

Scratching the Surface of Buckminsterfullerene: The Barriers for Stone–Wales Transformation through Symmetric and Asymmetric Transition States

Holger F. Bettinger,^{*,†} Boris I. Yakobson,^{‡,§,||} and Gustavo E. Scuseria^{‡,§}

Contribution from the Lehrstuhl für Organische Chemie II, Universitätsstrasse 150, 44780 Bochum, Germany, and Center for Nanoscale Science and Technology, Department of Chemistry, and Department of Mechanical Engineering, Rice University, Houston, Texas 77251-1892

Received October 9, 2002; E-mail: holger.bettinger@ruhr-uni-bochum.de

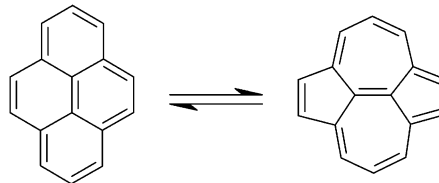
Abstract: General-gradient approximation (PBE) and hybrid Hartree–Fock density functional theories (B3LYP) in conjunction with basis sets of up to polarized triple- ζ quality have been applied to study the Stone–Wales transformation of buckminsterfullerene (BF) to yield a C_{60} isomer of C_{2v} symmetry with two adjacent pentagons (#1809). In agreement with earlier investigations, two different transition states and reaction pathways could be identified for the rearrangement from BF to C_{60} on the C_{60} potential energy surface (PES). One has C_2 molecular point group symmetry with the two migrating carbon atoms remaining close to the fullerene surface. The other one has a high-energy carbene-like (sp^3) structure where a single carbon atom is significantly moved away from the C_{60} surface. The carbene intermediate and the second transition state along the stepwise reaction path characterized previously at lower levels of theory do not exist as stationary points with the density functionals utilized here. The classical barriers of both mechanisms are essentially identical, 6.9 eV using PBE and 7.3 eV with B3LYP.

Introduction

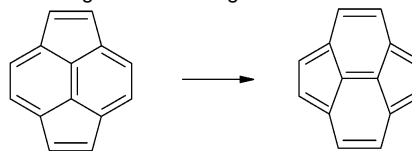
Carbon nanotubes, micrometer-long hollow filaments of carbon, have a large aspect ratio, and their mechanical properties make them promising candidates for applications in high-strength materials. Accordingly, the mechanical properties of nanotubes under large uniaxial tension have been studied intensively.¹ Yakobson and others have proposed by dislocation theory² and shown by extensive computer simulations^{3,4} that at high temperature the nanotube wall will yield to strain by formation of a dislocation dipole, a pentagon–heptagon pair. The formation of this 5/7/7/5 dislocation dipole can be considered to emerge from the regular hexagonal lattice comprising the nanotube wall by a 90° rotation of a C_2 unit (Scheme 1).

The rotation of a C_2 unit is known in the fullerene literature as a Stone–Wales (SW) transformation or pyracylene rearrangement,⁵ which enables a pair of hexagons and pair of pentagons to switch places (Scheme 2). It dates back to 1986, when Stone and Wales pointed out that there are many stable C_{60} isomers, which do not follow the well-known isolated

Scheme 1. Formation of a 5/7/7/5 Dislocation Dipole by Stone–Wales Transformation



Scheme 2. Stone–Wales Transformation in Buckminsterfullerene Interchanges Pentagons and Hexagons



pentagon rule, and which are related to the I_h form, buckminsterfullerene (BF), by transformations involving the rotation of two carbon atoms around the center of the bond connecting them.⁶

The prime SW dislocation, once “unlocked”, is known to ease further relaxation of the nanotube, either by brittle fracture or by plastic glide of the separated dislocations. This yield mechanism to large uniaxial strain has not only been identified in carbon, but also in boron–nitride nanotubes.^{7,8} However, as pointed out by Samsonidze et al.,⁹ the time it takes for a

[†] Lehrstuhl für Organische Chemie II.

[‡] Center for Nanoscale Science and Technology, Rice University.

[§] Department of Chemistry, Rice University.

^{||} Department of Mechanical Engineering, Rice University.

(1) Yakobson, B. I.; Avouris, P. *Top. Appl. Phys.* **2001**, *80*, 287.

(2) Yakobson, B. I. *Appl. Phys. Lett.* **1998**, *72*, 918.

(3) Nardelli, M. B.; Yakobson, B. I.; Bernholc, J. *Phys. Rev. B* **1998**, *57*, R4277.

(4) Nardelli, M. B.; Yakobson, B. I.; Bernholc, J. *Phys. Rev. Lett.* **1998**, *81*, 4656.

(5) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.

(6) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501.

(7) Zhang, P.; Crespi, V. H. *Phys. Rev. B* **2000**, *62*, 11050.

(8) Bettinger, H. F.; Dumitrica, T.; Yakobson, B. I.; Scuseria, G. E. *Phys. Rev. B* **2002**, *65*, 041406.

nanotube to fail depends decisively on the barrier of formation of the first dislocation dipole. The strength of nanotubes is essentially a kinetic rather than a thermodynamic effect. Thus, Samsonidze et al.⁹ have studied various modes of SW transformation in carbon nanotubes and have analyzed their barriers depending on tube chirality using the Tersoff–Brenner^{10,11} potential. The authors could then compute a critical strain for carbon nanotube failure within a given time, ranging from 1 ms to 1 year.

Accurate barrier heights for formation of the 5/7/7/5 dislocation dipole are highly desirable to allow a fairly reliable evaluation of the critical strain in carbon nanotubes. We thus decided to investigate here the SW transformation – concerted and stepwise pathways^{12,13} – in C₆₀, as even for this often studied molecule the literature does not agree on a barrier nor on a preferred reaction pathway (vide infra). We employ here density functional theory within the general gradient approximation and hybrid Hartree–Fock schemes with basis sets of up to polarized triple- ζ quality as these quantum chemical methodologies are known from a large body of data to give geometries, energies, and barrier heights in good agreement with higher level ab initio approaches.¹⁴ Although C₆₀ cannot be exposed to tensile forces, its isomerization can result from collisions with a thermostat, and the SW transformation can (metaphorically) be viewed as a basic scratch on the perfect surface of BF. The knowledge gained here will hopefully facilitate future studies of the SW transformation in carbon nanotubes. Before we begin to summarize our results, an introduction to the literature of the SW transformation in C₆₀ is pertinent.

Background

The SW transformation has originally been suggested as a hypothetical mechanism useful for deriving fullerene isomers.⁶ In this sense, it is applied in a formal way in topological studies to generate so-called Stone–Wales maps which illustrate possible interconversions of fullerene isomers.^{15–17} It also has been generalized and used to construct generalized SW maps.^{18–23} New isomerization transformations, expected to be of little physicochemical relevance, however, due to multiple bond breaking, have also been suggested for the use in topological studies.^{24–26}

The SW rearrangement has also been considered as an actual reaction mechanism involved in the efficient formation of the highly symmetric BF out of the chaos of condensing carbon vapor (consisting of atoms, dimers, and trimers)^{27,28} produced by laser ablation²⁹ or by an arc during the Krätschmer–Huffman³⁰ synthesis. Several mechanisms for fullerene formation have been put forward, for example, “pentagon road,”^{31,32} “fullerene road,”³³ “ring stacking,”^{34,35} and “cycloaddition,”^{36–39} and detailed descriptions and evaluations of these mechanisms with regard to their ability to explain experimental observations can be found in excellent reviews.^{18,40,41} From various drift tube ion-mobility experiments of Bower’s^{36,37} and Jarrold’s³⁸ groups, it is clear today that monocyclic carbon rings, their cycloaddition³⁹ to yield larger rings, and ring coalescence^{42–46} are essential for the formation of fullerenes. As BF is an especially small “target” in phase space to reach,¹⁸ it is regarded as very unlikely that the perfect BF is formed spontaneously.^{39,47–50} Rather, annealing of the cage is considered essential as it provides a means of exploring configuration space allowing the carbon cluster to reach its most stable form.⁴⁹ The SW transformation is usually thought to be a possible mechanism for achieving this annealing. However, Scott and Warren⁵¹ found that the pyracylene hydrocarbon does not rearrange according to the SW pathway at 1100 °C, and Scott stated in a 1996 literature survey that the SW transformation has not been observed at all in a polycyclic aromatic hydrocarbon.⁵² Recently, Dosa et al. invoked a formal Stone–Wales rearrangement in the high-temperature isomerization of angular [3]phenylene.⁵³ Finally, it should be noted that fullerenes form most likely by different mechanisms under experimental conditions found, for example, in combus-

- (9) Samsonidze, G. G.; Samsonidze, G. G.; Yakobson, B. I. *Phys. Rev. Lett.* **2002**, *88*, 065501.
 (10) (a) Tersoff, J. *Phys. Rev. B* **1988**, *37*, 6991. (b) Tersoff, J. *Phys. Rev. Lett.* **1988**, *61*, 2879.
 (11) Brenner, D. W. *Phys. Rev. B* **1990**, *42*, 9458.
 (12) Murry, R. L.; Strout, D. L.; Odom, G. K.; Scuseria, G. E. *Nature* **1993**, *366*, 665.
 (13) Murry, R. L.; Strout, D. L.; Scuseria, G. E. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 113.
 (14) Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 2936.
 (15) Fowler, P. W.; Manolopoulos, D. E.; Ryan, R. P. *Carbon* **1992**, *30*, 1235.
 (16) Fowler, P. W.; Manolopoulos, D. E.; Ryan, R. P. *J. Chem. Soc., Chem. Commun.* **1992**, 408.
 (17) Austin, S. J.; Fowler, P. W.; Manolopoulos, D. E.; Zerbetto, F. *Chem. Phys. Lett.* **1995**, *235*, 146.
 (18) Curl, R. F. *Philos. Trans. R. Soc. London* **1993**, *A343*, 19.
 (19) Balaban, A. T.; Schmalz, T. G.; Zhu, H. Y.; Klein, D. J. *THEOCHEM-J. Mol. Struct.* **1996**, *363*, 291.
 (20) Mitchell, D.; Fowler, P. W.; Zerbetto, F. *J. Phys. B: At. Mol. Opt. Phys.* **1996**, *29*, 4895.
 (21) Plestenjak, B.; Pisanski, T.; Graovac, A. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 825.
 (22) Osawa, E.; Ueno, H.; Yoshida, M.; Slanina, Z.; Zhao, X.; Nishiyama, M.; Saito, H. In *Proceedings of the Symposium on Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1998; Vol. 6, p 94.
 (23) Osawa, E.; Ueno, H.; Yoshida, M.; Slanina, Z.; Zhao, X.; Nishiyama, M.; Saito, H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 943.

- (24) Astakhova, T. Y.; Vinogradov, G. A. *Fullerene Sci. Technol.* **1997**, *5*, 1545.
 (25) Astakhova, T. Y.; Vinogradov, G. A. *Fullerene Sci. Technol.* **1998**, *6*, 1037.
 (26) Astakhova, T. Y.; Vinogradov, G. A. *THEOCHEM-J. Mol. Struct.* **1998**, *430*, 259.
 (27) Van Orden, A.; Saykally, R. J. *Chem. Rev.* **1998**, *98*, 2313.
 (28) Ebbesen, T. W.; Tabucki, J.; Tanigaki, K. *Chem. Phys. Lett.* **1992**, *191*, 336.
 (29) Kroto, H. W.; Heath, J. R.; O’Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1986**, *318*, 162.
 (30) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.
 (31) Heath, J. R.; O’Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *Comments Cond. Mater. Phys.* **1987**, *13*, 119.
 (32) Smalley, R. E. *Acc. Chem. Res.* **1992**, *25*, 98.
 (33) Heath, J. R. *ACS Symp. Ser.* **1992**, *481*, 1.
 (34) Wakabayashi, T.; Achiba, Y. *Chem. Phys. Lett.* **1992**, *190*, 465.
 (35) Wakabayashi, T.; Shiromaru, H.; Kikuchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *201*, 470.
 (36) Von Helden, G.; Gotts, N. G.; Bowers, M. T. *Nature* **1993**, *363*, 60.
 (37) Von Helden, G.; Hsu, M. T.; Gotts, N.; Bowers, M. T. *J. Phys. Chem.* **1993**, *97*, 8182.
 (38) Hunter, J. M.; Fye, J. L.; Jarrold, M. F. *Science* **1993**, *260*, 784.
 (39) Strout, D. L.; Scuseria, G. E. *J. Phys. Chem.* **1996**, *100*, 6492.
 (40) Schwarz, H. *Angew. Chem.* **1993**, *105*, 1475; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1412.
 (41) Goroff, N. S. *Acc. Chem. Res.* **1996**, *29*, 77.
 (42) Yeretzian, C.; Hansen, K.; Diederich, F.; Whetten, R. L. *Nature* **1992**, *359*, 44.
 (43) McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993**, *259*, 1594.
 (44) (a) Hunter, J. M.; Fye, J. L.; Jarrold, M. F. *J. Chem. Phys.* **1993**, *99*, 1785. (b) Hunter, J. M.; Fye, J. L.; Jarrold, M. F. *J. Phys. Chem.* **1993**, *97*, 3460. (c) Hunter, J. M.; Fye, J. L.; Roskamp, E. J.; Jarrold, M. F. *J. Phys. Chem.* **1994**, *98*, 1810. (d) Hunter, J. M.; Jarrold, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 10317.
 (45) Babic, D.; Trinajstić, N. *Fullerene Sci. Technol.* **1994**, *2*, 343.
 (46) Babic, D.; Trinajstić, N. *J. Mol. Struct.* **1996**, *376*, 507.
 (47) Maruyama, S.; Yamaguchi, Y. *Chem. Phys. Lett.* **1998**, *286*, 343.
 (48) Yamaguchi, Y.; Maruyama, S. *Chem. Phys. Lett.* **1998**, *286*, 336.
 (49) Walsh, T. R.; Wales, D. J. *J. Chem. Phys.* **1998**, *109*, 6691.
 (50) Krestinin, A. V.; Moravsky, A. P. *Chem. Phys. Lett.* **1998**, *286*, 479.
 (51) Scott, L. T.; Warren, H. B. *Seventh International Symposium on Novel Aromatic Compounds*; Victoria, British Columbia, Canada, 1992; abstr. no. 65.
 (52) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291.
 (53) Dosa, P. I.; Schleifenbaum, A.; Vollhardt, K. P. C. *Org. Lett.* **2001**, *3*, 1017.

Table 1. Energies (in eV) of C_{60} - C_{2v} with Respect to Buckminsterfullerene As Computed at Various Levels of Theory^a

theory	reference	energy (in eV)
Tersoff potential	71	around 0.8
QCFF/PI	17	1.7
DF-TB	49	1.2
MNDO	12, 13, 64, 65	1.89
AM1	78	2.1
HF/3-21G//MNDO	65	2.12
BLYP/DZ//MNDO	12, 13	3.2
LDA (Car-Parinello)	66	1.6
LSDA	67-70	1.47
B3LYP/6-311G**//B3LYP/6-31G*	this work	1.68 (1.66)
PBE/6-311G**//PBE/6-31G*	this work	1.55 (1.53)

^aZero-point vibrational energy corrected data are given in parentheses.

tion systems,⁵⁴⁻⁵⁶ naphthalene pyrolysis,⁵⁷ or the recently reported rational chemical synthesis of BF.^{58,59}

Austin et al.¹⁷ have generated the SW map for C_{60} and have shown that BF is within the same SW family as 1709 of the other unique 1811 fullerene isomers. Thus, 94% of all fullerene C_{60} isomers can rearrange to BF by at most 30 SW transformations.¹⁷ In addition, BF is connected to only one other C_{60} isomer, which has C_{2v} symmetry and two pairs of adjacent pentagons (C_{60} - C_{2v} , #1809). This isomer thus is the only one which can be reached by SW transformation from BF, or, alternatively, it must be the last one in any annealing process before BF is formed.^{15,60,61} Combining these graph-theoretical results with a semiempirical QCFF/PI energetic analysis of the 1812 fullerene C_{60} isomers,⁶² it has been shown that introduction of pentagon adjacencies by SW transformation results in an overall energy increase. Annealing to BF thus can proceed downhill energetically. While the average increase in energy for Stone-Wales steps away from BF was determined to be 33 kJ mol⁻¹, it is about 5 times this value for the first step, that is, for the formation of C_{60} - C_{2v} .^{17,62}

Semiempirical investigations employing the QCFF/PI^{17,62} and the MNDO⁶³ Hamiltonians suggested that the defect isomer C_{60} - C_{2v} is 1.7 or 1.9 eV less stable than BF.^{12,13,64,65} Single point calculations on MNDO optimized structures at the HF/3-21G⁶⁵ and 4s2p/BLYP^{12,13} levels of theory give larger energy differences of 2.1 and 3.2 eV, respectively (Table 1). On the other hand, local density approximations were applied by Yi and Bernholc⁶⁶ and by Heggie et al.,⁶⁷⁻⁷⁰ who arrived at energy differences of 1.6 and 1.5 eV, respectively. Even lower values were obtained by Walsh and Wales⁴⁹ when using density

Table 2. Barriers (in eV) for Formation of C_{60} - C_{2v} from Buckminsterfullerene through Symmetric (C_2) and Asymmetric Transition States As Computed at Various Levels of Theory^a

theory	reference	symmetric	asymmetric
Brenner potential	47		2.5 ^b
DF-TB	49		5.2
MNDO	12, 13	8.5	7.2
AM1	78	7.7	7.5
SAM1	79, 80		4.2 ^c
BLYP/DZ//MNDO	12, 13	8.1	7.6
LDA (Car-Parinello)	66	7.0	
LSDA	67	6.18	not found
Tersoff potential	71	is minimum	5.58

^aZero-point vibrational energy corrected data are given in parentheses.

^bFrom an Arrhenius plot. ^cFor the "extended pyracyclene" model rather than C_{60} .

functional tight-binding (1.2 eV) and by Marcos et al.⁷¹ using Tersoff's¹⁰ interatomic potential (less than 1 eV).

SW⁶ recognized that their transformation would involve a four-electron Hückel transition state and that it thus is a thermally forbidden rearrangement according to the orbital symmetry considerations of Woodward and Hoffmann.⁷³ Hawkins et al. gave a lower limit for the activation energy of the SW transformation of >83 kcal mol⁻¹ (>3.6 eV) based on the configurational stability of C_{84} at 700 °C.⁷⁴ They also found that C_{84} in hexane solution does not racemize photochemically at 193 nm.⁷⁴ An analysis of the SW transformation route using Hückel theory concluded that the transition state for a concerted process should have C_2 symmetry.⁷⁵ Yi and Bernholc⁶⁶ (YB) were the first to compute the barrier for SW transformation in BF using local density functional theory and the Car-Parinello method. YB identified a transition state (TS) where the rotating C_2 unit is halfway between its orientation in BF and C_{60} - C_{2v} . Their investigation showed that the total energy increased monotonically from BF to the TS, suggesting that the TS localized describes a concerted chemical reaction, rotation of the C_2 unit, without any intermediates. This rearrangement is thus an example of a dyotropic reaction.^{76,77} In agreement with the thermally forbidden character of the SW transformation, a very high activation barrier of 7.0 eV from BF to C_{60} - C_{2v} was obtained (Table 2). This result is in good agreement with an estimate of 7 eV given by Dresselhaus et al. based on bond energy considerations.⁵ Taking into account that C_{60} - C_{2v} is 1.6 eV higher in energy than BF at the level of theory employed by YB, the barrier for the reverse process is 5.4 eV. A similar value (6.9 eV) was obtained by Fowler and Baker for the degenerate SW transformation of C_{28} using PM3 and HF/STO-3G, albeit the transition state did not have the expected C_{2v} but rather C_1 symmetry.⁷²

- (54) Homann, K.-H. *Angew. Chem.* **1998**, *110*, 2573; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2435.
 (55) Vahlas, C.; Kacheva, A.; Hitchman, M. L.; Rocabois, P. *J. Electrochem. Soc.* **1999**, *146*, 2752.
 (56) Reilly, P. T. A.; Gieray, R. A.; Whitten, W. B.; Ramsey, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 11596.
 (57) Taylor, R.; Langley, G. J.; Kroto, H. W.; Walton, D. R. M. *Nature* **1993**, *366*, 728.
 (58) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500.
 (59) Boorum, M. M.; Vasil'ev, Y. V.; Drewello, T.; Scott, L. T. *Science* **2001**, *294*, 828.
 (60) Coulombeau, C.; Rassat, A. *J. Chim. Phys.* **1991**, *88*, 173.
 (61) Coulombeau, C.; Rassat, A. *J. Chim. Phys.* **1991**, *88*, 665.
 (62) Austin, S. J.; Fowler, P. W.; Manolopoulos, D. E.; Orlandi, G.; Zerbetto, F. *J. Phys. Chem.* **1995**, *99*, 8076.
 (63) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.
 (64) Stanton, R. E. *J. Phys. Chem.* **1992**, *96*, 111.
 (65) Raghavachari, K.; Rohlfing, C. M. *J. Phys. Chem.* **1992**, *96*, 2463.
 (66) Yi, J.-Y.; Bernholc, J. *J. Chem. Phys.* **1992**, *96*, 8634.
 (67) Heggie, M. I.; Latham, C. D.; Jones, B.; Briddon, P. R. In *Proceedings of the Symposium on Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1995; p 1218.

- (68) Eggen, B. R.; Heggie, M. I.; Jungnickel, G.; Latham, C. D.; Jones, R.; Briddon, P. R. *Science* **1996**, *272*, 87.
 (69) Eggen, B. R.; Latham, C. D.; Heggie, M. I.; Jones, B.; Briddon, P. R. *Synth. Met.* **1996**, *77*, 165.
 (70) Eggen, B. R.; Heggie, M. I.; Jungnickel, G.; Latham, C. D.; Jones, R.; Briddon, P. R. *Fullerene Sci. Technol.* **1997**, *5*, 727.
 (71) Marcos, P. A.; Lopez, M. J.; Rubio, A.; Alonso, J. A. *Chem. Phys. Lett.* **1997**, *273*, 367.
 (72) Fowler, P. W.; Baker, J. *J. Chem. Soc., Perkins Trans. 2* **1992**, 1665.
 (73) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
 (74) Hawkins, J. M.; Nambu, M.; Meyer, A. *J. Am. Chem. Soc.* **1994**, *116*, 7642.
 (75) Pinto, Y.; Fowler, P. W.; Mitchell, D.; Avnir, D. *J. Phys. Chem. B* **1998**, *102*, 5776.
 (76) Reetz, M. T. *Angew. Chem.* **1972**, *84*, 161; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129.
 (77) Reetz, M. T. *Angew. Chem.* **1972**, *84*, 163; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 130.

Murry et al. identified an alternative mechanism for SW transformation, which involves an energetically high-lying transient intermediate, a carbene, with a sp^3 hybridized (tetra-coordinated) and a dicoordinated carbon atom.^{12,13} The latter atom is moved considerably away from the fullerene surface. This pathway is not concerted but involves two [1,2]-C shifts: alkene \rightarrow carbene \rightarrow alkene. An important feature of this reaction path is the finding that the carbene intermediate links the SWT to the fragmentation of C_{60} into C_{58} and C_2 . Murry et al. concluded from computations using gradient-corrected density functional theory (BLYP) in conjunction with a double- ζ basis set (4s2p) on geometries obtained by the semiempirical MNDO method that the carbene pathway is more favorable than the concerted mechanism by 0.5 eV. Nonetheless, the lowest barrier for the SW transformation (via the carbene intermediate) was quite high, 7.6 eV. A few years later, Honda and Osawa⁷⁸ could confirm the existence of a carbene pathway using the semiempirical AM1 modification of the MNDO Hamiltonian in their 1996 study of the SW transformation in C_{60} . However, their barriers, 176.5 kcal mol⁻¹ (7.7 eV) and 172.5 kcal mol⁻¹ (7.5 eV) for the SW transition state and the highest energy transition state along the carbene pathway, respectively, are closer in energy than those found in the study of Murry et al. In subsequent papers, Osawa and co-workers^{79,80} used the AM1 and SAM1 models and focused on the carbene pathway in the so-called “extended pyracylene” model introduced by Murry et al.^{12,13} They obtained a significantly lower barrier of about 4.2 eV using the SAM1 method on the extended pyracylene. Honda et al. also studied the SW rearrangement of a hinge-opened [2 + 2] C_{60} dimer to the so-called wide-bridged C_{120} isomer.⁸¹

On the other hand, no indications for a carbene intermediate or asymmetric TSs could be obtained by Heggie et al. in 1995.⁶⁷ Using the local spin-density (LSD) approximation, these authors mapped out the ground-state potential energy surface (PES) between BF and C_{60} - C_{2v} by using constrained geometry optimizations. For each pair of bonds being interchanged in the SW transformation, Heggie et al. constrained the differences of the squares of the bond lengths to be constant. They obtained a smoothly varying PES with a saddle point (6.2 eV with respect to BF) connecting the two minima, in agreement with a concerted planar rearrangement.⁶⁷

A long-standing problem associated with the SW transformation was as follows: Why is BF exclusively formed if the barrier for SW transformation is larger than 5 eV with respect to C_{60} - C_{2v} ?^{79,80,82–84} Indeed, early molecular dynamics simulations of C_{60} relaxation failed to obtain BF, but ended with sometimes strongly distorted C_{60} cages.^{85–88} This was ascribed to the unfortunate interplay of high barriers for SW transformation and the short time scale which had to be used for the

simulations.⁴⁹ Later, successful fullerene annealing to BF has been achieved in molecular dynamics simulations.^{89,90} The finding of the autocatalysis mechanism by Eggen et al.,^{68–70,91} that is, that the presence of carbon atoms significantly catalyzes the SW transformation, was clearly a step forward in understanding the annealing of C_{60} clusters. Using local density functional theory, Eggen et al. arrived at a barrier of 3.9 eV in the presence of an additional carbon atom, amounting to a reduction of 2.3 eV (at their level of theory). Hence, they argued that the problematically high barrier might drastically be reduced under experimental conditions.⁶⁸ In 2000, Slanina et al. computationally probed a variety of elements and found that the nitrogen atom is particularly efficient in catalyzing the SW transformation.⁹²

Already a year after the discovery of Eggen et al., the need for an autocatalysis mechanism in fullerene annealing was questioned by Marcos et al.⁷¹ In their molecular dynamics simulation of the annealing of the SW defect in C_{60} - C_{2v} to yield BF using the Tersoff^{10,72} interatomic potential, these authors concluded that there are at least three intermediates (“intermediate metastable isomers”).⁷¹ The overall barrier was only 5.6 eV, while the barriers between transient intermediates are found not to exceed 2.6 eV. However, the intermediates were only located by constrained optimization in this study, and thus the findings of Marcos et al.⁷¹ should be taken with caution as long as they are not confirmed by full geometry optimizations.

The 1998 density functional tight-binding (DF-TB) study of Walsh and Wales obtained a barrier of 5.2 eV involving an asymmetric transition state. These authors, however, conceded that an improvement in the interaction potential would shift their values upward. Using the SW map and considering all isomers up to six SW steps away from BF and the transition states connecting these isomers, Walsh and Wales could study the relaxation dynamics of C_{60} using an RRKM master equation approach.⁴⁹ They found rather long relaxation times, in agreement with the experimental time scale of 0.001 s for fullerene formation, which were ascribed to the high barriers for SW transformations.

Maruyama and Yamaguchi⁴⁷ managed in their molecular dynamics study to anneal high-energy C_{60} isomers into BF by using a novel temperature control method and the Tersoff–Brenner^{10,11} potential. The relaxation appears to involve SW and generalized SW transformations with asymmetric transition states. An extremely low activation energy of only 2.5 eV was obtained from an Arrhenius plot for SW transformation. Walsh and Wales⁴⁹ argued that the simulations of Maruyama and Yamaguchi⁴⁷ only succeeded in annealing to BF due to the low barriers obtained with their potential.

Theoretical Methods

We employed the gradient-corrected exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE),^{93,94} as well as Becke’s⁹⁵ three-

(78) Honda, K.; Osawa, E. *Fullerene Sci. Technol.* **1996**, *4*, 925.

(79) Osawa, E.; Slanina, Z.; Honda, K. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. C—Mol. Mater.* **1998**, *10*, 1.

(80) Osawa, E.; Slanina, Z.; Honda, K.; Zhao, X. *Fullerene Sci. Technol.* **1998**, *6*, 259.

(81) Honda, K.; Osawa, E.; Slanina, Z.; Matsumoto, T. *Fullerene Sci. Technol.* **1996**, *4*, 819.

(82) Mishra, R. K.; Lin, Y. T.; Lee, S. L. *Chem. Phys. Lett.* **1999**, *313*, 437.

(83) Mishra, R. K.; Lin, Y. T.; Lee, S. L. *J. Chem. Phys.* **2000**, *112*, 6355.

(84) Mintmire, J. W. *Science* **1996**, *272*, 45.

(85) Chelikowsky, J. R. *Phys. Rev. Lett.* **1991**, *67*, 2970.

(86) Chelikowsky, J. R. *Phys. Rev. B* **1992**, *45*, 12062.

(87) Wang, C. Z.; Xu, C. H.; Chan, C. T.; Ho, K. M. *J. Phys. Chem.* **1992**, *96*, 3563.

(88) Jing, X.; Chelikowsky, J. R. *Phys. Rev. B* **1992**, *46*, 5028.

(89) Xu, C.; Scuseria, G. E. *Phys. Rev. Lett.* **1994**, *72*, 669.

(90) Laszlo, I. *Fullerene Sci. Technol.* **1997**, *5*, 375.

(91) Heggie, M.; Eggen, B. R.; Ewels, C. P.; Leary, P.; Ali, S.; Jungnickel, G.; Jones, R.; Briddon, P. R. In *Proceedings of the Symposium on Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1998; Vol. 6, p 60.

(92) Slanina, Z.; Zhao, X.; Uhlik, F.; Ozawa, M.; Osawa, E. *J. Organomet. Chem.* **2000**, *599*, 57.

(93) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(94) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396 (E).

Table 3. The C–C Bond Lengths (in Å) in BF As Obtained at Various Levels of Theory

	[6,6] C–C bond	[6,5] C–C bond
MP2/TZP ^a	1.406	1.446
B3LYP/3-21G	1.390	1.460
B3LYP/6-31G*	1.395	1.453
PBE/3-21G	1.401	1.465
PBE/6-31G*	1.405	1.457
NMR ^b	1.40 ± 0.015	1.45 ± 0.015
X-ray ^c	1.355(9)	1.467(21)
neutron powder diffraction ^d	1.391	1.455
gas-phase electron diffraction ^e	1.401(10)	1.458(6)

^a Reference 112. ^b Reference 104. ^c Reference 105. ^d Reference 107. ^e Reference 106.

Table 4. The Vibrational Frequencies (in cm⁻¹) and Infrared Intensities (in Parentheses, in km mol⁻¹) of Infrared Active T_{1u} Symmetry Modes of BF Computed in the Harmonic Approximation at Various Levels of Theory

expt. ^a	B3LYP/6-31G* ^b	PBE/6-31G*
526.5	539.1 (84.9)	513.0 (66.9)
575.8	588.3 (33.6)	577.5 (35.7)
1182.9	1213.6 (26.8)	1192.5 (26.4)
1429.2	1460.5 (35.6)	1447.2 (27.7)

^a C₆₀ solid film on KBr; ref 113. ^b See also refs 108, 109.

Table 5. Barriers (in eV) for Stone–Wales Transformation through Transition States 1–3 As Obtained at Various Levels of Theory^a

method	1 (C ₂ symmetry)	2 (S ₄)	3 ("carbenic")
PBE/3-21G	6.99 (6.79) ^b	6.98 (6.79)	6.97 (6.80)
PBE/6-31G* ^c	6.99 (6.80)	converges to 1	6.98 (6.82)
PBE/6-311G**// PBE/6-31G* ^c	6.91 (6.72)		6.92 (6.76)
B3LYP/3-21G	7.35 (7.14)	converges to 1	7.33 (7.15)
B3LYP/6-31G*	7.37 (7.15)		7.32 (7.14)
B3LYP/6-311G**// B3LYP/6-31G*	7.27 (7.06)		7.27 (7.09)

^a Zero-point vibrational energies (ZPVE) were obtained with the 3-21G basis set, and the ZPVE corrected data are given in parentheses. ^b Second-order stationary point. ^c The ZPVE correction used the ZPVE of 2; ZPVE of 1 is 0.01 eV smaller.

parameter hybrid functional as implemented in the Gaussian⁹⁶ program in conjunction with the correlation functional of Lee, Yang, and Parr (B3LYP).⁹⁷ The basis sets employed were the standard 3-21G,⁹⁸ 6-31G*,⁹⁹ and 6-311G**¹⁰⁰ basis sets. The largest computations employed 1080 basis functions. Molecular geometries were completely optimized within the respective molecular point group symmetries with the 3-21G and 6-31G* basis sets and the PBE and B3LYP functionals.¹⁰¹ Second derivatives of the energy with respect to nuclear coordinates

(95) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(96) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Rev. A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

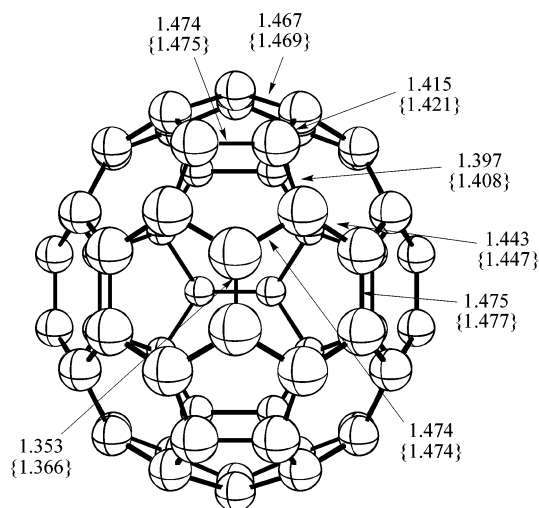
(97) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(98) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(99) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(100) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(101) The geometry optimizations employed the Gaussian keyword TIGHT (max. force < 0.000015, rms force < 0.000010, max displacement < 0.000060, rms displacement < 0.000040), while the default convergence criteria (max force < 0.00045, rms force < 0.00030, max displacement < 0.0018, rms displacement < 0.0012) were used in the IRC computations.

**Figure 1.** Structure of the C_{2v} symmetry isomer 1809 of C₆₀. Bond lengths were obtained at the B3LYP/6-31G* and PBE/6-31G* (in curly brackets) levels of theory and are given in Å.

were obtained analytically for all stationary points at the PBE/3-21G and B3LYP/3-21G levels of theory. In addition, the BF and C₆₀-C_{2v} harmonic vibrational frequencies were determined at the B3LYP/6-31G* and PBE/6-31G* levels of theory. Intrinsic reaction coordinates (IRC) were computed at PBE/3-21G for selected transition structures to establish the connectivity of minima and saddle points. The IRC computations employed the Gonzalez–Schlegel^{102,103} algorithm using the default step size (0.1 amu^{-1/2} Bohr).¹⁰¹ Energies were refined by single point computations at the B3LYP/6-311G** and PBE/6-311G** levels of theory employing the B3LYP/6-31G* and PBE/6-31G* geometries (B3LYP/6-311G**/B3LYP/6-31G* and PBE/6-311G**//PBE/6-31G*, respectively). Corrections for zero-point vibrational energies (ZPVE) were computed with the 3-21G basis set, and corrected energy differences are given in parentheses in Tables 1 and 5.

Results and Discussion

A. Buckminsterfullerene. An enormous amount of calculations on BF have been published since its observation in 1985. We have summarized our results on BF in Tables 3 and 4 to allow comparison with experimental bond lengths obtained by a wide variety of methods^{104–107} under varying conditions as well as infrared-active T_{1u} vibrational frequencies. Our B3LYP data are in agreement with previous investigations using this hybrid functional.^{108,109} For an in-depth discussion of the BF vibrational spectrum, the reader is referred to the recent work by Schettino et al.¹⁰⁹ and Ceulemans et al.¹¹⁰

B. C₆₀-C_{2v}. As can be seen from Table 1, the C₆₀-C_{2v} isomer arising from one SW transformation is 1.6–1.7 eV higher in energy than BF at our levels of theory. This energy difference is similar to results obtained previously with the local density approximation.⁶⁶ The ZPVEs of BF and C₆₀-C_{2v} differ by only

(102) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(103) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(104) Yannoni, C. S.; Bernier, P. P.; Bethune, D. S.; Meijer, G.; Salem, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 3190.

(105) Liu, S.; Lu, Y.-J.; Kappes, M. M.; Ibers, J. A. *Science* **1991**, *254*, 408.

(106) Hedberg, K.; Hedberg, L.; Bethune, D. S.; Brown, C. A.; Dorn, H. C.; Johnson, R. D.; De Vries, M. *Science* **1991**, *254*, 410.

(107) David, W. I. F.; Ibberson, R. M.; Matthewman, J. C.; Prassides, K.; Dennis, T. J. S.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, *353*, 147.

(108) Choi, C. H.; Kertesz, M.; Mihaly, L. *J. Phys. Chem. A* **2000**, *104*, 102.

(109) Schettino, V.; Pagliai, M.; Ciabini, L.; Cardini, G. *J. Phys. Chem. A* **2001**, *105*, 11192.

(110) Ceulemans, A.; Titeca, B. C.; Chibotaru, L. F.; Vos, I.; Fowler, P. W. *J. Phys. Chem. A* **2001**, *105*, 8284.

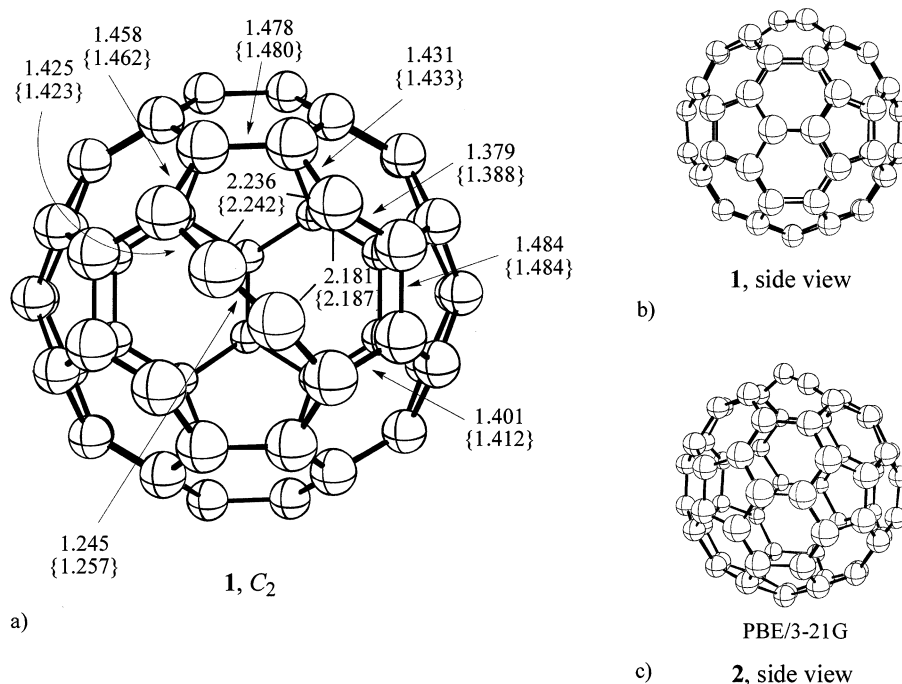
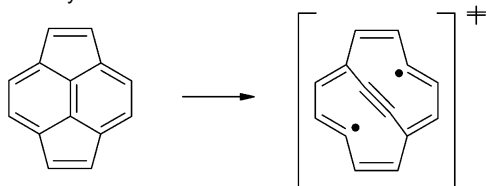


Figure 2. (a) Structure of the C_2 symmetry transition state **1** for concerted Stone–Wales transformation in buckminsterfullerene. Bond lengths were obtained at the B3LYP/6-31G* and PBE/6-31G* (in curly brackets) levels of theory and are given in Å. (b) Side view of **1**. (c) Side view of the transition state **2** obtained at the PBE/3-21G level of theory. Note that **2** converges to **1** upon geometry optimization at the PBE/6-31G* level of theory.

Scheme 3. The Transition State for Concerted Rotation of a C_2 Unit Is Formally a Diradical



0.02–0.03 eV, and hence consideration of these quantum effects changes the relative stability only marginally (Table 1). In Figure 1, the C–C bond lengths in and close to the SW defect are given; B3LYP/6-31G* data are used in the following discussion. The [5,5] bond, 1.474 Å, is significantly longer than the [6,6] bond (1.395 Å, given in Table 3) in BF. The length of the rotated C–C bond, on the other hand, is decreased to 1.353 Å, making it very similar in length to a regular carbon–carbon double bond (e.g., the C–C bond in ethylene is 1.330 Å).

C. Concerted Reaction to $C_{60}-C_{2v}$. The search for a transition state of the concerted SW transformation, a dyotropic rearrangement according to Retz,^{76,77} resulted in the C_2 symmetric structure **1** depicted in Figure 2. The rotating C_2 unit remains very close to the fullerene surface, in agreement with previous computational results.^{12,13,66} The distance between the migrating carbon atoms is reduced from 1.40 Å in BF to 1.25–1.26 Å in **1**. A similar value, 1.24 Å, was obtained for this transition state by Heggie et al. using the LSD approximation.⁶⁷ This bond length is close to the one found in alkynes (e.g., the C–C distance is 1.205 Å in acetylene at B3LYP/6-31G*), and hence the bond can be characterized as a stretched triple bond. Considering the Lewis structure given in Scheme 3, we found that the transition state for the concerted SW transformation formally is a diradical.

We therefore briefly have a look at the orbitals of this system, focusing on the interaction of the “in-plane” orbitals of the

transition structure and neglecting its radial π orbitals. The orbitals accommodating the two radical electrons may be combined in bonding and antibonding fashion, giving rise to orbitals transforming according to the a and b irreducible representations of the C_2 point group, respectively. If there were no interaction between the radical centers, both orbitals would be the degenerate frontier orbitals (I and II, left-hand side of Scheme 4). However, as the b symmetry orbital I is of the same symmetry as the in-plane π bonding MO (III) of the triple bond, these two orbitals can interact, giving rise to bonding and antibonding combinations (V and VI, center MOs in Scheme 4). Analysis of the computed MOs shows that orbital V corresponds to number 149 in the PBE/6-31G* description of **1**, while VI is a virtual orbital (#188).

To a first approximation, the a symmetry MOs (II and IV) are not affected, and thus their orbital energies do not change. MO II turns out to be the highest occupied molecular orbital (HOMO, #180) of **1**, while IV is a virtual orbital (#187). Consequently, the near-degeneracy situation hinted to on the left side of Scheme 3 is avoided by a through-space interaction with the in-plane MOs of the triple bond. Because of its nonbonding character, the HOMO in **1** is high-lying. Consequently, the gap to the LUMO, a radial π^* orbital, is small (0.58 eV at PBE/6-31G*; cf. 1.67 in BF). Accordingly, the lowest energy triplet state (3B) of **1** is only 15.5 kcal mol⁻¹ higher in energy (PBE/6-31G*). We find that the spin-unrestricted B3LYP solution breaks the singlet spin symmetry for **1**, while this is not the case for the PBE functional.¹¹¹ However, the energy thus gained is less than 0.01 kcal mol⁻¹. We note in passing that the small HOMO–LUMO gap of **1** should be kept in mind for possible future wave function studies as this might negatively

(111) Cremer, D. *Mol. Phys.* **2001**, *99*, 1899.

(112) Häser, M.; Almlöf, J.; Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *181*, 497.

(113) Wang, K.-A.; Rao, A. M.; Eklund, P. C.; Dresselhaus, M. S.; Dresselhaus, G. *Phys. Rev. B* **1993**, *48*, 11375.

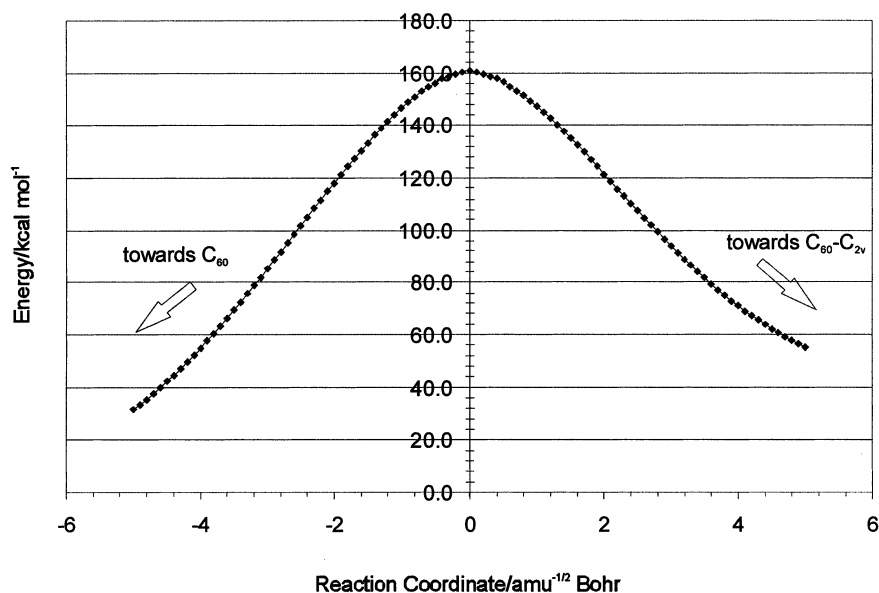
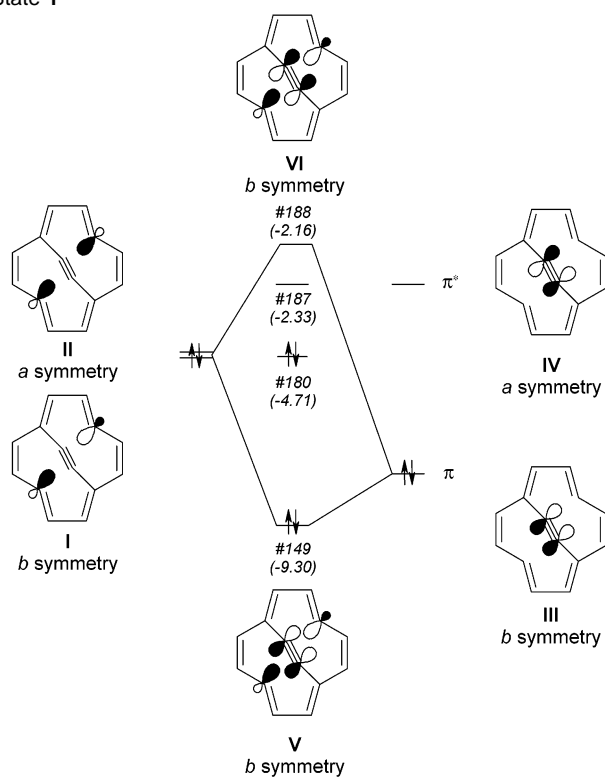


Figure 3. Plot of the intrinsic reaction coordinate (in $\text{amu}^{-1/2}$ Bohr) versus energy (in kcal mol^{-1} , relative to C_{60} buckminsterfullerene) starting from transition state **2** as computed at the PBE/3-21G level of theory.

Scheme 4. Schematic Representation (Not Drawn to Scale) of "In-Plane" Molecular Orbitals and Their Interactions in Transition State **1**^a



^a The MO numbers and their energies (in eV, in parentheses) as computed at the PBE/6-31G* level of theory are given in italics.

influence the reliability of the commonly used single determinant approximations.

Structure **1** is a first-order stationary point, that is, a true transition state, at the UB3LYP/3-21G level of theory with an imaginary harmonic vibrational frequency of $944i \text{ cm}^{-1}$ (transforming according to the A irreducible representation). Increasing the basis set to 6-31G* in the geometry optimization did not change the structure qualitatively using the B3LYP functional.

However, a qualitatively different PES in the vicinity of **1** was obtained using the PBE functional in conjunction with the 3-21G basis set. Here, **1** turns out to be a second-order stationary point: besides the $1014i \text{ cm}^{-1}$ imaginary mode (transforming according to the A irreducible representation), a second one ($65i \text{ cm}^{-1}$, B symmetry) exists. Following the latter mode in search of a first-order stationary point resulted in asymmetric (C_1 molecular point group) **2** (see Figure 2c), which is a first-order stationary point at PBE/3-21G ($1032i \text{ cm}^{-1}$). However, **2** is only 0.01 eV more stable than **1**, indicative of a very flat potential. In **2**, one of the two migrating carbon atoms is moved away from the C_{60} surface. Such a TS conformation has been considered by Samsonidze et al.⁹ for the SWT in carbon nanotubes and has been termed S_+ by these authors. The intrinsic reaction coordinate (IRC) mapped out in both directions for 50 steps (with a step size of $0.1 \text{ amu}^{-1/2}$ Bohr) away from the TS shows that **2** indeed connects BF and $\text{C}_{60}\text{-C}_{2v}$ without the involvement of any intermediates (Figure 3).

Increasing the basis set for geometry optimization of **2** from 3-21G to 6-31G*, however, changes the structure back to that of **1**. This indicates that **2** does not correspond to a stationary point on the C_{60} PES at the PBE/6-31G* level of theory. We also tried to locate the S_+ transition state **2** at the B3LYP/3-21G level of theory, but these computations also converged to **1** instead. To summarize, we find that the PES for the concerted rearrangement from BF to $\text{C}_{60}\text{-C}_{2v}$ differs qualitatively between PBE/3-21G, on one hand, and B3LYP/3-21G, B3LYP/6-31G*, PBE/6-31G*, on the other.

The barrier for the concerted rearrangement is very high with the B3LYP and PBE density functionals and the largest basis set (Table 5), as values of 7.27 eV ($167.7 \text{ kcal mol}^{-1}$) and 6.91 eV ($159.2 \text{ kcal mol}^{-1}$), respectively, are obtained. These data are in agreement with most previous density functional treatments (see Table 2 and Introduction).^{66,67} We note that the computed barriers do not significantly depend on the size of the basis set employed as the values differ by at most 0.1 eV between 3-21G, 6-31G*, and 6-311G**. Finally, correcting our barriers for ZPVE effects results in 7.06 eV (B3LYP) and 6.72

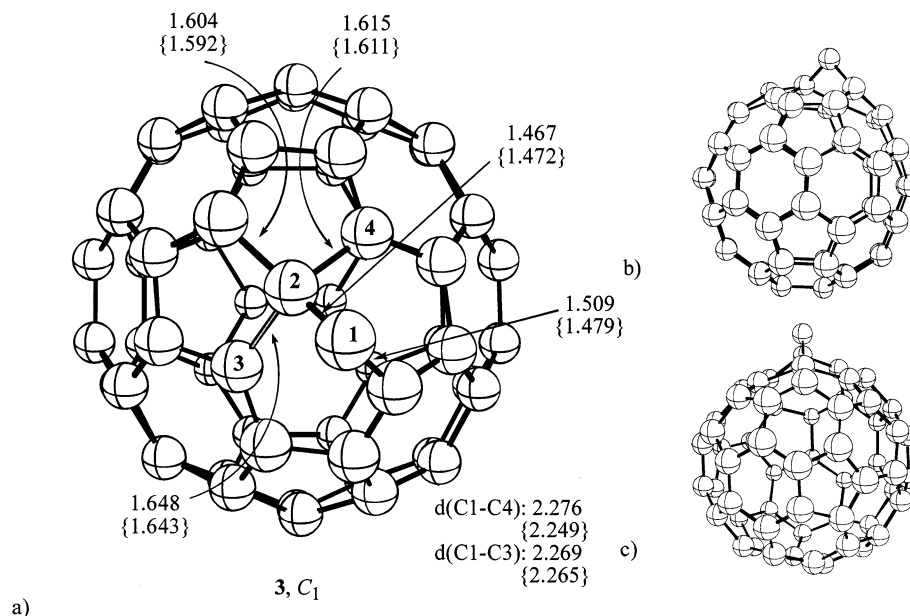


Figure 4. (a) Structure of the asymmetric transition state **3** for Stone–Wales transformation in C_{60} . Bond lengths were obtained at the B3LYP/6-31G* and PBE/6-31G* (in curly brackets) levels of theory and are given in Å. (b and c) Side views of **3**.

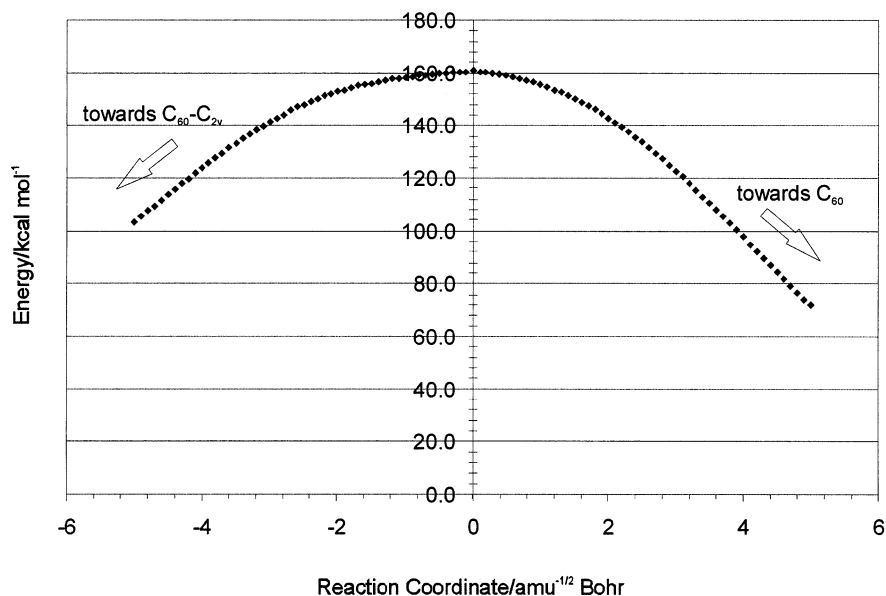
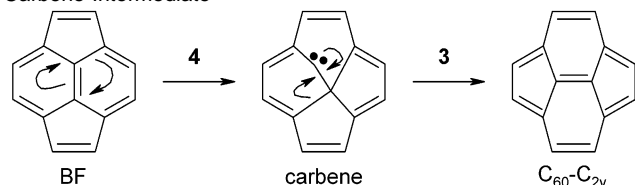


Figure 5. Plot of the intrinsic reaction coordinate (in $\text{amu}^{-1/2} \text{ Bohr}$) versus energy (in kcal mol^{-1} , relative to C_{60} buckminsterfullerene) starting from transition state **3** as computed at the PBE/3-21G level of theory.

Scheme 5. Stepwise Pathway of SW Transformation Involving a Carbene Intermediate



eV (PBE; we have used the ZPVE of **2**, but the difference in ZPVE between **1** and **2** is only -0.01 eV).

D. Stepwise Reaction from Buckminsterfullerene to $C_{60}-C_{2v}$. A stepwise pathway (Scheme 5) through a nonplanar carbene intermediate was discovered in 1993 by Murry et al.^{12,13} using the MNDO semiempirical method and later confirmed by Honda and Osawa⁷⁸ at the AM1 level. The C_{60} potential energy surface is extremely shallow in the vicinity of the carbene

intermediate. The barrier for rearrangement from the carbene to $C_{60}-C_{2v}$ through transition state **3** was found to be $5.9 \text{ kcal mol}^{-1}$ (AM1), while the barrier for formation of BF (via **4**) is as low as $0.01 \text{ kcal mol}^{-1}$.⁷⁸

We could locate one asymmetric transition state **3** (Figure 4) with an imaginary vibrational frequency of $414i \text{ cm}^{-1}$ and $445i \text{ cm}^{-1}$ at B3LYP/3-21G and PBE/3-21G, respectively. The dicoordinated carbon is moved away from the fullerene surface (Figure 4b and 4c), reminiscent of the structures computed previously.^{12,13,78} Structure **3** is characterized by three stretched C–C bonds (ranging between 1.6 and 1.65 Å, B3LYP/6-31G*) between the tetracoordinated carbon atom C2 and the atoms of the fullerene cage. An interesting point to note is that the distances between the dicoordinated carbon atom C1 and the migrating carbon atoms C3 and C4 are very similar (difference is 0.007 and 0.016 Å at B3LYP/6-31G* and PBE/6-31G*,

respectively), hinting to an almost symmetrical bridging arrangement. This differs somewhat from the AM1 geometries computed by Honda and Osawa,⁷⁸ where the dicoordinated C1 is tilted toward C3 or C4 in the corresponding transition states (differences of C1–C3 and C1–C4 distances are 0.206 and 0.170 Å). The HOMO–LUMO gap of **3** is larger than that of **1**, and no singlet spin-symmetry broken solutions were obtained for **3** with the B3LYP and the PBE functionals.

All of our attempts to locate the carbene intermediate and the second transition state (**4**) along the stepwise pathway for SWT turned out to be unsuccessful with the density functionals employed in this study. In view of the very low barrier of 0.01 kcal mol⁻¹ obtained at AM1, this result appears reasonable. We decided to compute the IRC at the PBE/3-21G level of theory to shed light on the PES in the vicinity of **3**. As can be seen from Figure 5, the forward path descends steeply towards BF. The reverse path, on the other hand, does not end at an asymmetric carbene intermediate (this should energetically be very similar to **3**), but passes through a flat area only to descend steeply thereafter. The energy and the geometry of the last points computed on the IRC suggest that at the PBE/3-21G level of theory transition state **3** connects C₆₀ and C₆₀-C_{2v} directly. More rigorous computational techniques are required to strictly rule out the existence of this intermediate, but unfortunately such methods are not feasible for systems as large as C₆₀ at this time. Hence, we tend to consider the DFT results described here to be indicative of a very flat potential energy surface, but note that the existence of the carbene intermediate and a second transition state (**4**) at higher levels of theory cannot strictly be ruled out.

The barrier for this reaction path is computed at the B3LYP/6-311G**//B3LYP/6-31G* level of theory to be 7.27 eV. A slightly lower barrier (6.93 eV) is obtained at the PBE/6-311G**//PBE/6-31G* level of theory. Again we find only little dependence of the barriers on the basis sets employed in the calculations: the 3-21G, 6-31G*, and 6-311G** results lie within 0.05 eV. Correction of these classical barriers by ZPVE results in 7.09 (B3LYP) and 6.76 eV (PBE); see Table 5. Comparing our results with previous investigations (Table 3), we find that an underestimation of barrier heights by empirical and some semiempirical interaction potentials is very likely as has already been suggested by Walsh and Wales.⁴⁹

Conclusions

We have studied the Stone–Wales rearrangement in buckminsterfullerene (BF) to yield the C_{2v} symmetry isomer #1809

and have confirmed earlier studies which identified two different channels for the reaction.^{12,13,78} One of these is the concerted 90° rotation of a C₂ unit with a C₂ symmetry transition state (**1**) in which the two rotating carbon atoms are located close to the fullerene surface. The other transition state (**3**) is asymmetric and has one tetra- and one dicoordinated carbon atom. The latter is significantly moved outward from the fullerene surface and can be considered to resemble a carbene species. The carbene intermediate, found earlier using semiempirical methods to be only 0.01 kcal mol⁻¹ lower in energy than the TS for rearrangement to BF,⁷⁸ could not be found with the density functionals employed here, but its existence cannot be ruled out. Our investigations of the two pathways using intrinsic reaction coordinate computations hint to concerted processes and do not support the involvement of multiple intermediates along the SW transformation pathway, as put forward by Marcos et al.⁷¹ based on constraint geometry optimizations. The two channels are found to have nearly identical energy requirements, 7.0 eV (at PBE) or 7.3 eV (at B3LYP). Hence, we conclude that there is energetically hardly any preference of one reaction path over the other.

The computations performed here are the most rigorous ones among those reported to date for Stone–Wales transformation in BF and hence can be considered to give the most reliable estimate of the barrier heights. The results are in agreement with previous density functional investigations (ranging from 6.2 to 7.0 eV)^{66,67} as well as with the semiempirical AM1 data.⁷⁸ On the other hand, empirical schemes, for example, the Tersoff–Brenner potentials,^{10,11,72} as well as density functional based tight-binding (DF-TB), underestimate these barrier heights (as mentioned already by Walsh and Wales⁴⁹). We thus suggest that for the study of the Stone–Wales transformation in carbon nanotubes such schemes should only be employed with some caution.

Acknowledgment. The authors greatly appreciate very helpful comments on the manuscript by Professor E. Osawa. H.F.B. thanks the Fond der chemischen Industrie for a Liebig Fellowship and Professor Sander for encouragement. This work was in part supported by the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number EEC-0118007, NSF-CHE9982156, and the Welch Foundation.

JA0288744