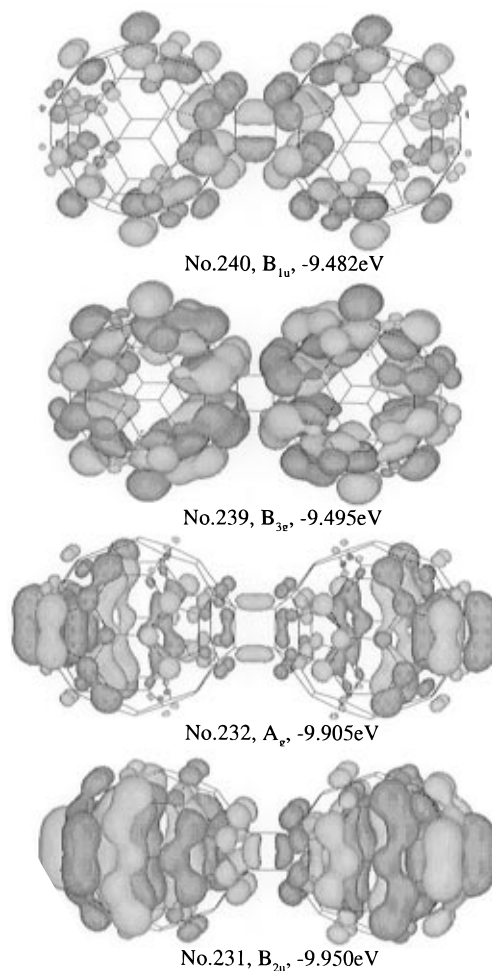

No.240, B_{1u}, -9.482eV

No.239, B_{3g}, -9.495eV

No.232, A_g, -9.905eV

No.231, B_{2u}, -9.950eV

Figure 1. Higher occupied π molecular orbitals of [2+2] C_{60} dimer **1** (AM1) relevant to the ordering diagnosis for the orbital-interaction-through-bond (OITB). The 240th orbital (HOMO) has a mirror symmetric property $\bar{1}11$ regarding σ^{xy}, σ^{xz}, and σ^{yz} planes (1 for symmetric and $\bar{1}$ for antisymmetric), while the 239th orbital is $\overline{111}$. These two orbitals differ only with respect to the symmetry property of the σ^{xz} plane, hence form an in-phase and out-of-phase combination of π orbitals of C_{60} cages, respectively, in unnatural order of energy level, which attests to the operation of OITB. The other pair of orbitals of Nos. 232 and 231 represent 111 and $1\bar{1}1$ mirror symmetry in unnatural order.

the bond elongation, which has actually been observed often, has never been conclusive due to the complexity of MOs of less symmetrical molecules. **1** provides a highly symmetrical framework amenable to a clear-cut analysis of MOs. There is other evidence that demonstrates the absence of bond elongation in the OITB.[31]

Thus, one problem is solved: our presumption of long distance for the pivot bond of **1** was wrong. Still another problem remains: why is the hinge bond of **1** abnormally long? We show below that an uneven hybridization of cyclobutane carbon atoms is responsible for the different bond distances in this ring.

3.2. Effect of Hybridization. We begin with a small model, dinaphthalene (**2**, 4a,8a-(4a′,8a′-naphthaleno)naphthalene). The use of a small model **2** for the dimer **1** is rationalized by experimental observations showing that changes in the structural parameters and charge distribution that occur by the 1,2-addition to C_{60} are limited to the close vicinity of the reaction site.[32]
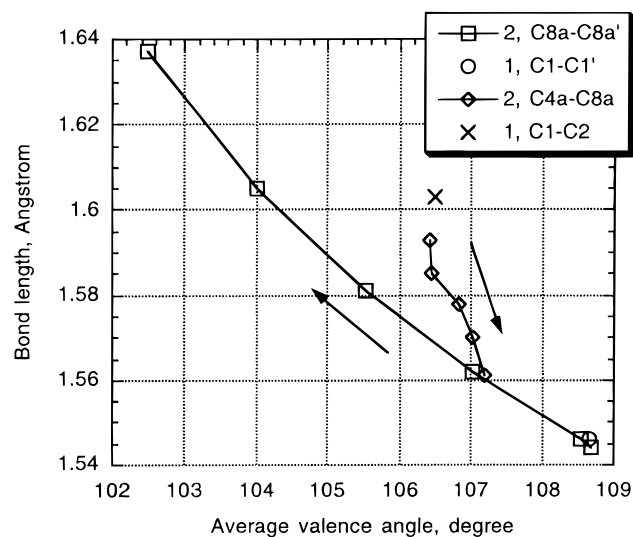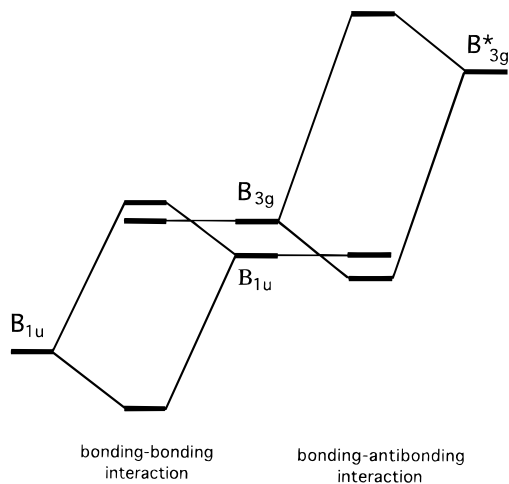
Figure 2. Dependence of the length (r) of pivot and hinge bonds in the [2+2] C_{60} dimer (**1**) and dinaphthalene (**2**) upon the average valence angle θ_{av} involving the bond in question. For example, θ_{av} of C8a along the bond C8a−C8a′ of **2** is obtained by ($\theta_{C8a′−C8a−C1}$+ $\theta_{C8a′−C8a−C4a}$+$\theta_{C8a′−C8a−C8}$)/3.

SCHEME 1

We first thought that its double-butterfly structure resembled the central portion of **1**. Geometry optimization revealed, however, structural features to the contrary: pivot bond C8a− C8a′ (1.581 Å) is slightly longer than hinge bond C4a−C8a (1.578 Å), and the folding angle of two six-membered rings (128.2°) was much larger than that of **1** (117.8°). While attempting to compare the bond lengths of **1** and **2** under identical folding angle by imposing the D_{2h} symmetry constraint, we noticed that the lengths (r) of cyclobutane bonds in **2** change peculiarly and sharply with the folding−unfolding motion of the naphthalene rings. In Figure 2 the computed r was plotted against the average θ_{av} of three valence angles involving the pivot and hinge bond, respectively, instead of being plotted against the folding angle.

The well-known inverse relation between bond length and bond angle[18] holds in such a complex case like the bridgehead carbon atoms of **2**, when the average angle θ_{av} was used. Pivot and hinge bonds form separate $r−\theta_{av}$ relations. The fact that the corresponding points of **1** fell on the respective curves of **2** proved that the selection of the model was right. Whereas a similar relation between r and θ_{av} of cage dimers has been noticed for some time by Mastryukov and others,[33] we were aroused by the countermovements displayed by the cyclobutane bonds in **2**: when the pivot bond lengthens,[30] the hinge bond
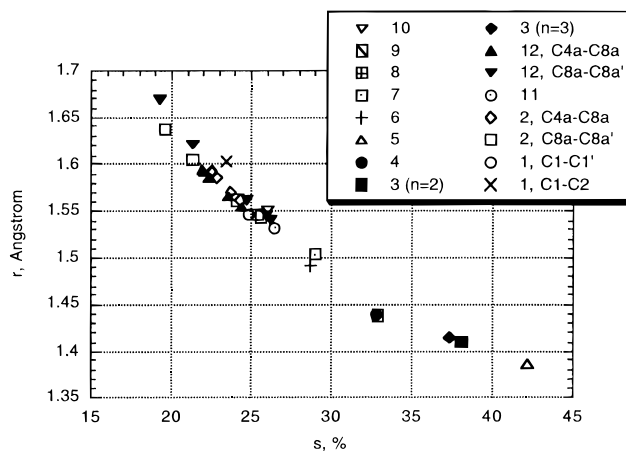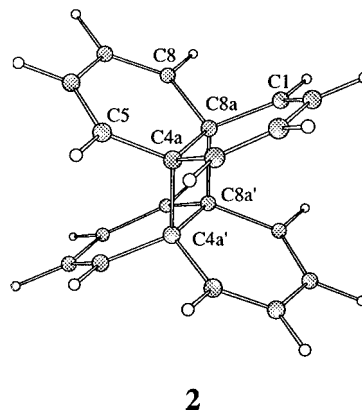

Figure 3. Dependence of distances (r, Å) of pivot and hinge bonds on s-character in doubly bonded C_{60} dimer (**1**), dinaphthalene (**2**), cage dimers (**3−10**), singly bonded C_{60} dimer (**11**), and octahydrodinaphthalene (**12**).

shrinks. Such a move strongly suggests an uneven distribution of hybridization among the valences at the carbon atom under unusual angle deformation.

2

Taking advantage of the centrally symmetric nature of σ bonds in question, we assigned s-characters to the bond based on the localized molecular orbitals and examined their correlation with the lengths. We were pleased to see that the two separate correlation lines that we obtained when the bond lengths were plotted against the average valence angles (Figure 2) now merged into one curve when plotted against s-% of the bond (Figure 3). Encouraged by this success, we included in Figure 3 the known r and s-% data of likewise symmetric $C_q−C_q$ pivot bonds in the strained (**3−5**, **8**, **9**) and unstrained (**6**, **7**, **10**) cage dimers.[34−37] Eventhough the r vs s-character relation has long been known for a limited body of data,[38] the present extension gives by far the broader perspective.

For all the compounds added, the pivot bond lengths have been determined by X-ray method. As summarized in Table 2, the X-ray bond lengths are slightly but systematically longer than the AM1 values, but the magnitude of differences, 0.02− 0.04 Å, is negligible compared to the total span of bond length variation among the compounds. For consistency, the bond distances used in Figure 3 are taken from the AM1-optimized structures. Replotting Figure 3 using X-ray values (Table 2) does not visibly affect the correlation. Thus, the $r−s$ relation presented in Figure 3 is not an artifact of computation but real. The results are gratifying: the plot can be taken to represent a single-valued relation between r and s. It may be noted that not all $C_q−C_q$ bonds fall on this line, but other types of compounds including [4+4] C_{60} dimer,[8] persubstituted cyclo-

TABLE 2: Lengths (r, Å), Percent s-Character (s, %), and Partitioned Two-Center Bond Energies (2CE, kcal/mol) of Pivot Bonds in Cage Dimers

	r		
dimer	expt[a]	ref	AM1[b]	diff[c]	s	2CE
1,1′-bi(tricyclo[4.1.0.0^{2,7}]heptyl) **3** ($n = 3$)	1.445(3)	34	1.414	0.031	37.36	−16.53
1,1′-bi(tricyclo[3.1.0.0^{2,6}]hexyl) **3** ($n = 2$)	1.440(2)	34	1.409	0.031	38.10	−16.66
bicubyl **4** (R = H)[d]	1.458(8)	35	1.440	0.018	32.73	−15.70
bitetrahedryl **5** (R = H)[e]	1.434[f]	36	1.386	0.048	42.17	−17.50
1,1′-binorbornyl **6**	1.515(5)	38a	1.492	0.023	28.68	−14.64
1,1′-biapocamphyl **7**	1.544(2)	38a	1.503	0.041	28.93	
1,1′-bi(cyclo[1.1.1]pentyl) **8** (X = Y = H)	1.474(6)	g	1.438	0.036	32.87	−15.61
4,4′-bis(homocubyl) **9**	1.460(1)	37	1.440	0.020	32.82	−15.70
biadamantyl **10**	1.578(2)	34	1.551	0.027	26.02	−13.68

[a] X-ray results unless otherwise noted. Standard deviation of the last digit given in parentheses. [b] This work. [c] Difference between X-ray-determined and AM1-computed bond distances. [d] Several derivatives are known: 2-*tert*-butyl-**4**, 1.464(5);[35] 4-bromo-**4**, 1.473(5) Å. Hassenrück, K.; Radziszewski, J. G.; Balaji, V.; Murthy, G. S.; McKinley, A. J.; David, D. E.; Lynch, V. M.; Martin, H.-D.; Michl, J. *J. Am. Chem. Soc.* **1990**, *112*, 873. [e] 2-Methoxycarbonyl **5** (R = CO$_2$CH$_3$), 1.441 Å.[36d] [f] High-level *ab initio* value. [g] An average of seven pivot bond lengths in 3,3′-X,Y-1,1′-bi(bicyclo[1.1.1]pentyl): 1.480(3) Å, X = Y = MeS, 1.469(6), X = Y = MeSO$_2$. Bunz, U.; Polborn, K.; Wagner, H.-U.; Szeimies, G. *Chem. Ber.* **1985**, *121*, 1785. 1.480(4), X = H, Y = CO$_2$Me, Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225. 1.476(7), 1.464(7), X = SCOMe, Y = MeCOSZ, Z = 1,3-bicyclo[1.1.1]pentylene group (this compound is a trimer of bicyclo[1.1.1]pentane; hence there are two pivot bonds), Friedli, A. C.; Kaszynski, P.; Michl, J. *Tetrahedron Lett.* **1989**, *30*, 455. 1.473(3), X = H, Y = CCl$_3$, 1.481(8), X = Cl, Y = CCl$_3$, Potekhin, K. A.; Maleev, A. V.; Kurkutova, E. N.; Struchkov, Yu. T.; Sadovaya, N. K.; Surmina, L. S.; Koz'min, A. S.; Zefirov, N. S. *Dokl. Akad. Nauk SSSR*, **1990**, *312*, 1147; *Chem. Abstr.* **1990**, *113*, 201873n.

butanes, and hexamethylethane form separate $r-s$ lines. Namely, the present relation holds only for the pivot bonds in the head-to-head cage dimers.

3

4

5

6 (gauche)

7 (trans)

8

9

10
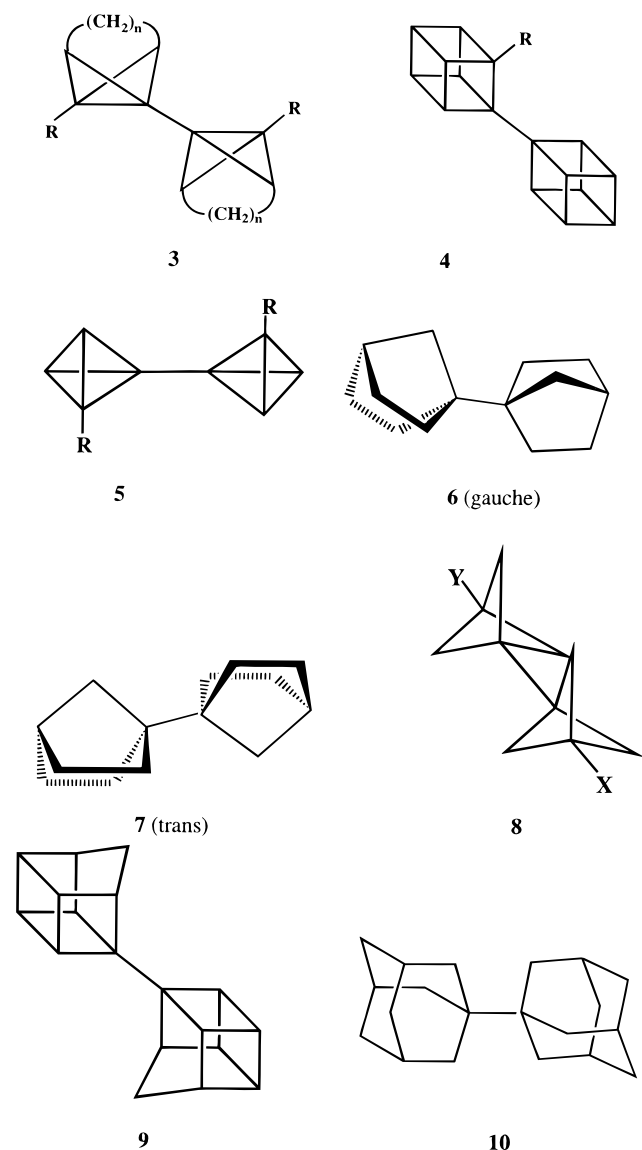
We further added two more imaginative compounds to Figure 3, a singly bonded C_{60} dimer **11** (H-$C_{60})_2$[8] and an octahydrodi-naphthalene (**12**, 1,4,5,8,1′,4′,5′,8′-octahydro-4a,8a-(4a′,8a′-naphthaleno)naphthalene). For **12**, the D_2 conformation shown is the global energy minimum. For the atom numbering of **12**, see the drawing of **2**. The effect of varying the folding angle in **12** upon the lengths of pivot and hinge bonds was followed as we did in **2**. Results were almost superimposable with those of **2** and fell on the same $r-s$ line. Since there should be no direct interaction between the double bonds and cyclobutane ring in **12**, this test establishes beyond doubt that the hybridization change imposed by the geometrical constraints overrides the OITB effect, if any, in determining the bond length in these compounds.

11

12
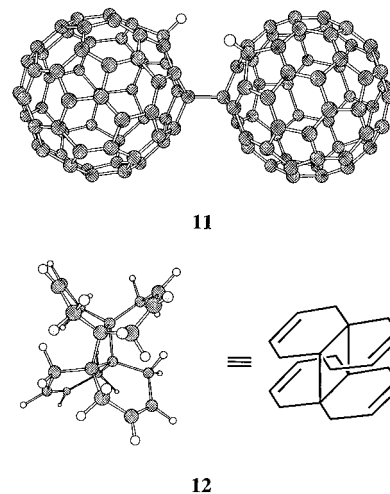
Now we reach the final solution to the problem posed in the Introduction. The lengths of pivot and hinge bonds of **1** are controlled by their valence angles, in accordance with the generally held idea.[18] For the head-to-head cage dimers like **1**, a convenient measure for the distances of bonds at the cage junction is the s-character of the valence in question. The hinge bond is longer than the pivot bond because the former has a smaller s-character than the latter. It may be noted that the magnitude of s-character primarily depends upon the three valence angles containing the valence in question. For example, that of the pivot bond of **1** is determined by the C2−C1−C1′
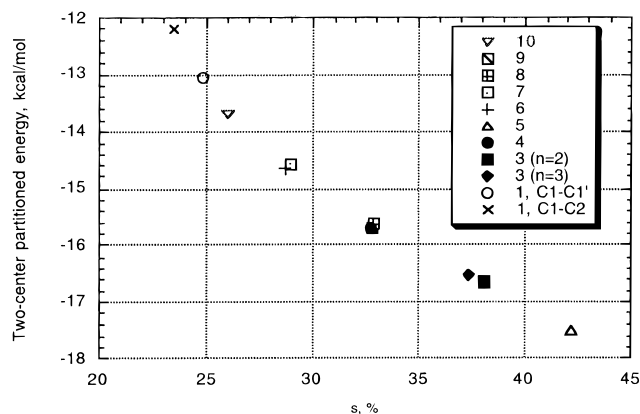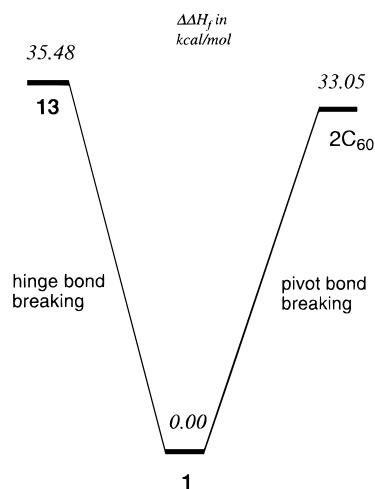
Figure 4. Relative energies of pivot had hinge bonds computed by the two-center energy partition scheme of Pople plotted against s-character of the bond.

SCHEME 2

angle and the two $C_{sp^2}-C1-C1'$ angles. These three angles are greatly deviated from the normal valence angle, but the combined effect gave an s-character that is almost identical to that of a purely sp^3 carbon atom. This is the reason why the pivot bond of **1** has practically the same value as that of biadamantyl **10**.

After confirming that the bond lengths we discussed here are the function of s-character only, we thought it worthwhile to confirm another general idea that the strength of a C−C bond is a function of distance only. Figure 3 presents plots of bond energies obtained by the two-center energy partition scheme originally proposed by Pople for semiempirical MO methods[39,40] (Table 2) against their s-characters (Figure 4). Combined with the single-value relations between *r* and s, simple dependence of the strength on the length of a pivot C-C bond in the head-to-head cage dimes has now been confirmed.

3.3. Fate of 1. It is now clear that the hinge bond of **1** should be weaker than the pivot bond. If the two hinge bonds in **1** break up, it is likely that a pair of double bonds will be produced at the bridge to give a C_{120} molecule (**13**), which is made up only of sp^2-hybridized carbon atoms and would be interesting as an entry into C_{120} fullerenes.[8] Comparison of the AM1-computed heats of reaction[8] indicates that this reaction is thermodynamically slightly less favorable than the breaking of pivot bonds to regenerate two molecules of C_{60} (Scheme 2). It would be interesting to study the thermal behavior of **1** *under kinetic control* to see if they produce **13** or its congeners.
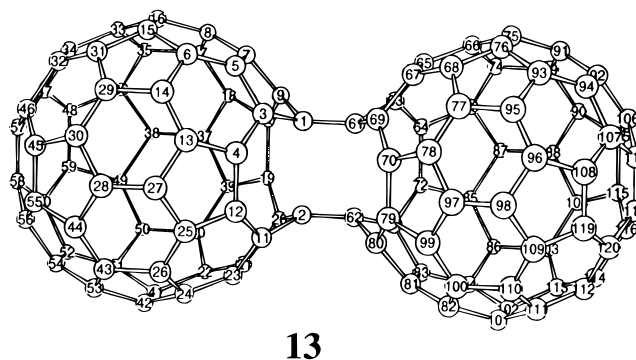
13

4. Conclusions

1. Significant orbital interactions have been detected between C_{60} cages in the neutral dimer of C_{60} (**1**) through the pivot bond by the reversal in several occupied MO levels. Contrary to the past ideas, we conclude that the $\pi-\sigma-\pi$ OITB must be dominated by bonding−bonding interactions and does not elongate the mediating pivot bond, at least in the case of **1**.

2. In the head-to-head cage dimers like **1**, the length of the pivot bond is a sole function of s-character in the localized bond, which in turn depends on all of the valence angles that include the bond in question. Due to the incidental balance among these valences, the pivot bond in **1** has almost the same s-character as that of a pure sp^3 bond. On the other hand, the hinge bond of **1** has relatively small s-character, hence is somewhat elongated.

3. The hinge bond of **1** is expected to be weaker than the pivot bond.

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