

## Radical-Promoted Stone–Wales Rearrangements

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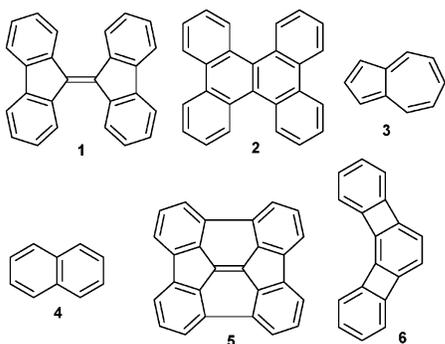
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**Abstract:** The mechanism of the known Stone–Wales rearrangement of bifluorenylidene to dibenzo[*g,p*]chrysene is assessed with the aid of B3LYP/6-31G(d) density functional calculations, and it is shown that a radical-promoted mechanism involving a sequence of homoallyl–cyclopropylcarbinyl rearrangement steps gives a realistic activation energy and can explain experimental observations, whereas a unimolecular mechanism has an improbably high activation energy. Radical-promoted mechanisms are then applied to the hypothetical Stone–Wales rearrangements of diindeno[1,2,3,4-*defg*;1',2',3',4'-*mno*]chrysene and C<sub>60</sub> itself. Severe steric constraints in these cases raise the activation energy for the radical-promoted pathways substantially, but they are still strongly preferred to uncatalyzed, unimolecular pathways

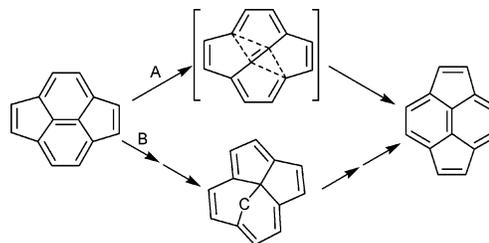
In 1986, Stone and Wales<sup>1</sup> used the bond switch process illustrated in Scheme 1 as a graph–theoretical device to generate a library of possible isomeric fullerene structural formulas.

Stone and Wales never proposed that this bond-switch might actually occur as a real rearrangement, but we reported an example of 90° rotation of a C<sub>2</sub> unit in the rearrangement of bifluorenylidene **1** to dibenzo[*g,p*]chrysene **2** more than 25 years ago.<sup>2</sup> This process occurred at temperatures as low as 400 °C and was accelerated in the presence of decomposing iodomethane, a convenient source of methyl radicals at that temperature. We proposed a radical-promoted mechanism that consists of a sequence of homoallyl–cyclopropylcarbinyl rearrangement steps. We also showed during the 1970s that the rearrangement of azulene **3** to naphthalene **4** (not a Stone–



Wales process but an example of conversion of one aromatic compound to another) was also strongly promoted by radicals and that product distributions in many cases could be accounted for by two mechanisms, the methylene walk and spiran pathways, both involving sequences of homoallyl–cyclopropylcarbinyl rearrangement steps.<sup>3–5</sup> We have recently revisited

**Scheme 1.** Pyracyclene or Stone–Wales Rearrangement



this rearrangement using B3LYP/6-31G(d) density functional calculations and have shown that all labeling studies can be reconciled using these two pathways.<sup>6</sup>

The facile radical-promoted rearrangement of **1** to **2** raises the possibility of the operation of related radical-promoted mechanisms for Stone–Wales rearrangements in fullerenes. In this contribution, we apply B3LYP/6-31G(d) methods to (a) the radical-promoted conversion of **1** to **2**, (b) the degenerate rearrangement of diindeno[1,2,3,4-*defg*;1',2',3',4'-*mno*]chrysene **5**, the smallest possible alkene-centered C<sub>60</sub> substructure with a curved  $\pi$ -system,<sup>7</sup> and (c) C<sub>60</sub> itself. Comparison of these cases permits us to evaluate the energetic consequences of the extra constraints in typical fullerenes. Although these constraints raise activation energies substantially, we will argue that radical-promoted mechanisms are intrinsically more efficient than unimolecular mechanisms for Stone–Wales rearrangements and should be given serious consideration in fullerene chemistry.

### Computational Methods

All calculations were performed with the Jaguar program package,<sup>8</sup> using Becke's three-parameter exchange functional<sup>9</sup> with the correlation

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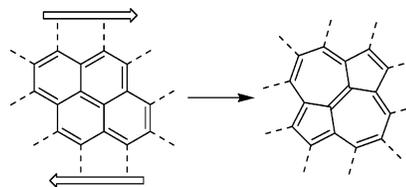
functional of Lee, Yang, and Parr (B3LYP).<sup>10</sup> All species were characterized by full geometry optimization with the standard 6-31G(d) basis set. In previous work on related rearrangements,<sup>6</sup> comparison to calculations with larger basis sets, other functionals, and MP2 suggested that this level of theory should give good results. Except for the large fullerene system, all stationary points were characterized by analytical frequency calculations. For singlet species, restricted DFT methods were used (unlike in our previous work on the azulene-to-naphthalene rearrangement, none of the singlet structures considered are strongly diradical in nature, so we did not need to consider any open-shell singlet solutions), while unrestricted methods were used for all radicals. Energies shown on the figures and schemes are derived from the B3LYP/6-31G(d) electronic energies by correction for zero-point energy (except for the C<sub>60</sub> system where no such correction was applied). Total energies and optimized geometries are given in the Supporting Information.

## Results and Discussion

There has been extensive discussion of Stone–Wales maps,<sup>11,12</sup> and of their relevance to the actual mechanism of fullerene formation.<sup>13,14</sup> On the other hand, two studies put limits on the occurrence of Stone–Wales rearrangements in well-defined aromatic hydrocarbons and fullerenes. Optically active C<sub>84</sub> is configurationally stable under conditions approaching its limit of thermal stability (600–700 °C). Given the potential racemization of D<sub>2</sub> C<sub>84</sub> by two consecutive Stone–Wales transformations, this sets a limit for the activation energy of the Stone–Wales transformation of >347 kJ mol<sup>-1</sup>.<sup>15</sup> Scott<sup>16</sup> has shown that flash vacuum pyrolysis at 1100 °C of 1,5-diethylnaphthalene labeled at all the acetylene carbons yields pyracyclene exclusively labeled in the five-membered rings. If Stone–Wales rearrangement had occurred under these conditions, the label would have appeared in the six-membered rings. Scott points out that pyracyclene may be a poor model for fullerenes as far as Stone–Wales rearrangements are concerned, due to the lack of curvature.

Although no examples of Stone–Wales rearrangements in aromatic hydrocarbons and fullerenes have been recorded, interest in the possibility of their occurrence has remained at a high level. Vollhardt et al.<sup>17</sup> recently invoked Stone–Wales-like steps in the flash vacuum rearrangement of [3]phenylenes such as **6**. It has also been proposed that 90° rotation of a C<sub>2</sub> unit in the regular hexagon lattice of a nanotube wall, Scheme 2, may be involved in distortion of nanotubes under high mechanical stress.<sup>18–20</sup>

**Scheme 2.** Stone–Wales Rearrangement in a Nanotube Wall under Stress

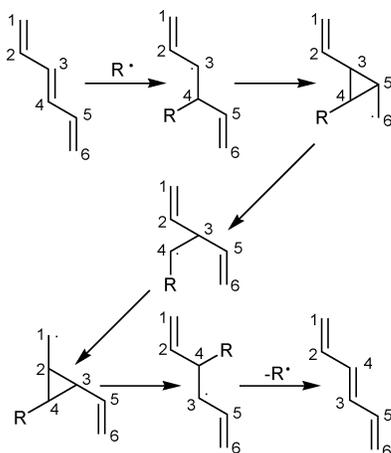


Several potential intramolecular mechanisms for the Stone–Wales rearrangement have been studied computationally. Kumeda and Wales<sup>14</sup> have recently presented geometry optimizations and pathway calculations for all the SW transition states and fullerene minima up to stack five (i.e. five SW transformations away from icosahedral C<sub>60</sub>), while Bettinger et al.<sup>18</sup> have made a careful study of the pathway between icosahedral C<sub>60</sub> and the next-lowest fullerene in SW stack two. These two reports provide an excellent summary of the current understanding of unimolecular mechanisms for the Stone–Wales transformation. A concerted in-plane dyotropic<sup>21</sup> bond switch (route A in Scheme 1) is forbidden by the Woodward–Hoffmann orbital symmetry rules<sup>22</sup> but is predicted to have a similar barrier for the case of C<sub>60</sub> (711 kJ mol<sup>-1</sup> at BLYP/6-31G(d)) to a nonconcerted process via a C(carbene)–C(sp<sup>3</sup>) intermediate (route B in Scheme 1, barrier 706 kJ mol<sup>-1</sup>).<sup>18</sup> These barriers are very high, and rearrangement could only be expected under extreme thermal conditions (>1500 °C). In light of this, it is not surprising that others have considered the possibility of catalysis of Stone–Wales rearrangements. Eggen and co-workers<sup>23</sup> have shown that the presence of a loosely bound single carbon atom can reduce the barrier to Stone–Wales rearrangement to below 400 kJ mol<sup>-1</sup>. In a subsequent report,<sup>24</sup> they discussed this process in more detail and showed how carbon atoms bind preferentially to paired pentagon regions, diffuse easily, and exchange with C<sub>60</sub> host atoms. Osawa and co-workers<sup>25</sup> suggested that these may be subject to “elemental catalysis” (i.e. catalysis by free elements or ions derived from them) but did not discuss the example of rearrangement of **1** to **2**. Using semiempirical (PM3) and DFT (B3LYP/6-31G(d)//PM3) calculations on a model C<sub>34</sub>H<sub>12</sub> bowl-shaped fragment, their calculated barrier came down from 519 kJ mol<sup>-1</sup> uncatalyzed to just 76 kJ mol<sup>-1</sup> for promotion by N<sup>+</sup> (at the B3LYP/6-31G(d) level).

The essence of a Stone–Wales rearrangement is the transposition of two sp<sup>2</sup>-hybridized carbon atoms within a framework of other sp<sup>2</sup>-hybridized atoms. A mechanism for achieving this through radical addition and a sequence of homoallyl–cyclopropylcarbinyl rearrangement steps is shown in Scheme 3 for the simple case of scrambling of C-3 and C-4 of hexatriene. The homoallyl–cyclopropylcarbinyl interconversion is a facile radical rearrangement (intrinsic barrier ≈ 40 kJ mol<sup>-1</sup>) that has been thoroughly studied experimentally and for which absolute rates are known for the parent and other simple examples.<sup>26,27</sup>

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**Scheme 3.** Radical-Promoted Process for Scrambling C-3 and C-4 of Hexatriene

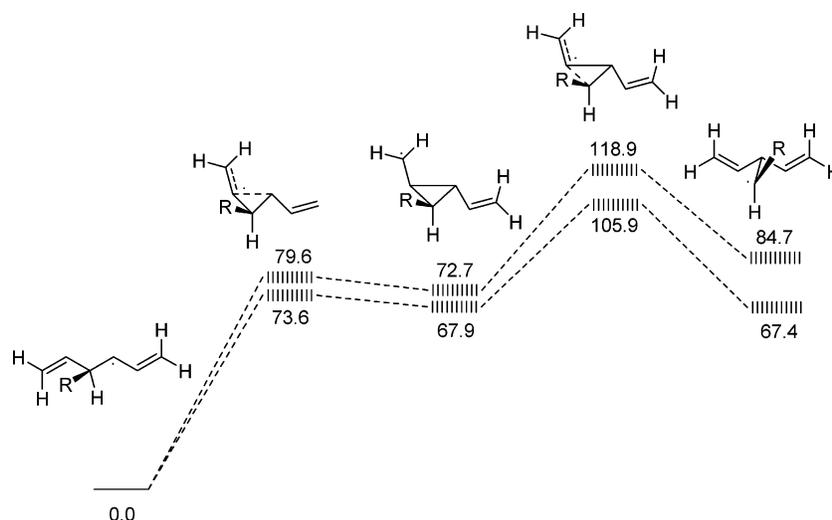
It has also been shown that hybrid DFT methods give a good account of the barriers in these processes;<sup>28</sup> in particular, we obtained good results at the same B3LYP/6-31G(d) level of theory used here in our studies of radical-promoted pathways for the azulene/naphthalene rearrangement.<sup>6</sup>

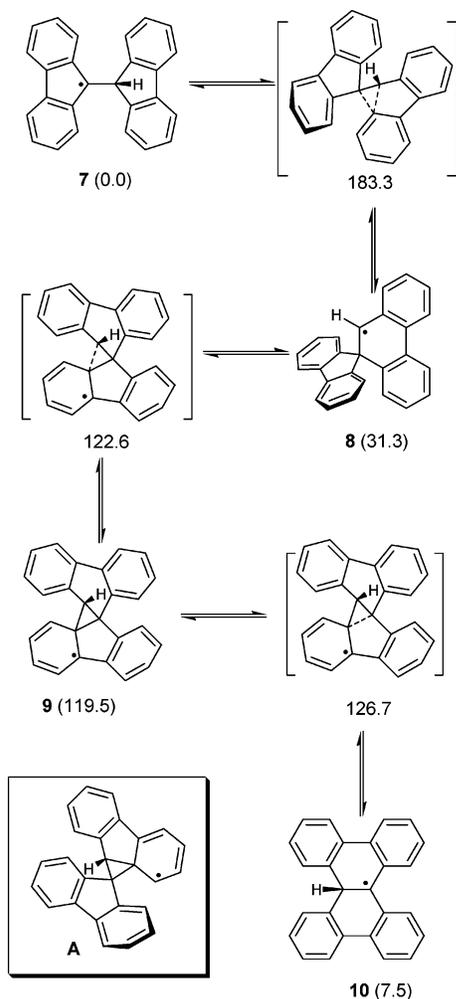
Apart from the radical addition and expulsion steps, there are a maximum of five intermediates and four transition states for the radical rearrangement steps, although in the case of the degenerate process illustrated in Scheme 3, the mechanism is symmetrical about the midpoint. We have investigated this degenerate rearrangement of hexatriene, as promoted by hydrogen atoms and by methyl radicals. The results are illustrated in Figure 1. As might be expected, the nature of the adding radical  $R^\bullet$  only has a major effect on the relative energies of the central intermediate and the transition states leading to it. It is reasonable to expect that the energetic consequences for various promoting radicals in other cases will be proportional to their normal radical-stabilizing properties, and in the remainder of this paper, the added radical will be represented by a hydrogen atom. We have deliberately chosen this case as least favorable to radical-promoted rearrangement and, thus, the most severe test of these processes. Note also that, for several of the species shown in Figure 1, several possible rotamers and/or

diastereoisomers can exist. We have studied all of these computationally but show only the results for what appears to be the lowest-energy pathway.

**The Rearrangement of Bifluorenylidene to Dibenzo[*g,p*]-chrysene.** Dibenzo[*g,p*]chrysene **2** is calculated to be 79.8 kJ mol<sup>-1</sup> more stable than bifluorenylidene **1** at the B3LYP/6-31G(d) level. Our computed pathway, Scheme 4, for the rearrangement is based on the sequence in Scheme 3, but we find that not all the potential intermediates are stable enough to exist. In particular, while the first hypothetical intermediate **A** can be located using semiempirical AM1 or PM3 methods, optimization at the B3LYP/6-31G(d) level always leads back to the initial adduct of a hydrogen atom to bifluorenylidene **7**. We have located a transition state at the B3LYP/6-31G(d) level for the conversion of (hypothetical) **A** to the spiran intermediate **8**, but when this transition state is disturbed slightly in the direction of **A**, it optimizes all the way back to **7**. We are unable to compute an IRC using the Jaguar program, but the repeated observation that attempts to optimize structure **A** at the B3LYP level lead instead to **7** shows that, even if **A** does exist, it can only be a very shallow minimum, with no relevance to reactivity. In view of the strain and loss of aromaticity incurred in its formation, the lack of discrete existence for **A** should occasion little surprise. We encountered similar examples of the nonexistence of intermediates anticipated from a purely stepwise mechanism in our studies of azulene-to-naphthalene rearrangement processes.<sup>6</sup> The remaining steps in Scheme 4 do appear to proceed by discrete ring-closing/ring-opening processes via the lower-energy intermediate **9** to the final radical **10** that is subject to hydrogen atom abstraction to give dibenzo[*g,p*]chrysene **2**.

It is noteworthy that the first “concerted” step is rate-limiting according to the calculations. The energy of this rate-limiting transition state relative to **7** (183.3 kJ mol<sup>-1</sup>) may be compared with the energy difference between bifluorenylidene and the C(carbene)–C(sp<sup>3</sup>) intermediate (effectively a singlet carbene analogue of **8**) in the nonconcerted uncatalyzed process (273 kJ mol<sup>-1</sup>). The energetic benefits of the radical-promoted mechanism are clear. The calculated free energy of activation for this mechanism ( $\Delta G^\ddagger$  169 kJ mol<sup>-1</sup> at 450 °C) leads to a

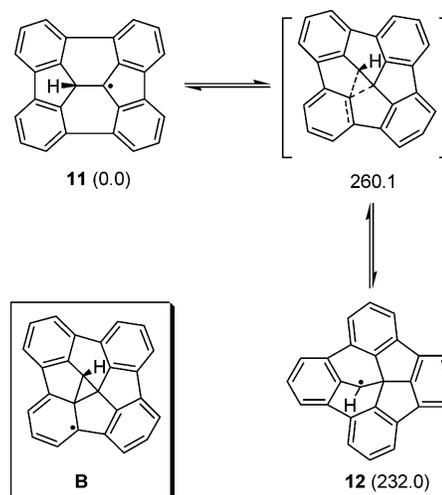
**Figure 1.** B3LYP/6-31G(d) relative energies (in kJ/mol) for the radical-promoted scrambling of C-3 and C-4 in hexatriene. The upper pathway is for  $R = H$ , and the lower for  $R = CH_3$ .

**Scheme 4.** Energies (B3LYP/6-31G(d) in  $\text{kJ mol}^{-1}$ ) Are Reported Relative to the Initial Radical Adduct **7**

predicted half-life of  $7 \times 10^{-2}$  s at that temperature, compared with about 66 h for the uncatalyzed process. Thus, radical-promoted rearrangement at that temperature appears to be entirely plausible. The azulene-to-naphthalene rearrangement proceeds under very similar thermal conditions, and the computed activation energies for the rate-limiting steps of the spiran and methylene walk mechanisms are 164.0 and 182.3  $\text{kJ mol}^{-1}$ , respectively.<sup>6</sup>

It should be noted that we have no experimental evidence concerning the nature of the radical or radicals ( $\text{R}^\bullet$ ) that serve to promote the reaction in the absence of deliberately added radical sources. The nature of  $\text{R}^\bullet$  will mostly affect the energetics of the steps around the spiran intermediate **8**, but since this intermediate already benefits from benzylic stabilization, these effects may be relatively small in this case.

**The Degenerate Rearrangement of Diindeno[1,2,3,4-defg;1',2',3',4'-mnop]chrysene.** Diindeno[1,2,3,4-defg;1',2',3',4'-mnop]chrysene, **5**, has been recently prepared in moderate yield<sup>7</sup> and is the smallest system which shows fullerene-like addition chemistry at the central double bond.<sup>29</sup> Degenerate Stone–Wales

**Scheme 5.** Energies (B3LYP/6-31G(d) in  $\text{kJ mol}^{-1}$ ) Are Reported Relative to the Initial Radical Adduct **11**

rearrangement of **5** can obviously occur by a stepwise mechanism related to Scheme 3, but a number of the intermediates will be significantly more strained than those for the bifluorenylidene-to-dibenzo[*g,p*]chrysene rearrangement. In particular, the central intermediate **12**, corresponding to **8** in Scheme 4, will lack any benzylic stabilization. Nevertheless, our computed mechanism for this case, Scheme 5, is quite similar to Scheme 4 in several respects.

Once again the anticipated first intermediate, **B**, can be located using AM1 or PM3 semiempirical methods but does not appear to exist on the B3LYP/6-31G(d) surface, and there is just one transition state between the initial adduct **11** and the central intermediate **12** (the second part of the rearrangement is, of course, simply the microscopic reverse of that shown). Intermediate **12** lies 200  $\text{kJ mol}^{-1}$  higher in energy relative to initial adduct **11**, when compared with **7** and **8** in Scheme 4 (the structure of **12** is compared with **8** in Figure 2). This difference can be attributed to the loss of benzylic resonance (a contribution of the order of 70  $\text{kJ mol}^{-1}$  is expected<sup>30,31</sup>) and to the extra strain in the  $\sigma$ -framework of **12**. It is worth noting that **12** does not possess  $C_s$  symmetry (Figure 2)—the nonconjugated radical center pyramidalizes toward  $\text{sp}^3$  hybridization. However, the  $C_s$  symmetric structure only lies 6.3  $\text{kJ mol}^{-1}$  higher in energy.

Despite the high energy of intermediate **12**, the calculated overall activation energy for the degenerate rearrangement of diindeno[1,2,3,4-defg;1',2',3',4'-mnop]chrysene (Scheme 5) is only 76.8  $\text{kJ mol}^{-1}$  higher than for the rearrangement of bifluorenylidene to dibenzo[*g,p*]chrysene (Scheme 4). The calculated free energy of activation ( $\Delta G^\ddagger$  249  $\text{kJ mol}^{-1}$ ) leads to a predicted half-life of 0.16 s at 750 °C.

Again, we can compare the energetics of this radical-promoted pathway (activation energy 260.1  $\text{kJ mol}^{-1}$ ) with a unimolecular process via a singlet carbene. In this case the carbene, with  $C_s$  symmetry, is a transition state rather than an intermediate, with an imaginary frequency of  $-250 \text{ cm}^{-1}$  and an energy 483.8  $\text{kJ mol}^{-1}$  higher than the starting hydrocarbon. The energetic advantages of the radical-promoted mechanism are even more striking here than in the bifluorenylidene to dibenzo[*g,p*]-

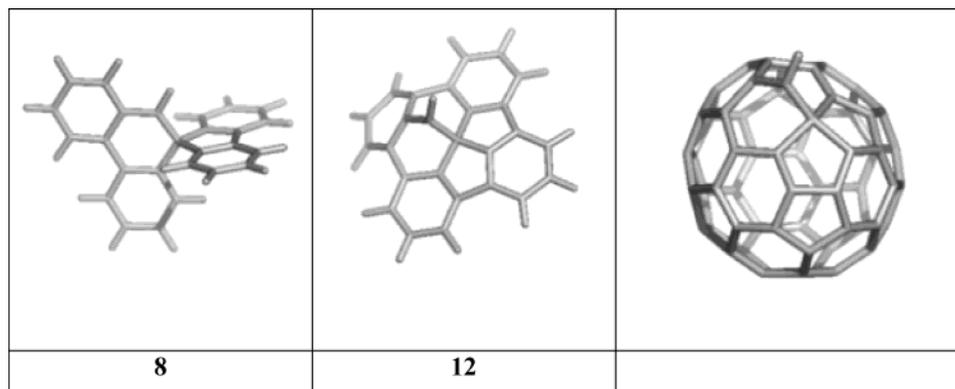
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**Figure 2.** Structures of the central intermediates for the rearrangement of bifluorenylidene, diindeno[1,2,3,4-*defg*;1',2',3',4'-*mnop*]chrysene, and C<sub>60</sub>.

chrysene case. Furthermore, we deliberately chose the least favorable case with hydrogen as our added radical. The lack of conjugation in **12** means that the nature of the added radical R<sup>•</sup> will have a larger effect on the energetics of rearrangement via **12** than via **8** in the bifluorenylidene case.

We also explored the concerted in-plane dyotropic<sup>21</sup> bond switch process (route A in Scheme 1) for diindeno[1,2,3,4-*defg*]chrysene, and found a structure with C<sub>2v</sub> symmetry 804.3 kJ mol<sup>-1</sup> above diindeno[1,2,3,4-*defg*]chrysene, which appeared to be a candidate for the expected transition state. However, this had two imaginary frequencies: -1441 cm<sup>-1</sup>, corresponding to movement along the expected reaction coordinate, and -357 cm<sup>-1</sup>, corresponding to a bend in a perpendicular plane. Further attempts to optimize this to a true transition state simply led back to the singlet carbene transition state mentioned above.

#### Radical-Promoted Stone–Wales Rearrangement of C<sub>60</sub>.

A major difference in the overall energetics of Stone–Wales rearrangement of C<sub>60</sub> and diindeno[1,2,3,4-*defg*;1',2',3',4'-*mnop*]chrysene should be noted at once: the Stone–Wales isomer of C<sub>60</sub> is 185.4 kJ mol<sup>-1</sup> less stable than fullerene itself. However the radical-promoted mechanisms are essentially the same: rearrangement taking a diindeno[1,2,3,4-*defg*;1',2',3',4'-*mnop*]chrysene fragment through the pathway shown in Scheme 5. The central intermediate (see Figure 2), corresponding to **12** in Scheme 5, is 469.3 kJ mol<sup>-1</sup> less stable than the initial radical adduct C<sub>60</sub>H. We can only locate one transition state leading to this from the initial radical adduct (480.5 kJ mol<sup>-1</sup> above C<sub>60</sub>H). There is just one further transition state between the intermediate and the Stone–Wales isomer of C<sub>60</sub> (526.1 kJ mol<sup>-1</sup> above C<sub>60</sub>H and 372.0 above the Stone–Wales isomer of C<sub>60</sub>H). Once again, the activation energy for the rate-limiting transition state of the radical-promoted process is considerably less than that calculated for the corresponding unimolecular reaction (711 kJ mol<sup>-1</sup>) even though we deliberately chose the least favorable example of a promoting radical (hydrogen atom). We are unable to calculate frequencies for this large system and hence cannot compute a free energy of activation ( $\Delta G^\ddagger$ ) in this case; thus, we cannot estimate a half-life directly. However, we observe that for the bifluorenylidene and diindeno[1,2,3,4-*defg*]chrysene cases, the thermal and entropic effects are quite small, so that  $\Delta E^\ddagger$  is very similar to  $\Delta G^\ddagger$ , as expected for unimolecular processes with “ordered” transition states. This is almost certainly true for the C<sub>60</sub>H case also, and on that basis, we suggest that radical-promoted rearrangement of Stone–Wales isomers of C<sub>60</sub> are probably feasible at temperatures of around 1000–1200 °C.

#### Conclusions

As already shown experimentally, formal Stone–Wales rearrangements of unsaturated hydrocarbons such as bifluorenylidene are predicted by computation to occur at fairly low energies. These rearrangements are, however, only favorable in the presence of a radical promoter, such as a hydrogen atom. Sources for the radical promoter can only be guessed, but experience shows that it would be hard to avoid the presence of a variety of carbon-based radicals under the high-temperature conditions necessary for these rearrangements. It is, of course, less clear that radicals would be present during the distortion of nanotubes under high mechanical stress.<sup>18–20</sup>

These reactions proceed, in formal terms, by a series of cyclopropylcarbinyl–homoallyl radical isomerizations, although in some cases the putative cyclopropylcarbinyl radicals are not stable intermediates. Strain and lack of resonance stabilization of the key intermediates makes the barriers to Stone–Wales-like rearrangements of diindeno[1,2,3,4-*defg*]chrysene and C<sub>60</sub> higher than in the rather favorable bifluorenylidene case, but the reaction is still predicted to be feasible at much lower temperatures than the corresponding uncatalyzed process.

Part of the reason for the high activation energy of the radical-promoted Stone–Wales rearrangement of the isomer of C<sub>60</sub> to buckminsterfullerene itself is the relatively unstrained nature of both of these hydrocarbons—the intermediates show significant extra strain. Nevertheless, the computed barrier is compatible with the occurrence of this process under high-temperature thermal conditions, and it is certainly expected that radical-induced processes will compete very effectively with the uncatalyzed reactions, as the latter have even higher energy demands. Rearrangement of other fullerenes, and of carbon nanotubes, is expected to be more facile than that of C<sub>60</sub>, as the effect of strain is expected to be at a maximum in the latter case. Also, catalysis by radicals other than the hydrogen atom should be somewhat more effective, so that the results presented here are a “worst-case scenario”.

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**Supporting Information Available:** Cartesian coordinates, SCF energies, zero-point corrections, and imaginary frequencies for transition states (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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