Combined topological and energy analysis of the annealing process in fullerene formation. Stone–Wales interconversion pathways among IPR isomers of higher fullerenes

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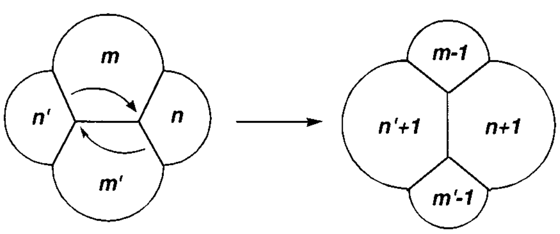
An algorithm for finding all the possible products from consecutive generalized Stone–Wales (GSW) rearrangements of any fullerene or closed cage precursor has been developed. Combined with energy-minimization, the program provides a versatile tool for the analysis of extremely complex interconversion pathways in the annealing process of fullerene formation. This paper presents results of the following preliminary applications of the program: (1) identification of the shortest pathway from Wang's C_{60} cage precursor to [60-I_h]fullerene, (2) availability of GSW cascades for a large number of sixty-carbon cage precursors leading to [60-I_h]fullerene, (3) generation of interconversion pathways among IPR isomers of higher [n]fullerenes (n = 78, 80, 82, 84, 90), and (4) enumeration of fullerene isomers. The pathways map of [84]fullerene solved the pending problem of why the high-energy isomer, [84-D_{2d}(I)]fullerene, has been detected using a helium-labelling technique in the product mixture and confirmed by IGOR calculation: this particular isomer is the dead-end product of a downhill bypath.

The Stone–Wales (SW) rearrangement was first conceived as a graphical method of generating isomeric structures of [60-I_h]fullerene,[1] but was soon recognized as a reaction potentially capable of separating abutted pentagonal rings, believed to occur frequently in the course of the fullerene formation process.[2] Although the SW rearrangement has not yet been confirmed experimentally, it is now considered to play a key role in the annealing process of fullerene formation, during which irregular 3D cage precursors undergo a series of SW rearrangements to perfect the pentagonal/hexagonal network of carbon atoms conforming to the isolated pentagon rule (IPR).

As the result of recent intensive computational studies on the SW rearrangement, the overestimation of activation energy has been corrected,[3] the scope of reaction extended to involve rings other than pentagons and hexagons [generalized Stone–Wales (GSW) rearrangement, Scheme 1],[4] and the ubiquitous nature



m, m', n, n' = four- to eight-membered rings

Scheme 1

of this type of reaction in graphitic systems proposed.[5] Recently we noticed that C_2 ingestion, another important reaction dominating in the fullerene road theory of fullerene formation,[6] also involves GSW rearrangements.[7]

The annealing process consists of a series of GSW rearrangements, which start from the primary ring-collapsed product of the planar mono- to multi-ring carbon clusters.[8] It may appear that any nonclassical fullerene may be transformed into a classical fullerene whenever a long enough sequence of consecutive GSW isomerization steps are carried out. Recently Plestenjak *et al.*[9] have mathematically proved this hypothesis for systems containing five-, six- and seven-membered rings. However, the actual annealing process is also controlled by another factor, energetics, and for this reason the freedom of choosing rearrangement pathways is limited. Nonetheless, it is hard to identify the most likely pathway due to the enormous number of combinations that arises from the fact that intermediates may contain various ring sizes, perhaps four- to eight-membered,[10] and that virtually every C–C bond in the intermediate can be the site of $\pi/2$ bond rotation. Is there a general way to determine the most likely GSW sequence for any irregular 3D cage precursor to reach an IPR fullerene? The problem is challenging, not only because it directly addresses the riddle of fullerene formation but also because there is virtually no chance of solving it by conventional experimental means.

We began the work by writing a topological program capable of generating all possible products of GSW reactions and storing unique structures with their complete history, but we prevented an explosive increase in the number of stored structures by imposing judicious constraints when running the program. The fullerene annealing process that we describe below has a remarkable resemblance to the *adamantane rearrangement*,[11,12] the multi-step transformation of a polycyclic hydrocarbon into the thermodynamically most favorable structure through a sequence of Wagner–Meerwein 1,2-CC bond shifts involving carbocations.[13]

Computational methods

Pathways of the GSW isomerization sequence were analyzed by using a path-generating GSW program and the results were visualized by using a graphic program N-GRAPH.[14] The former program is written in C++ language, and receives the structure of any 3D cage precursor and a set of search conditions[15] as input information to perform the following operations.

(1) Execute GSW isomerization on all the C–C bonds in the

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input structure and eliminate those products which do not satisfy the conditions given.

(2) Calculate Hückel molecular orbitals (HMO) for the remaining structures, and identify duplicates by comparing HMO total energy and HOMO/LUMO levels with those of the structures already produced.

(3) Store the structure of unique products together with their history of isomerization. If necessary, an improved set of atomic conditions of the product may be obtained using the topological coordinate method[16] for further elaboration of structure and energy.

(4) Repeat steps (1) to (3) until no new product is generated or until the predetermined number of steps are exhausted.[17]

Interconversion pathways can be visualized by using a sister program N-GRAPH. Written in the Java language, this program receives the pathway information from the GSW program and displays the interconversion map on the monitor screen at any desired level of simplification. Symbols of intermediates can be dragged using a mouse to any place on the screen. A pair of intermediates related by GSW isomerizations may be connected by an arc. Additional information like heats of formation and partial IUPAC nomenclature[18,19] may also be displayed. In the present version, vertical positions correlate with the computed energies of intermediates.

Energies of fullerene isomers were calculated by semiempirical HF-SCF (AM1, PM3 and SAM1)[20] as well as *ab initio* (4-31G) MO methods.[21] Activation energies of each GSW reaction were not calculated because the local environment of individual GSW reactions should be more or less alike for cases treated in this work, and good estimates of about 60 kcal mol^{-1} have already been reported.[3] All computations have been carried out on an Alpha Server 2100 5/250 from DEC.

Results and discussion

Conversion of [60]fullerene isomers to [60-I_h]fullerene

We planned to test the performance of the GSW program on the rearrangement of cage clusters often obtained during molecular dynamics simulation of fullerene formation, and chose the C_{60} cluster **1** reported by Wang *et al.*[22] which contained two heptagonal rings and an abundance of fused pentagonal rings. Execution of the GSW program on **1** allowing a maximum of two heptagonal rings readily produced a number of pathways of various lengths leading to [60-I_h]fullerene, among which eight-step paths are the shortest. The energy profile of these paths [Fig. 1(*b*)] represents the expected cascade with a high overall exothermicity (250 kcal mol^{-1}). The exothermicity of an individual GSW step is disturbed when a heptagon ring is generated: in the most likely path from **1** to [60-I_h]fullerene [Fig. 1(*a*), which corresponds to a bold line of Fig. 1(*b*)], one of the heptagons disappears in the first step and then the remaining heptagon in the third step, but a new heptagon is formed in the fifth step and disappears again in the sixth. In the course of these transformations, the AM1-energy decreases almost monotonously, except in the fifth step.

Unable to find a more attractive precursor model than **1**,[23] we decided to run the GSW program in the reverse direction, namely to trace the fullerene rearrangement backwards starting from [60-I_h]fullerene with the hope of finding many more paths of fullerene rearrangement. When the program had completed 10 isomerization steps, a total of 36 035 unique structures had been generated (Table 1). This result alone demonstrates the high degree of versatility of the GSW isomerization. Fig. 2 reproduces a small portion of the interconversion pathways obtained in this run. Isomerization steps are generally exothermic except for a few instances.

At this point, we decided that it would be always possible to find the most favorable annealing pathway(s) from any C_{60} or even C_{70} cage precursor to [60-I_h]- or [70-D_{5h}]-fullerenes by using the GSW program, and turned our attention to higher fullerenes.

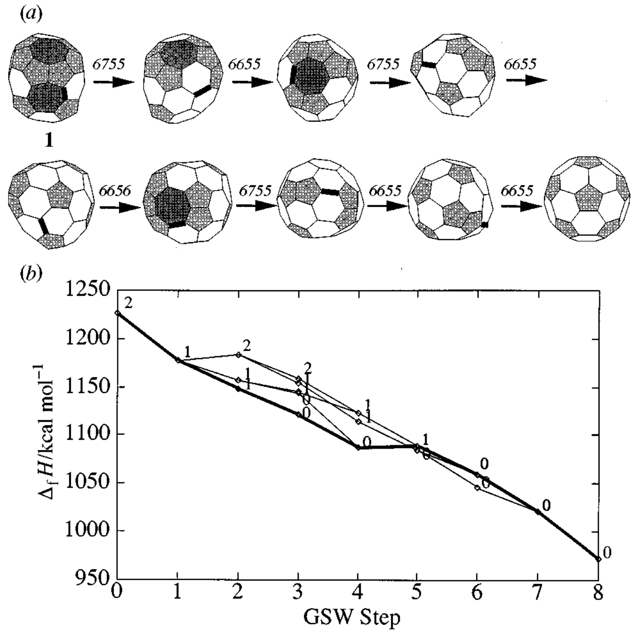


Fig. 1 (*a*) One of the eight-step pathways of conversion from Wang's C_{60} cluster **1** to buckminsterfullerene obtained by the GSW program. The sizes of the rings in the four-ring unit involved in the generalized SW isomerization (m, m', n, n') are marked above each step. The central bond in the four-ring unit to be rotated by $\pi/2$ in the next step is printed in bold. (*b*) AM1-energies of intermediates appearing in the fullerene rearrangement from Wang's C_{60} cluster **1** to buckminsterfullerene decrease sharply as the GSW step progresses. The numbers to the upper right of each point indicate the number of heptagonal rings in the structure. Only two paths are slightly endothermic and they generate one heptagonal ring.

Table 1 Numbers of C_{60} cage isomers generated in reverse run of the GSW program starting from buckminsterfullerene and classified according to the numbers of component rings[a,b]

f4	f5	f6	f7	f8	Count
0	12	20	0	0	108
0	13	18	1	0	35
1	13	16	1	1	1 839
1	12	18	0	1	3 379
1	11	19	1	0	27 778
1	10	21	0	0	2 896
				Total	36 035

[a] The following search conditions were imposed on the GSW program: (1) in addition to five- and six-membered rings, four-, seven- and eight-membered rings are allowed to appear but limited to one for each, (2) a maximum of five continuously abutting five-membered rings is allowed, (3) a maximum number of five groups of abutting five-membered rings are allowed. [b] fn = the number of n-membered rings.

Interconversion pathways in higher fullerenes

Because there is more than one IPR isomer for fullerenes higher than C_{76},[19] their annealing processes acquire an extra feature: interconversion among IPR isomers. The task of searching the extended reaction space can be accomplished by restarting the run from the new IPR isomer found and continuing the process until all of the known IPR isomers are found. Restart means searching the energy hypersurface around the starting point. Careful examination of the overlap among hypersurfaces of each IPR isomer eventually covers all of the short pathways connecting all these isomers.

Once the annealing process reaches one of the IPR isomers in the map, the most likely path therefrom to the global-minimum isomer can be traced by following the smallest number of exothermic GSW steps. Hence constructing comprehensive pathways is now the focus of our attention. Such a map becomes more and more complicated as the number of IPR isomers

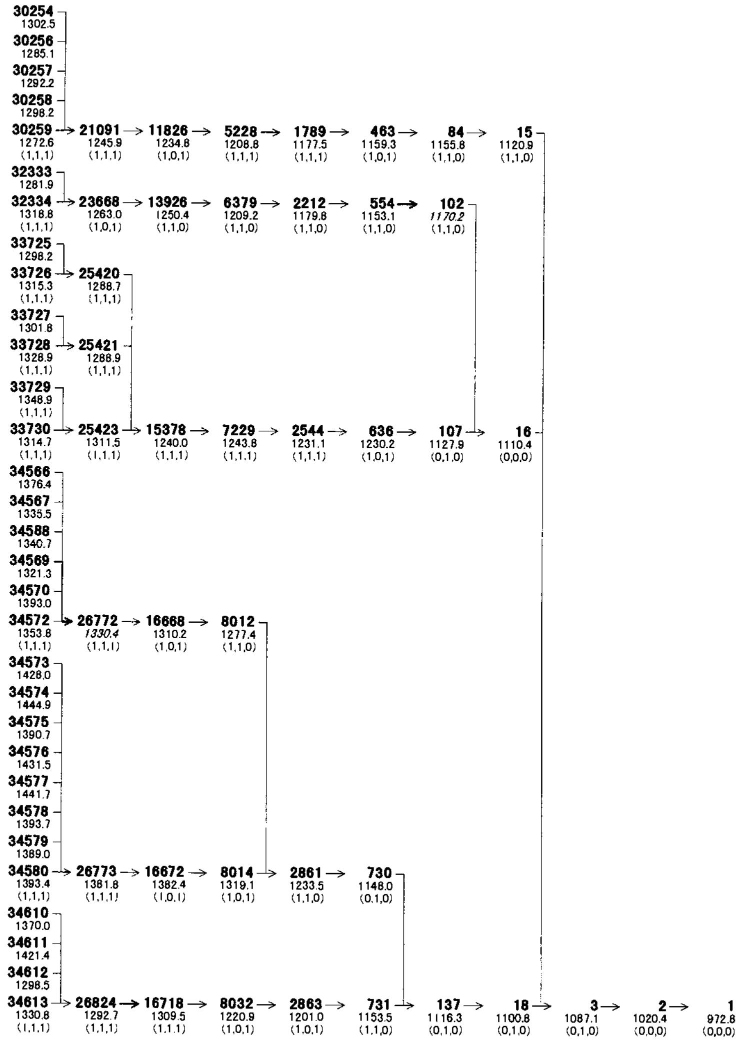


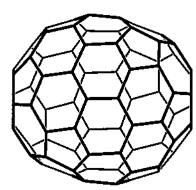
Fig. 2 Illustration of a part of the interconversion map from a variety of C_{60} isomers to buckminsterfullerene (No. 1) retrieved from Table 1. Each entry consists of our ID number, AM1 heat of formation in kcal mol^{-1}, and the number of nonclassical rings (f4, f7, 78) in this order.

increases. Complicated maps can be conveniently displayed by positioning all the IPR isomers according to their relative potential energies and indicating the GSW routes with arcs.

As can be seen in the maps thus prepared (Fig. 3), domains are sometimes formed, within which interconversion among IPR isomers takes place in one to a few GSW steps, but between which more steps involving unstable, non-IPR intermediates must be passed. Hence transfer from one domain to the other is considered difficult. Another notable aspect of Fig. 3 is that the relative free energy values are computed at 3000 K (column under the heading $\Delta\Delta G^{3000\,\mathrm{K}}$ in Table 2). Even though this temperature is still tentative, there is some reason to believe that this value represents the annealing temperature.[24]

As a preliminary test, we analyzed [78]-, [80]-, [82]-, [84]- and [90]-fullerenes for which product isomers have been separated. If the need arises to find the most favorable pathway from a particular cage precursor to a fullerene by a GSW mechanism, it is desirable to examine several routes each involving a different entrance to the interconversion pathways map of IPR isomers.

[78]Fullerenes. Experimentally, two isomers with C_{2v} symmetry and one isomer with D_3 symmetry have been separated.[25] Theoretical computations initially underestimated the stability of D_3 isomer **2** (see Table 2),[26] but inclusion of the temperature effect solved the problem: the stability order remains unchanged in the decreasing order of C_{2v}(II) **3**, C_{2v}(I), **4**, D_3 **2**, D_{3h}(II) **5**, D_{3h}(I) **6** over a temperature range of 1300 to 10 000 K.[27] Thus, experiment and theory agree as to the identity of the three separated isomers.



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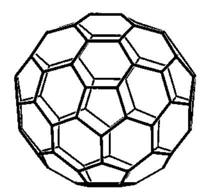

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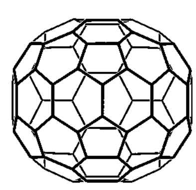

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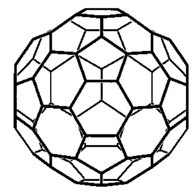

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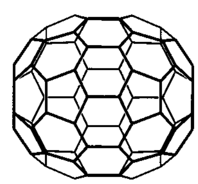

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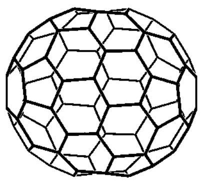
Fig. 3(*a*) provides the most comprehensive picture of the dynamics of IPR isomers of [78]fullerenes at 3000 K. The map shows that **3**–**6** form one domain, while **2** belongs to a different domain at least three steps away from the former. Hence it is quite reasonable to find that the two most stable of

3–6 (**3** and **4**) and the only IPR isomer in the latter domain (**2**) have been isolated. In view of the 'closeness' of **5** in the map to the two separated isomers, however, it would not be surprising if this is separated in the near future. Indeed, Saunders and co-workers observed a few minor peaks in the ^{3}He NMR spectrum of a He-labelled sample of C_{78} in addition to three large signals.[28]

[80]Fullerenes. The single isomer that has recently been separated has D_2 symmetry.[29] This isomer **7** belongs to the small



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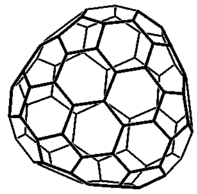

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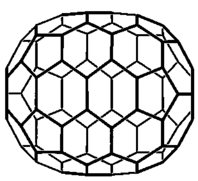

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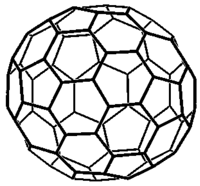

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domain in the interconversion map [Fig. 3(*b*)], which is separated from the other big domain by at least five GSW steps [Fig. 3(*b*)]. The failure to separate the D_3 isomer **8**, the global-minimum isomer above 3000 K,[30] to date suggests that the main course of annealing does not involve the latter domain.

A word of comment is due to the D_{5d} isomer **9** which has long been believed to be the outstanding global minimum of [80]fullerene.[26b] It is only recently that this particular isomer has lost its dominance in this respect relative to the other isomers at higher temperatures (Table 2).[30]

[82]Fullerenes. All of the nine IPR isomers belong to a single domain and are interconvertible by a single to a few GSW steps [Fig. 3(*c*)]. In the equilibrium at 3000 K, the C_2(II) isomer **10** should dominate. Hence there is little doubt about the identity of the only separated isomer of [82]fullerene which has been shown to have C_2 symmetry.[31] Isomer **10** holds the position of global minimum over a very wide temperature range of 0 to 7000 K.[32]

[84]Fullerenes. Experimental results are contradictory. HPLC separation gave two isomers having D_2 and D_{2d} symmetry,[25] and this observation appeared to have agreed with the result of computation which gave two outstanding global minima, D_2(IV) **11** and D_{2d}(II), **12** by a margin of at least 8 kcal mol^{-1} from the other isomers (see $\Delta\Delta H_f^0$ values in Table 2).[26] However, it was naturally wrong to discuss the product distribution at very high temperature in terms of computational results at low-temperature.[33] Then, it was reported that the ^{3}He NMR spectrum of a He-labelled sample of C_{84} mixture gave one major signal and several minor signals of a similar intensity ratio to the major signal.[28b] If the major signal is assigned to **11**, then **12** is not outstanding at all!

Fig. 3(*d*) is characterized by a large and closely knit domain, wherein all the members are connected by single-step arcs. Since this domain contains **11**, it follows that the major stream of annealing process passes through the domain. Interestingly enough, features at the bottom of the map fit better with the ^{3}He NMR results than with the picture of two outstanding global minima: four similarly stable isomers, **12**, C_1 **13**, C_s(V) **14** and C_2(IV) **15**, are located slightly above the global energy-minimum.

We find one other remarkable feature in the map, which solves a pending problem. Bühl and van Wüllen[34] had proposed that a small but characteristic signal at −24.35 ppm from dissolved ^{3}He in Saunders' ^{3}He NMR spectrum of the He-labelled C_{84} mixture[28b] came from [84-D_{2d}(I)]fullerene **16** based on good agreement of the computed ^{3}He chemical shift of −25.0 ppm for this structure with the observed value. However, **16** is one of the high-energy isomers (Table 2) and does not seem to be populated in detectable amounts in the equilibrium mixture. In the pathways map of Fig. 3(*d*), this particular isomer appears at the upper right corner as the dead-end product by way of a downhill bypath, hence it is indeed possible that **16** accumulates

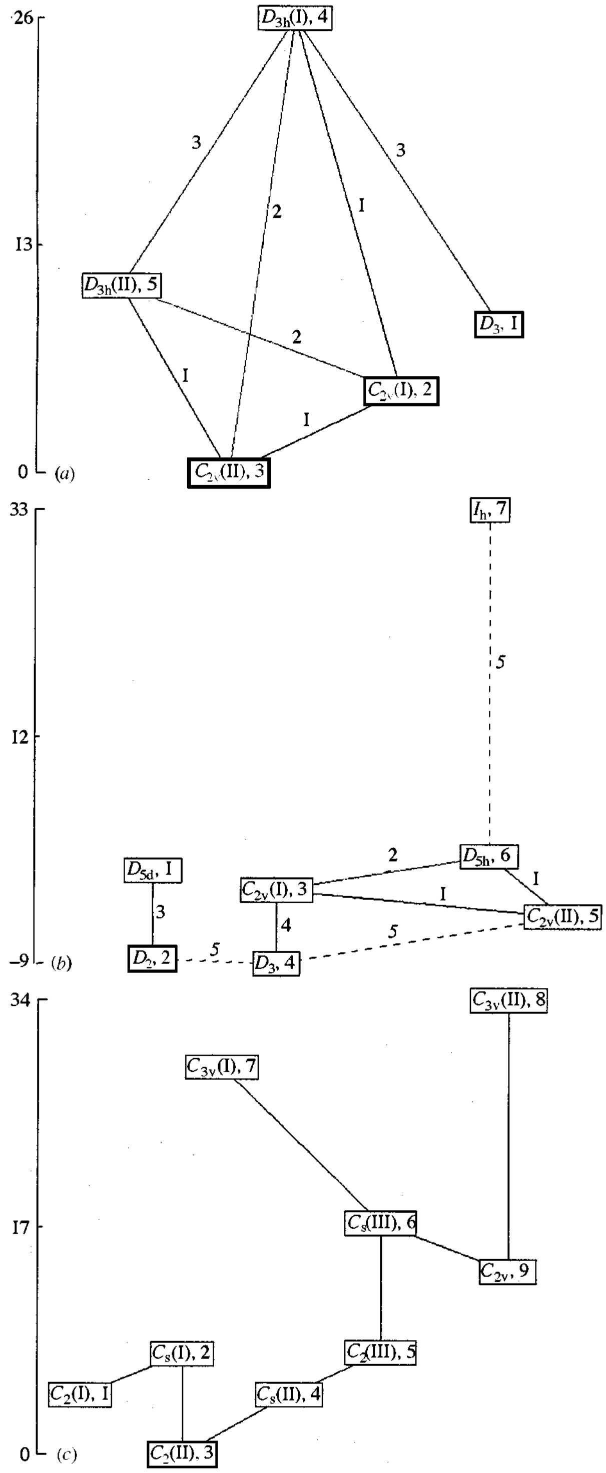
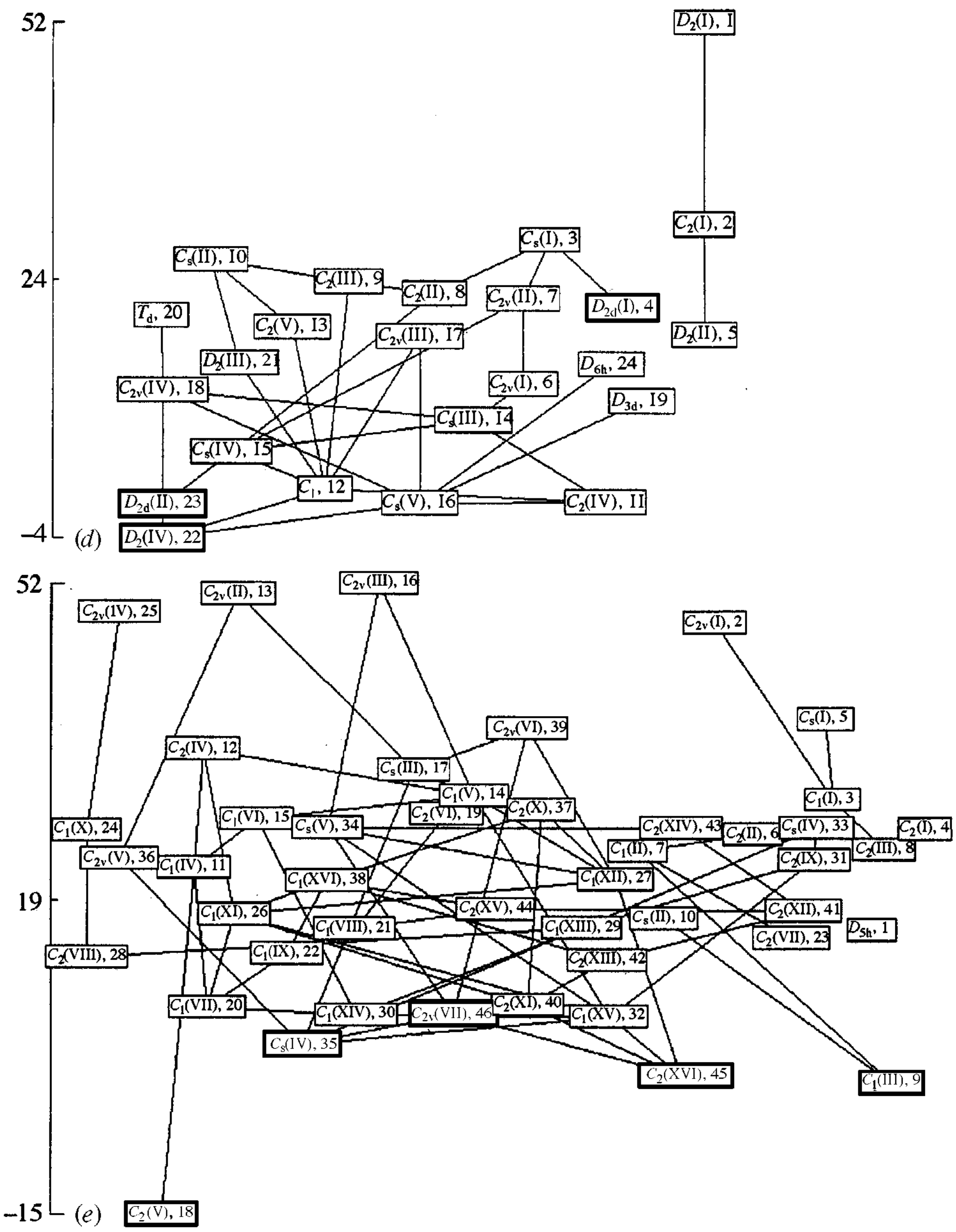


Fig. 3 Maps of interconversion pathways among IPR isomers of higher fullerenes. (*a*) [78]-, (*b*) [80]-, (*c*) [82]-, (*d*) [84]-, (*e*) [90]-fullerenes. Lines correspond to one to five generalized SW steps. The vertical height of each box is proportional to the computed free energy of formation in kcal mol^{-1} at 3000 K. Within the box are entered point group symmetry, sequential number in Roman according to the IUPAC rule,[18] and the Fowler–Manolopoulos ID number.[19]



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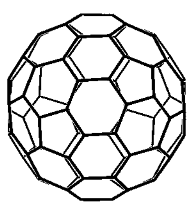
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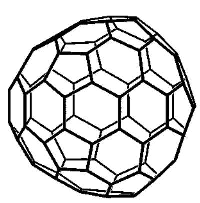
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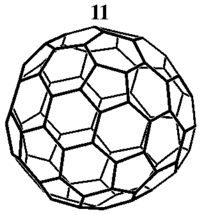
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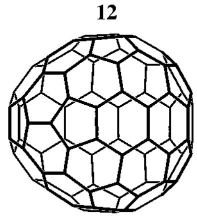
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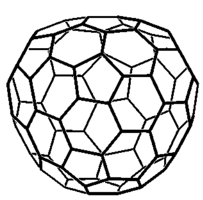
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during fullerene formation! There is no other downhill dead-end in this domain, therefore only this intermediate may kinetically accumulate despite its high energy-content (Fig. 4). This interpretation brings up an interesting possibility that the main annealing stream passes through C_s(I) isomer **17**.

In addition to the large domain, there is a very small domain consisting of three IPR [84]fullerene isomers at the right of Fig. 3(*d*). If there is any possibility of the annealing process touching this domain, then D_2(II) **18** would be the product. As a matter of fact, this structure could well be one of the other six isomers found by Saunders *et al.*[28b]

[90]Fullerenes. The largest of the higher fullerenes so far studied presents the most complicated and controversial case. Following Taylor *et al.*'s preliminary work,[35] Achiba and co-workers separated five isomers by HPLC: one C_{2v}, three C_2 and one C_1.[25b,36] Using SAM1 computations and re-interpreting the observed NMR pattern, we have assigned C_2(V) **19**, C_1(III) **20**, C_2(XVI), **21**, C_s(VI) **22** and C_{2v}(VII) **23** to the five separated isomers.[27]

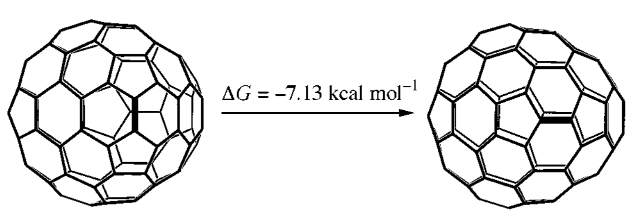
Almost all the isomers form a large domain, except for two isomers, C_2(I) **24** and D_{5h} **25**, which are completely isolated and for a small, high-energy domain including four isomers, C_2(III) **26**, C_1(1) **27**, C_s(I) **28** and C_{2v}(I) **29** [Fig. 3(*e*)]. These lone isomers are grouped at the upper right corner of the map. The main

Table 2 Computed potential energies of all IPR isomers in [78]-, [80]-, [82]-, [84]- and [90]-fullerenes at room temperature and at 3000 K [a]

Fullerene	PG [b]	F-M No. [c]	$\Delta\Delta H_f^0$	$\Delta\Delta G^{3000\,K}$	Structure
[78]	C_{2v}(II)	3	0.000	0.000	**3**
	C_{2v}(I)	2	3.773	4.651	**4**
	D_3	1	6.268	8.465	**2**
	D_{3h}(II)	5	5.640	10.541	**5**
	D_{3h}(I)	4	17.524	25.785	**6**
[80]	D_3	4	34.391	−8.532	**8**
	D_2	2	1.799	−8.185	**7**
	C_{2v}(II)	5	30.934	−4.120	
	C_{2v}(I)	3	19.621	−1.741	
	D_{5d}	1	0.000	0.000	**9**
	D_{5h}	6	45.495	1.387	
	I_h	7	90.230	33.219	
[82]	C_2(II)	3	0.000	0.000	**10**
	C_2(I)	1	4.037	4.419	
	C_s(II)	4	6.525	4.458	
	C_s(I)	2	6.018	7.524	
	C_2(III)	5	11.990	7.720	
	C_{2v} [d]	9	21.757	13.377	
	C_s(III)	6	16.574	17.340	
	C_{3v}(I) [e]	7	31.043	28.994	
	C_{3v}(II) [e]	8	35.557	34.018	
[84]	D_2(IV)	22	0.421	−3.547	**11**
	D_{2d}(II)	23	0.000	0.000	**12**
	C_s(V)	16	8.182	0.206	**14**
	C_2(IV)	11	8.562	0.398	**15**
	C_1	12	14.788	1.720	**13**
	C_s(IV)	15	14.415	5.646	
	C_s(III)	14	16.563	9.084	
	D_{3d}	19	8.790	11.133	
	C_{2v}(IV)	18	15.625	12.220	
	C_{2v}(I)	6	16.467	12.946	
	D_{6h}	24	7.960	15.035	
	D_2(III)	21	21.096	15.190	
	C_{2v}(III)	17	22.783	18.000	
	D_2(II)	5	22.113	18.214	**18**
	C_2(V)	13	29.193	19.047	
	T_d [f]	20	31.299	20.297	
	D_{2d}(I)	4	21.022	21.196	**16**
	C_{2v}(II)	7	27.879	22.046	
	C_2(II)	8	33.616	22.581	
	C_2(III)	9	35.086	23.892	
	C_s(II)	10	42.382	26.202	
	C_s(I)	3	39.293	28.325	**17**
	C_2(I)	2	38.280	30.050	
	D_2(I)	1	54.701	51.830	

Fullerene	PG [b]	F-M No. [c]	$\Delta\Delta H_f^0$	$\Delta\Delta G^{3000\,K}$	Structure
[90]	C_2(V)	18	26.430	−14.754	**19**
	C_1(III)	9	43.940	−0.831	**20**
	C_2(XVI)	45	0.000	0.000	**21**
	C_s(VI)	35	4.604	3.280	**22**
	C_1(XV)	32	9.784	6.262	
	C_1(XIV)	30	8.867	6.374	
	C_{2v}(VII)	46	3.496	6.565	**23**
	C_1(VII)	20	23.483	7.190	
	C_2(XI)	40	9.975	7.484	
	C_2(XIII)	42	20.917	12.222	
	C_2(VIII)	28	11.073	12.474	
	C_1(IX)	22	31.875	12.858	
	C_2(VII)	23	47.265	14.572	
	D_{5h}	1	6.368	15.358	**25**
	C_1(VIII)	21	47.200	15.444	
	C_1(XIII)	29	18.822	15.610	
	C_s(II)	10	48.551	16.543	
	C_1(XI)	26	22.491	17.058	
	C_2(XII)	41	31.428	17.355	
	C_2(XV)	44	31.303	17.481	
	C_1(XVI)	38	30.079	20.534	
	C_1(XII)	27	22.511	20.642	
	C_1(IV)	11	34.197	21.953	
	C_2(IX)	31	20.252	22.771	
	C_{2v}(V)	36	21.653	22.842	
	C_1(II)	7	48.285	23.715	
	C_2(III)	8	23.586	23.774	**26**
	C_2(II)	6	35.328	25.413	
	C_1(X)	24	41.872	25.819	
	C_2(I)	4	25.586	25.918	**24**
	C_2(XIV)	43	43.692	26.059	
	C_s(IV)	33	24.164	26.075	
	C_s(V)	34	22.666	26.115	
	C_1(VI)	15	28.431	27.046	
	C_2(VI)	19	35.492	27.624	
	C_2(X)	37	28.881	27.990	
	C_1(I)	3	30.072	29.065	**27**
	C_1(V)	14	30.862	29.519	
	C_s(III)	17	30.133	32.247	
	C_2(IV)	12	34.532	34.420	
	C_{2v}(VI)	39	29.686	36.594	
	C_s(I)	5	35.984	37.468	**28**
	C_{2v}(I)	2	36.097	47.665	
	C_{2v}(IV)	25	65.810	48.797	**29**
	C_{2v}(II)	13	47.457	50.761	
	C_{2v}(III)	16	39.867	51.876	

[a] Separated isomers are underlined. For reference to experimental works, see text. Computational methods are not uniform but consistent within isomers of the same fullerene: PM3, [78]fullerene; HF/4-31G, [80]fullerene; AM1, [82]fullerene; SAM1, [84]- and [90]fullerenes. Energies are given in kcal mol^{-1}. [b] Point group. Notation partially follows IUPAC nomenclature of fullerenes. [c] According to Fowler and Manolopoulos, ref. 19. [d] In our hands, the symmetry changed into C_2 point group upon geometry-optimization. [e] Symmetry changed into C_s. [f] Symmetry changed into C_1.



17 **16**

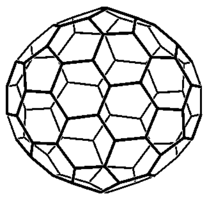
Fig. 4 Downhill Stone–Wales rearrangement from [84-C_s(I)]- **17** to [84-C_{2d}(I)]-fullerene **16**. This corresponds to an expansion of the upper right corner of the major domain in Fig. 3(*d*). The free energy change is based on the SAM1 potential energy (Table 2) and refers to 3000 K.

domain contains all the separated isomers, hence one would expect that thermodynamic equilibrium will quickly drive all the intermediates downstream to give a only a few separable products. In this regard, four of the low energy isomers **19**–**22**, are the primary candidates of separable products and they agree with our previous prediction.[37] One of the isomers that we have previously thought to have been separated, **23**, now seems to be a bit dubious. It may be noted, however, that the composition of the low energy isomers of [90]fullerenes is highly sensitive to temperature in the range between 1000 to 4000 K.[37] For this reason, we have to postpone further discussion on [90]fullerenes until a more reliable estimate of annealing temperature is obtained or ^{3}He NMR experiments are carried out.

Other uses. As can be readily guessed, the GSW program can also be used to enumerate fullerene isomers as well by imposing appropriate constraints. For example, GSW produced the total numbers of structural isomers of C_{60} and C_{70} containing only pentagonal and hexagonal rings as being 1812 and 8149, respectively. When one seven-membered ring is allowed, the numbers increased to 36 294 and 289 705, respectively. These results agree well with those of previous methods.[17]

Conclusions

1. Our topological algorithm for exhaustively generating products of GSW rearrangement from a cage molecule could be executed for a multi-step sequence without leading to divergence as long as appropriate constraints were imposed.



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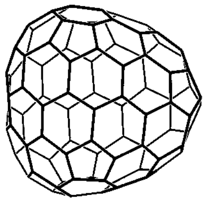

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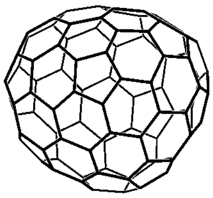

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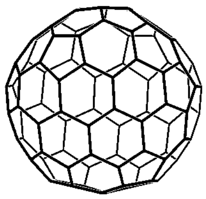

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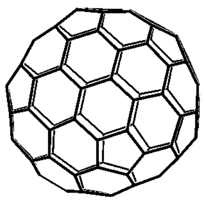

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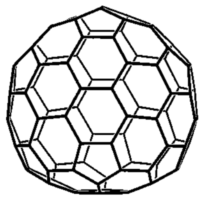

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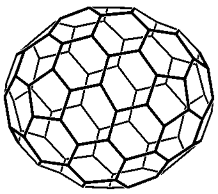

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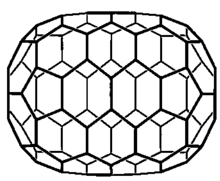

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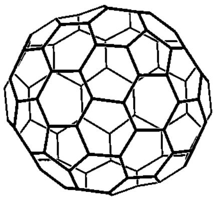

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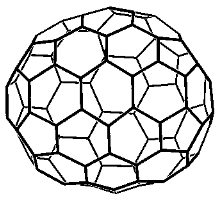

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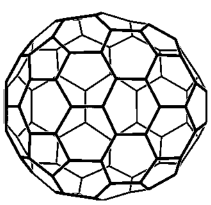

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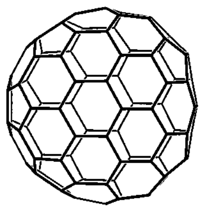

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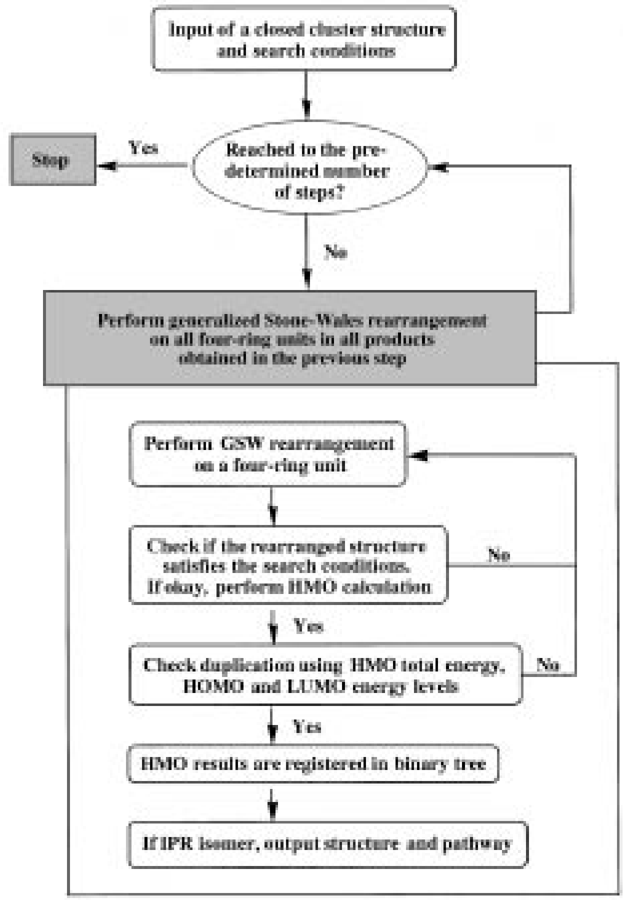
2. It should always be possible to find the most favorable annealing pathway by consecutive GSW mechanisms from any given cage precursor to a classical fullerene. It is important to evaluate relative stabilities of intermediates and fullerenes at the temperature of GSW reaction.

3. GSW interconversion pathway maps of several higher fullerenes solved a few enigma carried over from the time when relative energies were evaluated in terms of energy calculations at low-temperatures.

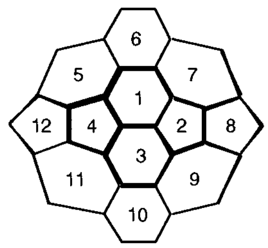
Appendix

Flowchart of program GSW

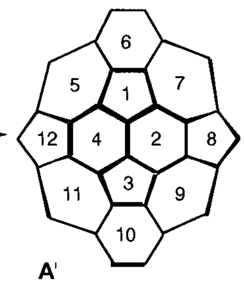


Topological representation of fullerene structure

The generalized Stone–Wales isomerization changes the size and adjacency of the four rings involved, hence it can be conveniently handled by using the information about the ring distribution. The component rings are termed *face*. The two matrices shown above illustrate the principle of designating a SW step in terms of face information. In the matrix on the left, four lines of numbers represent a pyracylene (cyclopent[*fg*]-acenaphthylene) unit (bold lines) in the extended pyracylene model **A**. The first column denotes face numbers, 1 to 4, the second column gives the ring size, 5 or 6, and the third and further columns face numbers of adjacent rings. Thus, face 1 is fused with six faces: 2, 3, 4, 5, 6 and 7. The matrix on the right corresponds to product (**A′**) of SW isomerization operated on the pyracylene unit 1–4: face 1 is now a pentagon and misses face 3 from the immediate neighbors' list. A complete history of interconversion for all unique products is stored and can be retrieved.



A



A'

```
1 6   6 7 2 3 4 5
2 5   7 8 9 3 1
3 6   1 2 9 10 11 4
4 5   1 3 11 12 5
```

```
1 5   6 7 2 4 5
2 6   7 8 9 3 4 1
3 5   2 9 10 11 4
4 6   1 2 3 11 12 5
```


Acknowledgements

This work was supported by a grant from the Japan Society for the Promotion of Science (RFTF97R11601) and by Grants-in-Aid for Scientific Research from the Ministry of Education (08554030, 09238219).

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Paper 7/06423C
Received 2nd *September* 1997
Accepted 29*th January* 1998