9. This is a slight modification of the formula appearing in B. Zellner, T. Gehrels, J. Gradie, *ibid.* **79**, 1100 (1974).
10. P. R. Weissman, M. F. A'Hearn, L. A. McFadden, H. Rickman, in *Asteroids II*, R. Binzel, T. Gehrels, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1989), pp. 880–920.
11. C. W. Allen, *Astrophysical Quantities* (Athlone, London, ed. 3, 1976), p. 162.
12. G. Tancredi, M. Lindgren, C.-I. Lagerkvist, *Int. Astron. Union Circ. 5892* (1993).
13. V. S. Safronov, "Evolution of the Protoplanetary Cloud and Formation of the Earth and Planets," *NASA TT F-677* (1972) (the original Russian article was published in 1969); P. Goldreich and W. R. Ward, *Astrophys. J.* **183**, 1051 (1973).
14. M. C. Festou, *Astron. Astrophys.* **95**, 69 (1980); J. Crovisier, *ibid.* **213**, 459 (1989).
15. S. Wyckoff, R. M. Wagner, P. A. Wehinger, D. G. Schleicher, M. C. Festou, *Nature* **316**, 241 (1985).
16. H. U. Keller *et al.*, *Astron. Astrophys.* **187**, 807 (1987).
17. T. R. Lauer, *Publ. Astron. Soc. Pac.* **101**, 445 (1989).
18. M. E. Vanhoosier, J.-D. F. Bartoe, G. E. Brueckner, D. K. Prinz, *Astrophys. Lett. Commun.* **27**, 163 (1988).

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Theoretical Evidence for a C_{60} "Window" Mechanism

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On the basis of semiempirical and high-level ab initio calculations, theoretical evidence is presented of a "window" mechanism operable on the surface of C_{60} and other fullerenes. Through this mechanism, large holes may be formed in fullerenes excited to their triplet state, openings through which atoms and small molecules can pass. This work provides a theoretical foundation for experiments that have prepared endohedral noble gas compounds of C_{60} under thermal excitation. A method is proposed that could increase the efficiency of the process of noble gas insertion into C_{60} and provide a more general means to create endohedral fullerene compounds.

Nature may abhor a vacuum, but fullerene (*1, 2*) researchers find the vacancies inside these hollow carbon cages one of the molecules' most attractive features. The discovery of the metallofullerenes (*3, 4*), fullerenes with metal atoms trapped inside them, was nearly concurrent with that of C_{60} and equally exciting. Numerous metallofullerenes (*5, 6*) have been synthesized by the inclusion of metal sources in the graphite used for fullerene generation, and several noble gases (*7–10*) and small metal atoms (*11*) have also been implanted with ion beam collision experiments. Nevertheless, it seems that only elements with Pauling electronegativities of less than ~1.5 (that is, in general, elements on the left side of the periodic table) are spontaneously trapped inside fullerenes by resistive heating or in arc experiments (*12*), and ion implantation has been limited to He, Ne, Li, Na, and K insertion (*13*). Research into alternative routes to custom-fill the fullerenes' void with a variety of atoms and molecules continues at a rapid rate, for such endohedral species could tailor the physical and chemical properties of fullerenes to specific applications. The filled fullerene cages could have applications as superconductors, drug-delivery agents, medical imaging compounds, or molecular containers. But as of now, no general experimental means for making any X@C_{60} compound exists, and synthesizing endohedral fullerene compounds in macroscopic quantities is difficult at best.

A series of experiments by Saunders *et al.* (*14*) has revealed a method of creating endohedral fullerene compounds. By heating C_{60} soot under atmospheres of He, Ne, Ar, Kr, or Xe to ~600°C for a few hours, significant quantities of He@C_{60} or other noble gas endohedral fullerenes are formed (*14, 15*). Further heating of these endohedral compounds can cause the molecules to release the noble gases, and Saunders *et al.* calculated the Arrhenius activation barrier of helium release to be ~3.5 eV (*14*). Thus, under those relatively mild conditions, a "window" of sorts is formed on the fullerene surface through which the atoms may pass in and out. Because the barrier for direct helium insertion through a six-membered carbon ring is very high (~8.7 eV) (*16, 17*), and barriers for insertion of the other noble gases must be even higher, such a brute force mechanism does not seem to be a satisfying explanation of these experiments.

In this report, on the basis of theoretical calculations, we present evidence for a window mechanism that may occur on the surface of fullerenes. Specifically, we have found that opening the C–C bonds in the fullerene cage to create 9- and 10-membered rings is a relatively low energy process in the triplet state potential energy surface. We have confirmed this theoretical finding both in model fullerene systems and in C_{60}. Furthermore, a minimum exists in the triplet C_{60} potential energy surface with the single C–C bond open to 2.48 Å. We propose that the holes in such metastable species may allow the insertion of atoms and small molecules into the fullerene cage more easily than through direct penetration at the center of a pentagon or hexagon.

The theoretical tools used in this work include the semiempirical MNDO procedure (*18, 19*), the ab initio direct self-consistent field (SCF) Hartree Fock method (*20, 21*), and the local density approximation (LDA) (*22*) and nonlocal Becke-Lee-Yang-Parr (BLYP) (*23, 24*) density functional theory. The SCF method has proven reliable for predicting fullerene structures (*25, 26*), and the BLYP method has been shown to reproduce the experimental thermochemistry of chemical reactions to within a few kilocalories per mole (*23*).

To investigate the energetics of opening a bond on the C_{60} surface, we optimized the C_{60} geometry using the MNDO method with selected bonds held open to fixed distances while the rest of the cage was allowed to relax. We have examined the opening of both types of bonds on C_{60}, between a pentagon and a hexagon (a 5–6 bond) and between two hexagons (6–6). A plot of the energy of each structure against the length of the open bond

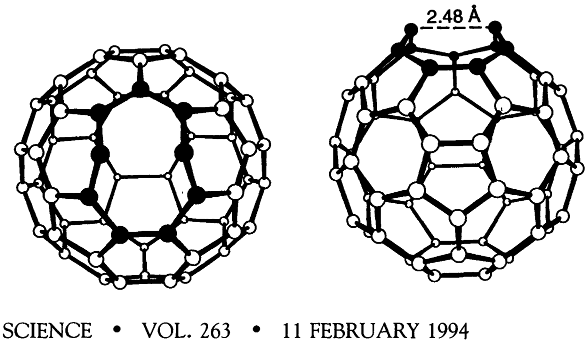

Fig. 1. The C_{60} window. By breaking a pentagon-hexagon bond on C_{60}, a large nine-membered ring is obtained. This structure with the bond open to 2.48 Å is a minimum on the MNDO unrestricted Hartree Fock (UHF) potential energy surface for the triplet state of C_{60}.

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provides a cut of the potential energy surface along the reaction coordinate for the proposed window mechanism. A C_{60} molecule with a 5–6 bond open creates a nine-membered ring "hole" in the surface (Fig. 1). A plot of the relative energy in electron volts against bond distance as the bond is opened for both the 5–6 and 6–6 bonds is shown in Fig. 2. As might be expected, breaking a bond in the C_{60} singlet ground state is costly in energy, about 5.5 eV to open the 5–6 bond to 2.5 Å. For comparison, at the same level of MNDO theory, previous calculations indicate that rearrangement of C–C bonds in the C_{60} surface is a process with a 7.2-eV barrier (*27*), and the C_2 fragmentation energy of C_{60} is 11.8 eV (*28*).

However, similar calculations on the 5–6 bond for C_{60} in the triplet (biradical) state reveal a different picture (Fig. 3). The activation barrier to open the bond is quite low (~3.5 eV), and a minimum at the MNDO level of theory (characterized by analytic second derivative methods) exists in the potential energy surface with a 5–6 bond open to 2.48 Å (Fig. 1). To further examine these features, we did ab initio calculations on a model system for fullerenes: a 20-carbon atom sheet of polygons (corannulene-like), identical to a section of the C_{60} surface. The features of the potential energy surface for this model were qualitatively similar to that of C_{60} for both the singlet and triplet states at all levels of theory. Table 1 presents MNDO, SCF Hartree Fock, LDA, and BLYP energy points at the MNDO optimized geometries for some representative key points on the 5–6 triplet surface. All ab initio levels of theory indicate the presence of a minimum in the triplet state when the 5–6 bond is open to ~2.4 Å. The relative energies in the model system are slightly higher than for C_{60}, and we attribute this to the difference in curvature of the two systems. Forcing a bond open causes the carbon structure to buckle and curve away from the bond, and the addition of this extra curvature is better accommodated by the C_{60} cage than the relatively flat model system, making the relative energies of the latter higher than those of C_{60}. Also, geometry reoptimization at the ab initio levels of theory would change these energies somewhat. Nevertheless, the results are qualitatively similar to the MNDO predictions for C_{60}, strong evidence for the validity of both the model system and the proposed mechanism. They also reveal that this window mechanism should be operable on many fullerenes, not just C_{60}; indeed, thermal noble gas insertion into C_{70} has also been observed (*15*).

On the basis of these calculations, we can interpret the thermal insertion experiments as occurring by means of this triplet mechanism. The large amount of vibrational energy in C_{60} could push a 5–6 bond open, and the system may cross to the triplet state, from which the shallow minimum shown in Fig. 3 may be reached. Elementary analysis on the basis of density of states will predict a predominance of the singlet state of these molecules, which may account in part for the relatively low yield of Saunder's experiments that created a few endohedral fullerenes per million unfilled cages after several hours of heating (*14*). However, despite the favoring of the singlet state at the geometry where the singlet and triplet curves cross, opening the bond further makes jumping back to the singlet state (now much higher in energy) less likely. Once this minimum is reached, the bond may vibrate from ~2.3 to 2.9 Å with relative ease (Fig. 3).

Our best estimate for the overall barrier to reach this minimum is obtained from the experimental singlet-triplet excitation energy of C_{60} (1.7 eV) (*29*) plus our MNDO ~3.5-eV barrier to open the bond in the triplet state. This barrier is higher than the experimental result (3.5 eV), a clear indication that further calculations will be necessary to elucidate this point. However, our qualitative model remains the same: a minimum exists in the triplet potential energy surface of C_{60} with one C–C single bond held wide open, and atoms may enter the fullerene cage much more easily through this hole than through a hexagon or pentagon, which should outweigh the energy cost of opening the bond to create the hole. Furthermore, because the low efficiency of the observed experimental process probably comes from attempting to thermally produce the intersystem crossing, we predict that experiments done with a large triplet population of C_{60} (as under photolysis, see below) should give much better yields than those currently obtained (*15*).

In addition to this, multiple windows may be created on the C_{60} surface by opening two or more bonds, making 12-, 13-, 14-, and larger membered rings. We have examined these "double window" processes at the MNDO level of theory for C_{60} and our preliminary results show the same

Table 1. Energetics of 5–6 bond opening for a corannulene model system in the triplet state. Geometries optimized at the MNDO level of theory with the pentagon-hexagon (5–6) bond held open and the rest of the cage allowed to relax. The energy in electron volts is that above the C_{60} triplet at the same level of theory. SCF basis set contracted from *7s3p* in (*31*). LDA and BLYP were implemented in our program (*32*).

Method	Relative energy (eV) as a function of bond opening			
	2.05 Å	2.25 Å	2.38 Å	2.65 Å
MNDO	3.2	4.2	3.8	3.9
4s2p SCF	3.0	4.2	3.6	4.0
4s2p LDA	2.3	4.1	3.8	4.1
4s2p BLYP	2.2	3.9	3.6	3.8

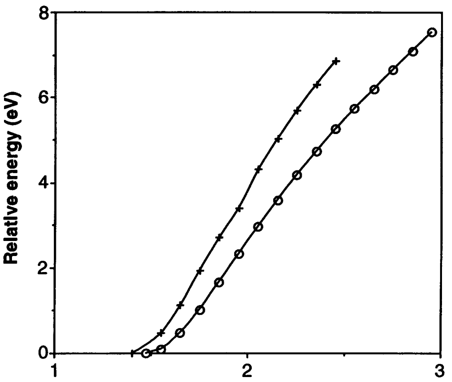

Fig. 2. Energetics of the singlet C_{60} bond opening. Relative energy (eV) to C_{60} is plotted against the length of the open bond at the MNDO (restricted Hartree Fock) level of theory. The 6–6 (hexagon-hexagon) bond is harder to open because it is shorter at equilibrium and has more double bond character. 6–6 bond, +; 5–6 bond, O.

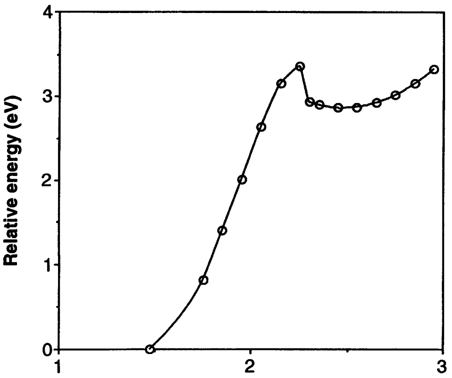

Fig. 3. Energetics of the triplet C_{60} window. Relative energy to the C_{60} triplet is plotted against the length of the 5–6 bond at the MNDO (UHF) level of theory. The barrier to open a bond is relatively low (3.5 eV), whereas a broad minimum exists (Fig. 1) with the bond open. This result was confirmed at ab initio levels of theory in a model system (Table 1), 5–6 bond, O.

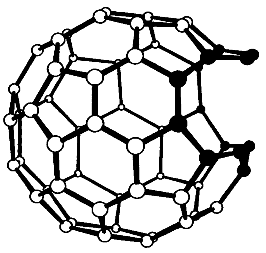

Fig. 4. One of several possible C_{60} "double windows." Breaking two pentagon-hexagon bonds creates a 13-membered ring in the cage structure through which large atoms or molecules may pass. The upper two *sp* carbons may bend back easily, opening the hole further.

qualitative features—a relatively low barrier to open the second bond and a minimum with both bonds open—in the triplet state along the second reaction coordinate as well. An example of such a double window structure with a 13-membered ring hole, for which the barrier to open the second bond (measured from the minimum with the bond open) is ~4 eV, is shown in Fig. 4. Some atoms or molecules may require such large windows for insertion.

Our theoretical predictions suggest an improved method of making endohedral fullerene compounds through this triplet window mechanism. We propose using a laser to irradiate C_{60} clusters in the gas phase and create a large population of the triplet state. By first producing an excited singlet state that intersystem crosses to the triplet, this process occurs with near quantitative yield (*30*), and it has the additional advantage of generating hot molecules, because the crossing releases energy. Heating this system to the sublimation point would ensure excellent thermal excitation and also keep unfilled cages cycling through an atmosphere of atoms to be inserted. With a large excess of such atoms, much of the material should react to X@C_{60}. Such a setup might allow the insertion of many different atoms and perhaps even small molecules. Furthermore, the *sp* carbons of the window minimum structure should be very reactive. Similar experiments under reactive atmospheres (such as H_2, F_2, or Li) might create compounds such as $C_{60}H_2$ or $C_{60}Li_2$, with addition across a 5–6 bond, in macroscale quantities. Thus, the existence of a C_{60} window mechanism described herein may open new avenues for the generation of both known and undiscovered endohedral and exohedral fullerene compounds.

REFERENCES AND NOTES

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1985).
2. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *ibid.* **347**, 354 (1990).
3. J. R. Heath *et al.*, *J. Am. Chem. Soc.* **107**, 7779 (1985).
4. F. D. Weiss, J. L. Elkind, S. C. O'Brien, R. F. Curl, R. E. Smalley, *ibid.* **110**, 4464 (1988).
5. Y. Chai *et al.*, *J. Phys. Chem.* **95**, 7564 (1991).
6. E. G. Gillan *et al.*, *ibid.* **96**, 6869 (1992).
7. T. Weiske, D. K. Böhme, J. Hrusák, W. Krätschmer, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **30**, 884 (1991).
8. M. M. Ross and J. H. Callahan, *J. Phys. Chem.* **95**, 5720 (1991).
9. K. A. Caldwell, D. E. Giblin, C. S. Hsu, D. Cox, M. L. Gross, *J. Am. Chem. Soc.* **113**, 8519 (1991).
10. E. E. B. Campbell, R. Ehlich, A. Hielscher, J. M. A. Frazao, I. V. Hertel, *Z. Phys.* **D23**, 1 (1992).
11. Z. Wan, J. C. Christian, S. L. Anderson, *J. Chem. Phys.* **96**, 3344 (1992).
12. T. Guo, R. E. Smalley, G. E. Scuseria, *ibid.* **99**, 352 (1993).
13. Z. Wan, J. F. Christian, Y. Basir, S. L. Anderson, *ibid.*, p. 5858.
14. M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, R. J. Poreda, *Science* **259**, 1428 (1993).
15. M. Saunders *et al.*, in preparation.
16. J. Hrusák, D. K. Böhme, T. Weiske, H. Schwarz, *Chem. Phys. Lett.* **193**, 97 (1992).
17. T. Weiske, J. Hrusák, D. K. Böhme, H. Schwarz, *Helv. Chim. Acta* **75**, 79 (1992).
18. M. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4907 (1977).
19. M. J. Frisch *et al.*, Gaussian 92, Revision C, Gaussian Inc., Pittsburgh, PA, 1992.
20. J. Almlöf, K. Faegri Jr., K. Korsell, *J. Comput. Chem.* **3**, 385 (1982).
21. R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).
22. See, for example, R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford Univ. Press, New York, 1989).
23. B. G. Johnson, P. M. W. Gill, J. A. Pople, *J. Chem. Phys.* **98**, 5612 (1993), and references therein.
24. G. E. Scuseria, *ibid.* **97**, 7528 (1992).
25. ______, in *Buckminsterfullerenes*, W. E. Billups and M. A. Ciufolini, Eds. (VCH, New York, 1993), p. 103.
26. T. Guo *et al.*, *Science* **257**, 1661 (1992).
27. R. L. Murry, D. L. Strout, G. K. Odom, G. E. Scuseria, *Nature* **366**, 665 (1993).
28. R. E. Stanton, *J. Phys. Chem.* **96**, 111 (1992).
29. R. E. Haufler *et al.*, *Chem. Phys. Lett.* **179**, 449 (1991).
30. J. W. Arbogast *et al.*, *J. Phys. Chem.* **95**, 11 (1991).
31. F. B. van Duijneveldt, *IBM Research Report RJ 945* (1971).
32. G. K. Odom and G. E. Scuseria, unpublished results.
33. G.E.S. is a Camille and Henry Dreyfus Teacher-Scholar. Supported by NSF and the Welch Foundation.

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Suppression of Rupture in Thin, Nonwetting Liquid Films

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Stabilization against the rupture and breakup of thin, nonwetting liquid films spread on surfaces is generally sought by modification of equilibrium interfacial properties. A mechanism for suppressing rupture in such films that uses surface-attached polymers together with free chains in the bulk of the film is reported. Films of an oligostyrene liquid, which rupture within several minutes when spread on a silicon wafer, may be stabilized for many months by a polystyrene brush attached to the substrate, together with some free polystyrene in the liquid. The effect may arise from entanglements of the free chains with the immobilized brush.

A liquid spread thinly on a surface that it does not wet will spontaneously rupture and break up into droplets. This everyday observation has practical importance in areas as diverse as detergency, greenhouse efficiency, and resist-lithography in microelectronic applications. Where nonretarded van der Waals interactions are dominant, the free energy U per unit area of a film of thickness h is given by

$$U(h) = -A/(12\pi h^2) \qquad (1)$$

Here, A is the difference between the liquid-liquid and solid-liquid Hamaker constants (*1*). If A is positive, the van der Waals interactions thin the film, enhancing surface fluctuations, and after a characteristic time, the film ruptures (*2–5*). Dewetting of the surface takes place as the resulting holes grow. The rupture and breakup of such films have been extensively studied and are reasonably well understood (*2–10*).

An outstanding issue concerns the prevention of film rupture. Methods to stabilize nonwetting films have invariably focused on modification of the interactions at the liquid interfaces. This can be done with surface-active agents or with treatments that modify the substrate chemistry and thereby change the wettability (*4, 11*). Our strategy relies on a very different mechanism for suppressing the breakup of thin fluid layers. Liquid films can be stabilized by formation of a polymer "brush" together with small amounts of free polymer in the liquid. This effect does not result from changes in the surface tension, as in usual surfactant action. It may result from long-ranged entanglement coupling of the surface-attached brush with

Table 1. Molecular characteristics of oligostyrene and polystyrenes.

Sample	Weight-averaged molecular weight	M_w/ M_n*
PS(580)†‡	580	1.02
PS(7 × 10^5)†	710,000	1.05
dPS(5 × 10^5)†	500,000	1.04
PS-X(2.6 × 10^4)§	26,500	1.02
dPS-X(3.8 × 10^5)§	380,000	1.05

*The ratio of weight-averaged molecular weight to number-averaged molecular weight is a measure of sample polydispersity. †Purchased from Polymer Laboratories (Church Stretton, United Kingdom) and used as received. Manufacturer's molecular weight data, based on size exclusion chromatography and light scattering. ‡Glass transition temperature, T_g = −18°C. §Synthesized as described in (*16*). Molecular weight data based on size exclusion chromatography and light scattering.

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