Dimerization of C_{60}: Symmetry Considerations

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Dedicated to Professor *Edgar Heilbronner* on the occasion of his 80th birthday

Orbital-symmetry analysis (OCAMS) of the dimerization of C_{60} *via* [2 + 2] cycloaddition indicates that the reactant monomers should approach one another along a pathway in which C_{2h} symmetry is conserved. Point-by-point computations (AM1/UHF) confirm this prediction: a low-energy pathway leads to a single-bonded dimer **2** with C_{2h} symmetry. Closure to the stable D_{2h} dimer **1** is effected by relatively facile rotation about the single bond. A similar symmetry analysis was performed on a second isomer **3** with D_{2h} symmetry, the moieties of which are linked by two two-atom chains. It raises the possibility that **3**, the so-called 'window' isomer, may be interconvertible with **1** along a pathway that retains C_i (S_2) symmetry. Although the computational results indicate that C_{60} is in thermal equilibrium with its stable dimer **1** at moderate temperatures, the latter is not observed in the gas phase for thermodynamic reasons. According to THERMO computations (AM1/RHF), the equilibrium is shifted strongly towards the monomer pair at temperatures where vaporization of the solid C_{60} is observed (>400°).

Preface. – I welcome the opportunity to include in this dedicatory issue of *Helvetica Chimica Acta* a modest tribute to my good friend, Professor *Edgar Heilbronner*, in partial recompense for the valuable advice that he gave me over a quarter of a century ago. Soon after *Woodward* and *Hoffmann*'s seminal monograph [1] introduced the ideas of orbital symmetry into Organic Chemistry, I devised a systematic extension of *Longuet-Higgins* and *Abrahamson*'s application of symmetry considerations to the analysis of organic reaction mechanism [2]. My method, which I named *Orbital Correspondence Analysis in Maximum Symmetry (OCAMS)*, aroused objections on the part of journal editors and referees, partly because it seemed to be stepping on hallowed toes and partly because of perceived flaws in the underlying theory.

During the *2nd IUPAC Conference on Physical Organic Chemistry*, held at Nordweikerhout in the summer of 1974, I related my difficulties to *Edgar Heilbronner* and convinced him of the theoretical validity of OCAMS, which was soon to be justified formally in a joint publication with my colleague *Jacob Katriel* [3]. *Edgar* raised several useful points on terminology and presentation, and concluded with the following practical suggestion: '*Join the Swiss Chemical Society and submit your paper to Helvetica Chimica Acta*'. I promptly acted as advised; the first paper on OCAMS was published [4], opening the way to a development of the method over the years and its eventual publication in a monograph [5].

Introduction. – a) *OCAMS Revisited*. The essential feature of OCAMS is as follows: when a reaction path is constrained to a given symmetry point group, it is *forbidden* by orbital symmetry if the irreducible representations (irreps) of two or more molecular orbitals (MOs) of the reactant(s) differ from those of the product(s). However, the *forbiddenness* can be lifted by a nuclear displacement to a subgroup in which the orbital mismatch has been eliminated. In a commutative group, the irrep of the required displacement is the direct product of the irreps of the non-correlating orbitals. For example, the paradigmatic suprafacial [2 + 2] cycloaddition of ethylene is *forbidden*, because an occupied molecular orbital of the reactant (the highest, though it need not be) correlates with a vacant MO of the product, and *vice versa* [1a]. As illustrated in *Fig. 1* [4a][5a], the *forbidden* suprafacial [2s + 2s] approach can be made *allowed* by reduction of symmetry along the reaction path from D_{2h} to $C_{2h}^{(y)}$, *i.e.*, by imposing a b_{2g} displacement, because b_{2g} is the direct product of b_{1u} and b_{3u} – the respective irreps of the mismatched MO's – both of which map onto b_u in $C_{2h}^{(y)}$.

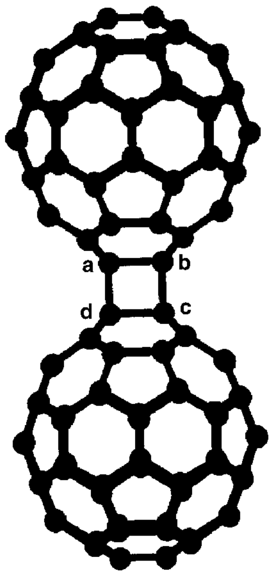
The formal *allowedness* achieved in this way, does not imply that the pathway will necessarily retain $C_{2h}^{(y)}$ symmetry, but only that no pathway of higher symmetry is compatible with the conservation of orbital symmetry. Moreover, [2 + 2] cycloaddition cannot be suprafacial, because a b_{2g} displacement favors bonding across the diagonal to form a *trans*-biradical, which then closes in a second step to generate the antarafacial product. This mechanistic sequence has been confirmed experimentally in a variety of cycloadditions [5b], perhaps most convincingly by stereochemical evidence in the dimerization of haloalkenes [6].

b) *Dimerization of C_{60}.* Though orbital-symmetry conservation is an important factor governing the reaction mechanisms of small organic molecules, it cannot be assumed *a priori* to hold for the reactions of large polyatomic species. The dimerization of C_{60} is an excellent case for testing this question. A variety of C_{60}-dimers have been computed by different methods in several laboratories [7–12], with widely divergent results. These results have been discussed critically by *Patchkovskii* and *Thiel* [12], who undertook an extensive exploration of the potential energy surface using MNDO/3 × 3 CI. They identified a number of structures as lying on extrema. Four of them, **1** and **3** with D_{2h} symmetry and two variants of **2** (C_{2h} and C_2), were characterized as stable dimers. Other conformers of **2**, including several with C_{2v} symmetry, were identified as first- and second-order transition states.

The authors explain the necessity for employing at least a minimal level of configuration interaction in pathway computations as due to the different orbital occupations of the reactant and product. However, this requirement holds strictly only if the original symmetry point group is retained along the reaction path. If the orbital mismatch between reactant(s) and product(s) is removed by desymmetrization of the reaction path to an appropriate subgroup of the original group, *Restricted Hartree-Fock* (*RHF*) computations should yield qualitatively reliable information, provided that the intervening transition states and intermediates retain their closed-shell character. Determining the nature of the appropriate symmetry-breaking nuclear displacement in any particular case, and thus of the symmetry species of the transition state, is precisely the province of OCAMS.

To date, the only C_{60}-dimer that has been identified and characterized experimentally is **1**, which has D_{2h} symmetry [13]. The present communication is concerned with the pathway to its formation by dimerization of two C_{60} monomers.

Procedure, Results, and Discussion. – a) *Symmetry Analysis of the Dimerization.* The dimer is oriented with its long axis aligned along *z* and the central four-membered ring in the *xz* plane. The two separated buckyballs are aligned similarly in the symmetry point group of the dimer, D_{2h}. Since the reactant pair and product each has 240 doubly



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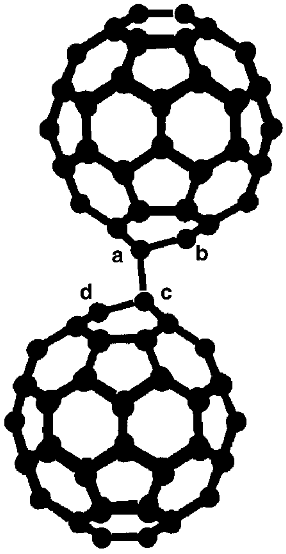

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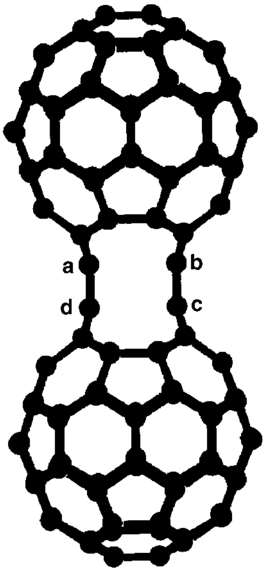

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occupied valence MOs in its closed-shell ground state, the construction of a *correspondence diagram* such as is shown in *Fig. 1* is impractical. Instead, they were optimized separately with AM1 and their orbital occupations recorded. (The reactants were brought close enough together that each of the MOs of the weakly interacting pair could be assigned to one of the symmetry species of D_{2h}).

The electronic configurations are as follows:

$2 \times C_{60}$: $[37 \times a_g^2\ 25 \times b_{1g}^2\ 29 \times b_{2g}^2\ 29 \times b_{3g}^2\ 25 \times a_u^2\ 37 \times b_{1u}^2\ 29 \times b_{2u}^2\ 29 \times b_{3u}^2]$

C_{120} (**1**): $[37 \times a_g^2\ 25 \times b_{1g}^2\ 29 \times b_{2g}^2\ 29 \times b_{3g}^2\ 25 \times a_u^2\ 36 \times b_{1u}^2\ 29 \times b_{2u}^2\ 30 \times b_{3u}^2]$.

The orbital occupancies of the dimer differ from that of the interacting monomers by just one less b_{1u}-MO and one more b_{3u}-MO. It follows – as in *Fig. 1* – that a nuclear displacement of symmetry species b_{2g}, the direct product of b_{1u} and b_{3u}, should remove the *forbiddenness.* A b_{2g} displacement takes the reacting system from D_{2h} into its subgroup $C_{2h}^{(y)}$ in which symmetry to inversion through the origin, rotational symmetry about the y-axis, and reflection symmetry in the xz-plane are retained.

Two reaction pathways that retain $C_{2h}^{(y)}$ symmetry should be taken into account:

1) A one-step reaction, in which the reacting C_{60} molecules approach one another with the four interacting atoms forming a parallelogram, and eventually snap back into a rectangular arrangement as the new 'pivot' bonds are formed.

2) A two-step reaction, analogous to those commonly observed in [2 + 2] cycloadditions of small molecules, *i.e.*, formation of a *transoid* intermediate that then rotates about its newly formed single bond and closes to the product. The most reasonable candidate for such an intermediate is isomer **2** [9][10].

Pathway *1* has not been observed computationally, whereas a two-step mechanism has been proposed by *Patchkovskii* and *Thiel* [12]. However, although they identify the

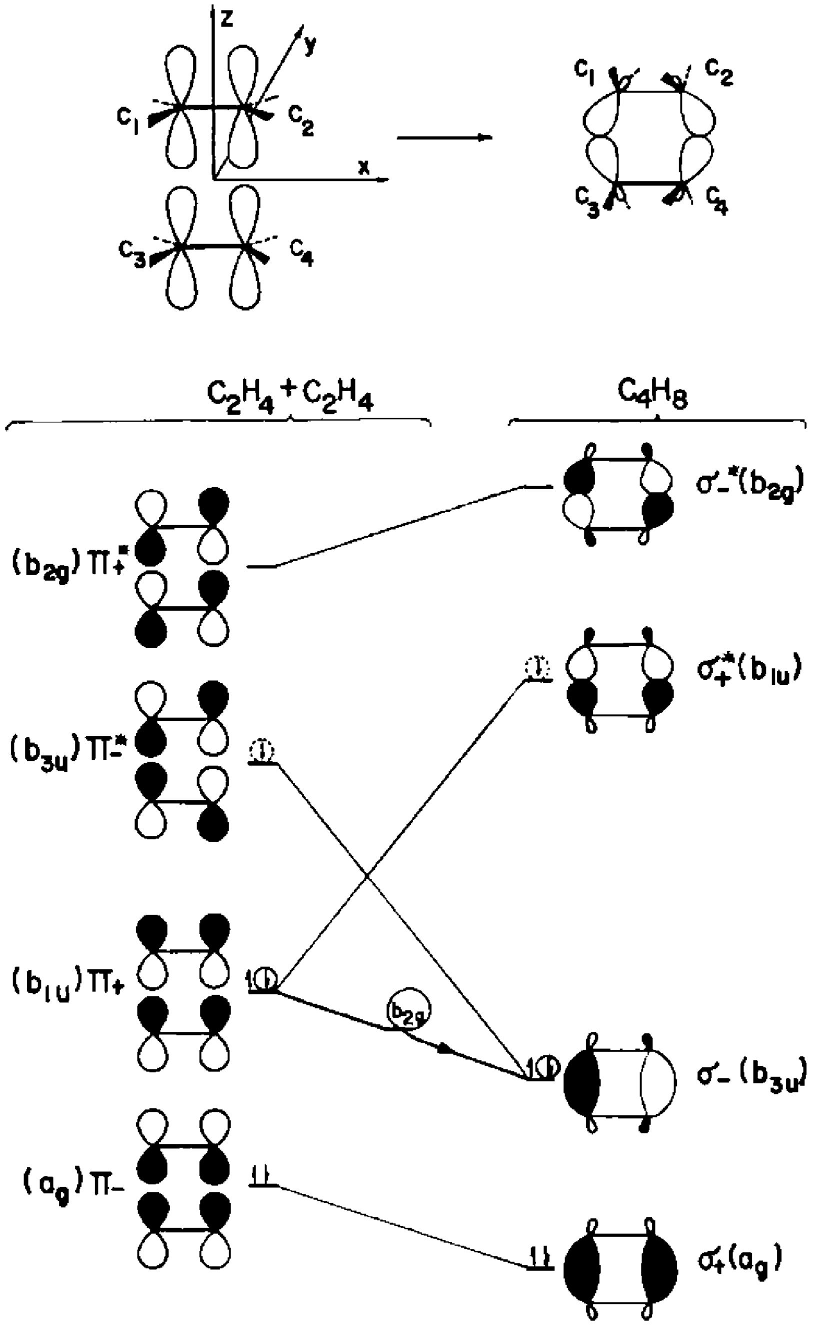

Fig. 1. *Correspondence diagram for [$_\pi 2 + _\pi 2$] cycloaddition of ethylene* [4][5a]

C_{2h} isomer of **2** as a stable species, they do not consider it to be an intermediate on the reaction pathway. Instead, they present the following sequence of transition states: a symmetry-conserving (D_{2h}) second-order stationary point, relaxation to another second-order saddle point (C_{2v}), followed by relaxation to an intermediate (C_2), and crossing over low barrier to generate the stable dimer **1**.

In view of the symmetry analysis presented above, there seems to be no requirement for retention of D_{2h} symmetry in the initial approach of the two monomers, or for passing through extrema on the potential-energy surface that can be avoided by reduction of symmetry along the reaction path. It was, therefore, decided to undertake a series of step-by-step pathway computations in order to determine whether or not desymmetrization to $C_{2h}^{(y)}$ plays a role in the mechanism of the reaction.

b) *Dimerization Pathway Computations.* Pathway computations with AM1/RHF yielded erratic results. This is hardly surprising in view of the substantial open-shell character of **2** [12a]. Given the limited computational facilities available to the author, point-by-point optimization with configuration interaction, even at the minimal 3 × 3 CI level, was out of the question. The only remaining practical option was to apply the *Unrestricted Hartree-Fock* procedure (*UHF*), despite concern that spurious spin polarization might affect the validity of the computations [12] [14]. Some confidence in the qualitative reliability of the AM1/UHF results can be derived, however, from the similarity of the computed energy of dimerization ($\Delta\Delta H_f = -42.2$) to the MNDO values that had been calculated with and without CI ($\Delta\Delta H_f = -49.1$ and -44.5 kcal/mol, resp.) [12a].

The upper curve in *Fig. 2* is a point-by-point plot of the reaction path constrained firmly to $C_{2h}^{(y)}$. It passes over a barrier to a shallow minimum, 36 kcal/mol above the energy of two non-interacting buckyballs, which is adopted as the energy 'zero'. When the center-to-center distance between the moieties is decreased further, with strict retention of $C_{2h}^{(y)}$ symmetry, the energy rises by an additional 53 kcal/mol before dropping to dimer **1**. This structure was identified as a second-order saddle point with a small off-D_{2h} component (towards C_s). Somewhat below it, at 83.52 kcal/mol, there is a first-order transition state with C_2 symmetry ($r_{ab} = 1.375$ Å, $r_{ad} = 2.044$ A, $r_{ac} = 2.276$ Å, $r_{bd} = 2.843$ Å), which is presumably the lowest pass on the direct, one-step pathway. In view of its high energy and the availability of a much less demanding two-step mechanism, this pathway can be disregarded, except perhaps at very high temperatures.

The lower curve in *Fig. 2* represents a pathway in which the symmetry constraint was reduced from C_{2h} to C_2. It should be kept in mind that the restriction of a pathway to a particular symmetry point group does not define it uniquely. With a system of 120 atoms in a low-symmetry point group, the danger of straying onto pathways of higher energy than the lowest is ever present. Measures taken to ensure that the pathway shown in *Fig. 2* is indeed the lowest are described below in the *Computational Part*.

The C_2 and C_{2h} pathways coincide up to a bonding distance of 2.5 Å or so, after which the former rises less steeply to a maximum of 19 kcal/mol at 2.0 Å, and settles into a potential well 9 kcal/mol below the reactant pair. If the 'intermediate' or the upper pathway is optimized in C_2, the energy drops to the lower minimum at -9 kcal/mol. Full optimization of this structure (the symmetry of this structure is nearly

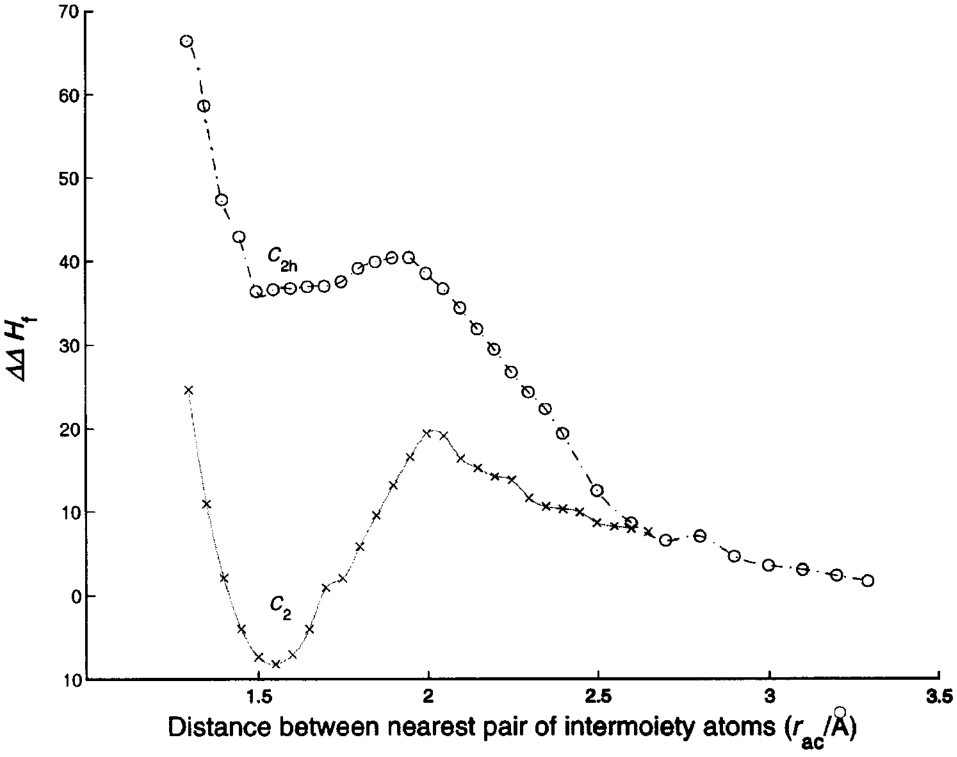

Fig. 2. *Computed* $C_{2v}^{(y)}$ *and* C_2 *pathways for dimerization of* C_{60} *to intermediate* **2**

indistinguishable from C_{2h}), led to a stable single-bonded dimer, listed as **2** in *Table 1*[1]). Regrettably, the electronic configuration of **2** could not be determined with MOPAC 93, so it was not possible to ascertain whether it is compatible with that of **1** and/or of the loosely interacting monomers.

Table 1. *Stable and Metastable Dimers of* C_{60}

		$\Delta\Delta H_f$[a])	r_{ab} [Å]	r_{ad} [Å]	r_{ac} [Å]	r_{bd} [Å]
1	(D_{2h})	– 42.2	1.60	1.55	2.22	2.22
2	(C_{2h})	– 14.5 (– 9.0[b]))	1.50	2.55	1.54	3.85
2a	(C_2)	– 14.4 (– 7.9[b]))	1.49	2.54	1.54	2.69
3	(D_{2h})[c])	+ 2.5	2.65	1.34	2.97	2.97

[a]) Heats of formation [kcal/mol] relative to two C_{60} molecules. [b]) Calculated with restriction to C_2 (see text). [c]) Calculated with AM1/RHF.

The computed C_{2h}-C_2 approach, illustrated by the lower curve in *Fig. 2*, evidently represents an upper bound to the energy along the first section of the reaction path, in

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[1]) The additional stabilization obtained with full optimization may be an artifact of AM1/UHF, which tends to disfavor symmetrical structures. (See *Computational Part.*)

the course of which the first intermoiety bond is formed. The second stage, rotation about the single bond from *trans* to *cis* and closure of the second bond, which – as will be seen – can apparently proceed along several different pathways, was not followed in as much detail.

On internal rotation about the newly formed central bond, with retention of C_2 symmetry, the energy rises to a broad plateau 8 kcal/mol or so above the monomer pair. A search for a funnel in the potential surface through which the C_2 pathway might pass would have called for mapping out an extensive region on the surface with a prohibitive number of computations. Instead, full optimizations in Cartesian coordinates were carried out at selected points. The results depended on the initial geometry, specifically on the dihedral angle τ_{bacd}. When it was set at 0°, a locally stable dimer **2a** with C_2 symmetry – virtually isenergetic with **2** – was formed, which was stabilized by several kcal/mol when the restriction of τ_{bacd} to 0° was lifted. Although its central ring remained planar, the overall geometry of the system was far from $C_{2\mathrm{v}}$. As the distance between atoms b and d was gradually decreased, closing the second bond took place after crossing a barrier of *ca.* 8 kcal/mol. Alternatively, when the initially chosen dihedral angle was 13°, corresponding to a dip on the plateau, the intermediate **2a** was bypassed, and dimer **1** was obtained directly. It is, therefore, a reasonably safe conclusion that, although rotation about the single bond is not as free as might have been expected, the second step of the reaction is more facile than the first.

Despite serious reservations about the quantitative accuracy of the data, the qualitative features of the mechanism appear firm enough to substantiate the prediction of the symmetry analysis. The computations indicate that Pathway *2* is a viable dimerization mechanism thermally accessible at moderate temperatures. Needless to say, confirmation with computational methods that include configuration interaction would be desirable.

c) *Diversion: the Window Isomer*. The 'window' isomer, **3**, which has $D_{2\mathrm{h}}$ symmetry, has been proposed by *Patchkovskii* and *Thiel* [12] as an intermediate for the incorporation of noble-gas atoms in fullerenes. Although it has the same symmetry as the stable isomer **1**, the authors found that it is not formed from the latter along a totally symmetric pathway. They propose that it passes through a transition state in which the four bonding atoms lie in a plane; in our axis convention its symmetry is $C_{2\mathrm{v}}^{(z)}$. It was of interest to see whether this departure from total symmetry could be rationalized by OCAMS.

The orbital occupancies of isomers **3** and **1** are as follows:

C_{120} (**1**): $[37 \times \mathrm{a}_{\mathrm{g}}^2\ 25 \times \mathrm{b}_{1\mathrm{g}}^2\ 29 \times \mathrm{b}_{2\mathrm{g}}^2\ 29 \times \mathrm{b}_{3\mathrm{g}}^2\ 25 \times \mathrm{a}_{\mathrm{u}}^2\ 36 \times \mathrm{b}_{1\mathrm{u}}^2\ 29 \times \mathrm{b}_{2\mathrm{u}}^2\ 30 \times \mathrm{b}_{3\mathrm{u}}^2]$

C_{120} (**3**): $[37 \times \mathrm{a}_{\mathrm{g}}^2\ 29 \times \mathrm{b}_{1\mathrm{g}}^2\ 25 \times \mathrm{b}_{2\mathrm{g}}^2\ 29 \times \mathrm{b}_{3\mathrm{g}}^2\ 25 \times \mathrm{a}_{\mathrm{u}}^2\ 29 \times \mathrm{b}_{1\mathrm{u}}^2\ 35 \times \mathrm{b}_{2\mathrm{u}}^2\ 31 \times \mathrm{b}_{3\mathrm{u}}^2]$

We write only the mismatched MOs:

C_{120} (**1**): $[4 \times \mathrm{b}_{2\mathrm{g}}^2\ 7 \times \mathrm{b}_{1\mathrm{u}}^2]$

C_{120} (**3**): $[4 \times \mathrm{b}_{1\mathrm{g}}^2\ 6 \times \mathrm{b}_{2\mathrm{u}}^2\ 1 \times \mathrm{b}_{3\mathrm{u}}^2]$, which in $C_{2\mathrm{u}}^{(z)}$ map onto:

C_{120} (**1**): $[4 \times \mathrm{b}_1^2\ 7 \times \mathrm{a}_1^2]$

C_{120} (**3**): $[4 \times \mathrm{a}_2^2\ 6 \times \mathrm{b}_2^2\ 1 \times \mathrm{b}_1^2]$.

The symmetry analysis is clearly inconsistent with one-step isomerization of **1** to **3** *via* a $C_{2\mathrm{u}}^{(z)}$ transition state. The largest subgroup of $D_{2\mathrm{h}}$ that satisfies the requirement of configuration correlation is C_{i} (S_2), in which inversion symmetry is the only non-trivial symmetry element. In this subgroup:

C_{120} (**1**): $[4 \times a_g^2\ 7 \times a_u^2]$
C_{120} (**3**): $[4 \times a_g^2\ 7 \times a_u^2]$.

Note that, in the point group C_i, the interacting pair of C_{60} molecules also has this same electronic configuration, suggesting that **3** may conceivably be an intermediate for dimerization to **1** along a pathway in which this symmetry point group is retained. Whether or not such a pathway exists, and – if so – whether it is energetically accessible, has yet to be investigated.

d) *Conclusion: Symmetry, Kinetics, and Thermodynamics.* If dimer **1** is so much more stable than C_{60}, and the barrier to dimerization is so low, why does spontaneous dimerization not occur? If – as predicted by the symmetry analysis – reaction *via* the single-bonded isomer **2** is the preferred dimerization pathway, it is clear why the reaction does not take place in the solid state, even at temperatures at which the buckyballs are rotating freely. Isomer **2** may indeed be formed momentarily, but rotation about the newly formed single bond would be prevented by crystal forces, which would probably be sufficiently strong to remove the dislocation by breaking the central bond of **2** and regenerating a pair of C_{60} molecules.

Failure to observe C_{120}, in the gas phase can only be ascribed to unfavorable thermodynamics. Accordingly, THERMO computations (AM1/RHF) were carried out on C_{60} and C_{120} (**1**) over the temperature range of 298–900 K, through which the *Gibbs* free energy of dimerization (ΔG_{dim}) varied smoothly from -18 to $+15$ kcal/mol. The factor principally responsible for the variation is the relatively rapid decrease of ΔS_{dim} with temperature. As the temperature rises, the low rotational entropy of C_{60} at low temperatures, due in large part to the high symmetry number (60) of icosahedral molecules, is offset by the entropy increase due to thermal motion. C_{60} begins to vaporize at *ca.* 400° and attains a substantial vapor pressure near 600° [16], at which temperature (ΔG_{dim}) has increased to such an extent that the concentration of C_{120} in thermal equilibrium with C_{60} would be undetectably low.

Computational Part

The computations were carried out with the MOPAC 93 package, according to the unrestricted *Hartree-Fock* (UHF) procedure with the AM1 hamiltonian. A cartesian coordinate system was set up with fixed dummy atoms. In the direct approach, the C_{60} units, centered on dummy atoms equidistant from the origin, were allowed to move in concert towards each other along the z-axis or – in some computations – at a fixed angle to it. In this way, all three translational motions are precluded, as is rotation about the x- and y-axes; the remaining free rotation (R_z) is blocked by constraining one of the C-atoms to the zx-plane.

To ensure that the reaction path does not stray from the prescribed symmetry point group, the number of independent internal coordinates (*i.e.*, geometric degrees of freedom) must be specified correctly. This was done with the aid of an algorithm published by *Pople*, *Sataty* and the author [15]. Each symmetrically disposed set of atoms contributes 1, 2, or 3 degrees of freedom, resp., depending on whether they lie on an axis of symmetry, on a plane of symmetry, or on neither. Subtraction of the number of totally symmetric external coordinates (translation and rotation), if any, yields the total number of independent coordinates. The requirements for the present system of 120 C-atoms in the symmetry point groups of interest are listed in the *Table 2*.

Occasionally, sets of consecutive computed points diverged from what appeared to be the lowest-energy pathway. This was checked, and corrected as necessary, by spacing the points more closely, recalculating with a different choice of the nominal reaction coordinate (distance between centers, distance between selected atoms, or bond or dihedral angle), and/or reversing the direction of motion along the pathway. Reproducibility to within 2 kcal/mol at non-stationary points was considered adequate. Stationary states were fully optimized.

Table 2. *The Number of Independent Variables in the Relevant Symmetry Point Groups*

Point group	Sets of atoms a)	Degrees of freedom
D_{2h}	2 on xy-plane (4)	4
	2 on zx-plane (4)	4
	13 off-plane (8)	39
		Total: 47
C_{2h}	4 on xy-plane (2)	8
	28 off-plane (4)	84
		Total: 92 – 1 b) = 91
C_2	60 off-plane (2)	180
		Total: 180 – 1 b) = 178
$C_1(S_2)$	60 off-plane (2)	180
		Total: 180 – 3 b) = 177
C_1	120 off plane (1)	360
		Total: 360 – 6 b) = 354

a) The number of atoms in each set is in parenthesis. b) The number of totally symmetric external coordinates (translations and rotations).

Several drawbacks of the computational procedure were encountered in addition to that of spin contamination: MOPAC 73 does not always specify the symmetry point group of large molecules correctly²). A related limitation is the fact that the irreducible representations of all of the occupied molecular orbitals are not always identified. When this happens, the electronic configuration cannot be established for comparison with that of related species. Finally, the energy of symmetric structures calculated with full optimization were usually by several kcal/mol lower than those obtained when symmetry was specified. This inconsistency is disturbing, but should not detract from the qualitative conclusions of the present investigation.

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[2] This flaw has been corrected in subsequent versions of MOPAC 2000 [17].