Energetics of the Stone–Wales Pyracylene Transformation

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Semiempirical and *ab initio* calculations show that the Stone–Wales (pyracylene) rearrangement of the chiral form of the C_{28} fullerene cage has a large activation energy [525 (PM3) or 664 (STO-3G) kJ mol⁻¹] and proceeds *via* a totally asymmetric transition state.

The Stone–Wales (or pyracylene) rearrangement[1] (**1**) has been proposed as a possible mechanism for interconversion between fullerene isomers. It effects pairwise interchange of pentagons and hexagons on the surface of these pseudospherical carbon cages and may be important in determining the experimentally observed distributions of isolated-pentagon isomers of the higher fullerenes.[2] There have been several topological studies of the selection rules and symmetry characteristics of fullerene isomerisation *via* the Stone–Wales transformation.[3–5] Although some estimates of the activation energy for the process have been made using Hückel theory,[5] we are not aware of calculations at a higher level for the energy profile of this potentially important rearrangement. This communication examines the energetics of isomerisation in D_2 C_{28}, which is the smallest fullerene cage to support the transformation.

1   **2**

3   **4**
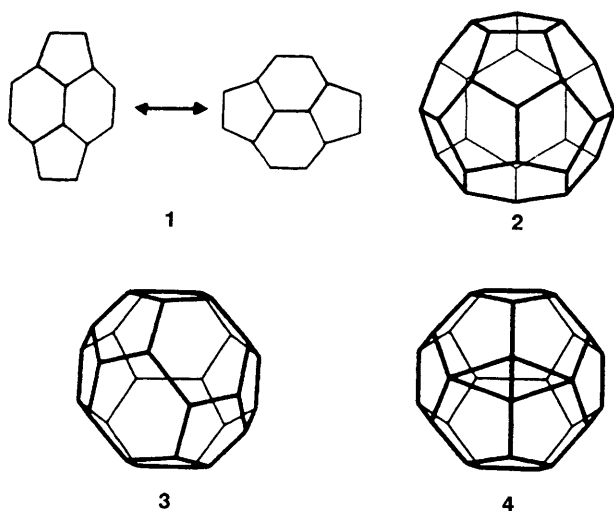
The complete potential energy hypersurface for C_{28} has many features of interest, of which only a few affect directly the present discussion. There are two topologically distinct fullerene cages with 28 vertices. Both have adjacent pentagons, as must all fullerene cages with fewer than 60 atoms, and both clusters are much less stable than C_{60} and C_{70}. One isomer has T_d symmetry, with abutting triples of pentagons and four isolated hexagons (**2**). The other is of D_2 symmetry (and hence chiral) and also has pentagon triples, but the four hexagons occur as two pairs (**3**). *Ab initio* restricted Hartree–Fock calculations[6] indicate that tetrahedral C_{28} is the more stable isomer, and the lowest energy reported so far is for a $^5A_2$ state in which the frontier a_1 and t_2 orbitals (accidentally degenerate in the Hückel
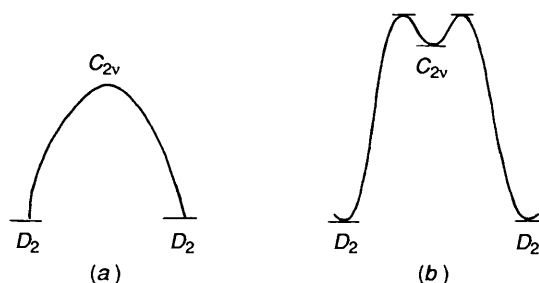
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Fig. 1 Energy profile for racemisation of D_2 C_{28} *via* (*a*) a C_{2v} transition state as predicted by topological Hückel theory, (*b*) a C_{2v} intermediate as predicted at PM3 and STO-3G levels

model) are all singly occupied. There is evidence from mass spectra of laser-ablated graphite that C_{28} is the smallest fullerene to form in significant amounts in dense carbon vapour, and it is suggested that the tetrahedral cage may be further stabilised by external addition of four hydrogen atoms, or by internal trapping of one tetravalent atom. The transformation D_2 C_{28} ⟷ T_d C_{28} is not allowed under mechanism **1** without making and breaking several more bonds and so C_{28} provides the first example both of fullerene isomerism and of a selection rule for isomer interconversion.

Under the Stone–Wales rearrangement D_2 C_{28} simply converts between isoenergetic forms, and a purely topological Hückel model based on a concerted process predicts a C_{2v} transition state[5] (**4**). Using appropriate starting structures, full geometry optimisations (within the respective symmetry constraints) were carried out at both the semiempirical PM3[7] and *ab initio* HF/STO-3G (Hartree–Fock with the STO-3G basis set[8]) levels on **3** and **4**. In the Abelian D_2 point group there is no formal orbital degeneracy and hence C_{28} has a closed shell. The optimisations were performed in Cartesian coordinates[9] using the eigenvector-following (EF) algorithm[10] and all stationary points located were characterised by vibrational analysis. PM3 was used as a quick way of obtaining a general survey of the potential surface and providing reasonable starting guesses for the *ab initio* calculations. The semiempirical surface mimics the *ab initio* surface fairly successfully in this instance, and all special points that were checked were found to be present on both surfaces with similar geometric characteristics.

At both PM3 and STO-3G levels the C_{2v} 'transition state' was in fact found to be a minimum, lying respectively 453 (PM3) and 574 (STO-3G) kJ mol⁻¹ above the D_2 minimum. Examination of the C_{2v} structure **4** shows the presence of two (symmetry-related) carbon atoms—involved in the Stone–Wales transformation—having only two formal C–C single bonds each and large distances (in excess of 2 Å) from all other atoms. Such a conformation is unlikely to be very stable and this immediately suggests a modification to the reaction profile from that given in Fig. 1(*a*) to that shown in Fig. 1(*b*), in which

the 'true' transition state lies very close (geometrically and energetically) to the C_{2v} structure.

A small distortion of the C_{2v} geometry along the direction of the lowest vibrational mode—which has A_2 symmetry—followed by a further transition-state search, resulted in a C_2 structure lying 100 kJ mol⁻¹ above the C_{2v} structure at PM3. However, this turned out to be a third-order saddle point and a further distortion (of B symmetry) to C_1 was required to give the true transition state on this surface, which was found to be 28 kJ mol⁻¹ lower in energy (72 kJ mol⁻¹ above the C_{2v} minimum in this PM3 calculation). The corresponding C_s transition state in STO-3G lies 90 kJ mol⁻¹ above the C_{2v} minimum.

Thus, our calculations indicate a reaction profile for the Stone–Wales rearrangement in D_2 C_{28} as shown in Fig. 1(b), in which two enantiomers of D_2 symmetry are linked to one another via C_1 transition states connected in turn by a metastable C_{2v} minimum. The activation energy is 525 kJ mol⁻¹ at PM3 and 664 kJ mol⁻¹ at the STO-3G level. These figures are close to what might be expected for the loss of one double or two single bonds in the transition state. Whether the C_{2v} structure remains a minimum on the true PES is a moot point, as unstable minima of this type have a habit of disappearing when more advanced levels of theory are applied. It is likely that the STO-3G activation energy is an overestimate: electron correlation is likely to stabilise preferentially the transition state and structures in which several atoms have unsatisfied valencies, and so lower the barrier. The calculations can undoubtedly be improved in accuracy, but they already give the first semiquantitative estimate of the activation energy, and show that it is large, as expected for a formally thermally forbidden reaction.[1,5] Although the Stone–Wales transformation is the only candidate advanced so far for interconversion of large fullerene cages (one author terms it 'the only game in town'[11]), and although the conditions under which fullerenes are formed are violent, isomerisation by this route is unlikely to be facile.

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