Predictions of Spectal Signatures of Fullerenes. Second-order Jahn–Teller Effects on the Structures of C_{44}, C_{56}, C_{68} and C_{92}

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It is argued that pseudo closed-shell fullerenes (those with two electrons in every occupied bonding orbital but with a bonding LUMO in Hückel theory) often fulfil the conditions for second-order Jahn–Teller distortion. Semiempirical (MNDO, AM1 and PM3) calculations on isomers of C_{44}, C_{68} and C_{92} yield optimal structures of C_2 symmetry (C_{44}) and D_2 symmetry (C_{68} and C_{92}), rather than the maximal possible T symmetry while C_{56} and a second C_{92} isomer give structures of S_4 rather than the maximal T_d symmetry. The distortions to lower symmetry are accompanied by a smoothing out of inequalities in atomic charge. Tetrahedral (T_d) C_{84} has a properly closed shell in Hückel theory and shows no loss of symmetry in a semiempirical calculation. Consequences of the distortions for spectroscopic signatures are discussed.

Much can be learned about the systematics of the fullerene series by the use of simple models. Graph theory allows the enumeration of isomers,[1] assignment of point-group symmetry and spectroscopic signature and even the calculation of approximate cage geometry.[2] Purely topological Hückel theory exposes regularities in electronic structure.[3–5] In addition to their aesthetic appeal, such models have practical importance since any attempt at outright prediction of the most stable structure of a fullerene by high-level *ab initio* methods would be thwarted by the huge number of isomers. C_{100}, for example, has over a quarter of a million distinct fullerene topologies[6] of which many will correspond to local minima on the potential-energy hypersurface. In practice, the *ab initio* and semiempirical calculations that have been performed have been forced to deal with small subsets of isomers selected according to some qualitative filtering criterion, *e.g.*, on five isolated-pentagon isomers of C_{78},[7–9] 30 particularly highly symmetric fullerenes[10] or the 24 isolated-pentagon isomers of C_{84}[11–13] derived from the ring-spiral algorithm.[2,14]

In the characterisation of higher fullerenes achieved so far, it has been the qualitative prediction of symmetry and spectral signature that has been most useful to experimentalists. A maximal point-group can be assigned to a fullerene graph and this leads straightforwardly to the numbers of ^{13}C NMR peaks, IR-active and Raman-active normal modes.[2] However, even within the topological model, symmetry and electronic structure are interdependent. The simplest example of this is when a molecule in maximal symmetry is predicted to have a Jahn–Teller-active open shell; distortion to a lower symmetry will take place according to the epikernel principle[15] and a larger number of ^{13}C NMR peaks must be expected for the true equilibrium closed-shell structure. In the present paper, we explore the case where the π configuration for the maximally symmetric molecule is predicted to be a closed shell but with a small HOMO–LUMO gap. Qualitative MO theory then indicates second-order Jahn–Teller distortion to a structure with lower symmetry but a larger band gap.[16–18]

This prediction is checked against semiempirical calculations and found to be correct for the five smallest pseudo closed-shell 'tetrahedral' fullerenes: C_{44}, C_{56}, C_{68} and C_{92} (two isomers), each of which would have orthorhombic equilibrium geometries after such a distortion, and hence a ^{13}C NMR spectrum with more than the small number of peaks expected of a cage with cubic symmetry. In contrast, a closed-shell tetrahedral isomer of C_{84} is shown not to distort. Although the particular isomers studied here are not likely to be the most stable forms of their respective fullerenes, and indeed C_{84} isomers found in experiments are known to have other topologies,[19] the phenomenon of symmetry-breaking illustrated by these cases may be widespread in the fullerene series.

Fullerene Electronic Structure

Fullerenes are geometrically closed-shell trivalent polyhedral cages of n carbon atoms in which 12 of the faces are pentagonal and the remaining $(n/2 - 10)$ are hexagonal. Their electronic structure can be pictured as an electron-precise system of $3n/2$ two-centre, two-electron σ bonds spanning the polyhedral edges and a surface π system containing the remaining n valence electrons. Cages of this sort are possible for all values of $n = 20 + 2k$ $(k \neq 1)$; isomers are possible for all cages with $n \geq 28$ and their numbers grow rapidly[2] with n.

Simple Hückel calculations on a range of fullerenes show three types of π electronic configuration: (*i*) a fullerene may have an open shell in which the HOMO is degenerate and only partly filled; (*ii*) a fullerene may have a properly closed shell in which all bonding orbitals are doubly occupied and all non-bonding orbitals are empty; (*iii*) a fullerene may have a pseudo-closed shell in which all orbitals up to and including the HOMO are filled, but in which the empty LUMO is bonding.[20] No cases are known in which the fullerene HOMO is antibonding at the Hückel level of theory; it seems that the presence of the 12 pentagons makes all fullerenes electron-deficient to some degree.

Open-shell configurations require little comment here. An open-shell cluster will undergo first-order Jahn–Teller distortion if it can thereby reach a non-degenerate electronic state. The icosahedral series C_{20}, C_{80}, C_{140}, . . . have g^2 π configurations and would be expected to distort to T_h or D_{3h} symmetries, opening up a gap between HOMO and LUMO at the equilibrium geometry.

Closed-shell cages occur for specific numbers of carbon atoms and for specific isomers. For fullerenes below 112 atoms a complete list of closed shells is given by the leapfrog and cylinder rules. The leapfrog rule[4] states that there will be one closed-shell isomer at $n = 60 + 6k$ $(k \neq 1)$ for every isomer of the smaller fullerene with $20 + 2k$ $(k \neq 1)$ atoms, and that the symmetry and connectivity of the larger fullerene follow from those of the smaller. Chemical rationalisations and a mathematical proof showing that leapfrogging a fullerene will always lead to a properly closed shell have been given.[21,22] A second and smaller class of closed shells comprise the carbon cylinders[5] C_{70}, C_{100}, C_{130}, . . . derived by longitudinal expansion of I_h C_{60}, and their sixfold-symmetric analogues C_{84}, C_{120}. . . . At each carbon number $n = 70 + 30m$ (all $m \geq 0$) and $84 + 36m$ (all $m \geqslant 0$) a closed π shell with a non-bonding LUMO is predicted for one specific cylindrical isomer. Several 'extra' closed shells outside these series have recently been found in Hückel calculations in cages with large n.[6,23] They have LUMO energies that are bonding by only tiny fractions of the Hückel β parameter and may be 'accidental'. Further discussion of this third series wll be published elsewhere.

Most fullerenes are neither open- nor closed-shell but fall into the pseudo-closed class. All fullerenes with adjacent pentagons are at best pseudo-closed, and the majority of fullerenes with isolated pentagons are pseudo-closed too. Other things being equal, it can be expected that closed-shell fullerenes will have larger band gaps than pseudo-closed cages with the same number of carbon atoms and this expectation is borne out by explicit Hückel calculations on, *e.g.*, the isolated pentagon isomer of C_{84}. When the term pseudo-closed was first introduced,[20] it was argued that such a fullerene would tend to distort from its maximal symmetry so as to maximise the bonding energy of its HOMO and minimise the 'wasted' bonding energy of its LUMO. This is in effect a restatement of several earlier concepts, *e.g.*, Pearson's principle of maximum hardness,[18] and the second-order Jahn–Teller effect.[17]

Put more formally, a structure that has been optimised in a high symmetry will be susceptible to geometric distortion (even if the electronic state is non-degenerate) if there is a non-totally symmetric vibrational coordinate q of symmetry species Γ_q belonging to the product $\Gamma_1 \times \Gamma_2$ where 1 is an occupied orbital (usually the HOMO) and 2 is an empty orbital (usually the LUMO) and if the gap in orbital energies $\varepsilon_2 - \varepsilon_1$ is 'small'. The distorted structure will belong to a sub-group of the original point group, one in which q is totally symmetric and orbitals 1 and 2 are equisymmetric. For a large molecule such as a fullerene there will always be a vibration of any required symmetry and so second-order Jahn–Teller distortion is likely to occur whenever the HOMO and LUMO are of different symmetries and separated by a small band gap. Another possibility is that HOMO and LUMO, although already equisymmetric in the higher group, are split by a distortion leading to further interaction and stabilisation of the HOMO components.

As the majority of the higher fullerene isomers isolated so far are pseudo-closed* and only two† have closed shells, these qualitative arguments are potentially relevant to questions of experimental assignment. Loss of symmetry would change the number of ^{13}C NMR peaks expected for an isomer of given topology. In the cases of C_{76}, C_{78} and C_{84} the computed HOMO–LUMO gaps are comparatively large for the most stable isomers, and these isomers retain their maximal symmetry in semiempirical and *ab initio* calculations.[7–13] Loss of symmetry has been mentioned in reports of calculations on non-optimal isomers of C_{84}[13] and other fullerenes.[10] The present work describes a systematic search for cases where the simplest theory can be checked against explicit calculation; second order Jahn–Teller distortion is found in exactly the cases where Hückel theory leads us to expect it.

Tetrahedral Fullerene Isomers

A complete enumeration of all fullerene isomers with maximal tetrahedral symmetry (T, T_d or T_h) point-group symmetry can be made by a method based on the triangulation of the sphere.[20] A tetrahedral fullerene cage C_n is possible for all vertex numbers n of the form where $i > 0$, $j \geq 0$, $(il - jk) > 0$ and if each cluster is to be counted once only, certain additional conditions must be imposed on i, j, k and l. Eqn. (1) includes icosahedral

$$n = 4[i^2 + ij + j^2 + k^2 + kl + l^2 + 3(il - jk)] \quad (1)$$

fullerenes as special cases since T is a subgroup of I and T_h is a subgroup of I_h. The first few tetrahedral fullerenes are C_{20} (I_h), C_{28} (T_d), C_{40} (T_d), C_{44} (T), C_{52} (T), C_{56} (T_d), C_{60} (I_h), C_{68} (T), C_{68} (T_d), C_{76} (T), C_{76} (T_d), C_{80} (I_h), C_{84} (T_d) and C_{92} (T, T_d and T_h). All clusters with fewer than 256 atoms have been listed.[20] Amongst the early members of this series, C_{60} (I_h) and C_{84} (T_d) have properly closed shells in Hückel theory, C_{44}, C_{56}, C_{68} and C_{92} (T and T_d isomers) have pseudo-closed shells with small HOMO–LUMO gaps and are therefore candidates for distortion, while the others have open shells.

Table 1 summarises the Hückel π electronic configurations of the various tetrahedral fullerenes in maximal symmetry. These configurations are obtained within the simplest version of the Hückel model, one in which all the atoms are assumed to have equal Coulomb integrals (α) and all bonds equal resonance integrals (β). For many tetrahedral fullerenes, with carbon environments varying from pyramidal (at the fusion of three pentagons) to planar (at the fusion of three hexagons) extremes, this assumption is likely to be a poor one. The general description of the symmetries of orbitals at or near the frontier is expected to be preserved in more sophisticated calculations, but the detailed ordering may not be. As a consequence, HOMO and LUMO symmetry labels in parameterised semiempirical calculations may differ from Hückel predictions; several such differences are noted in the following section. It is clear from Table 1 that the isomers with the pseudo-closed shells have the smallest HOMO–LUMO gaps. Idealised tetrahedral structures of C_{44}, C_{56}, C_{68} and C_{92} (T and T_d) are shown in Fig. 1. C_{44} comprises two sets of four equivalent atoms and three sets of 12 equivalent atoms; the ^{13}C NMR spectrum if symmetry is maintained should therefore consist of five lines with intensities in the ratio (3 : 3 : 3 : 1 : 1). Its vibrations span all the irreducible representations of the T group. C_{56} (T_d) has two sets of four atoms, two sets of 12 and one set of 24 equivalent atoms. The idealised ^{13}C NMR spectrum of tetrahedral C_{56} would therefore consist of five lines with relative intensities (6 : 3 : 3 : 1 : 1), and all irreducible representations of T_d are present in its vibrational representation. C_{68}, like C_{44}, belongs to the T group; it consists of two sets of four equivalent atoms and five sets of 12 equivalent atoms giving a ^{13}C NMR spectrum of seven lines with an intensity ratio (3 : 3 : 3 : 3 : 3 : 1 : 1). Likewise, the two pseudo-closed isomers of C_{92} would have idealised ^{13}C NMR spectral signatures, (3 : 3 : 3 : 3 : 3 : 3 : 3 : 1 : 1) and (6 : 6 : 3 : 3 : 3 : 1 : 1) in maximal T and T_d symmetries, respectively.

Semi-empirical Calculations

In order to check the qualitative expectation that fullerenes with small HOMO–LUMO gaps in Hückel theory should exhibit distortion from maximal symmetry, valence electron calculations were performed for C_{44}, C_{56}, C_{68}, C_{84} and the two isomers of C_{92}. As will be described in detail below, the calculations confirm the qualitative prediction. Given the variety of semiempirical Hamiltonian parametrisations used (MNDO, AM1, PM3)[24] and the similarity of the results, it seems unlikely that the broad conclusions would change at a higher level of theory.

C_{44}.—The geometry of the fullerene cage was first optimised in tetrahedral (T) symmetry. At convergence a structure with a

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* C_{76} (D_2), C_{78} (C_{2v}, C_{2v} and D_3), C_{84} (D_2 and D_{2d}).

† C_{60} (I_h) and C_{70} (D_{5h}).

Table 1 Hückel π electronic configurations of tetrahedral fullerenes with pseudo-closed or properly closed shells. *G* is the maximal point group, *Γ* is the representation and ε the energy of an orbital (HOMO or LUMO). *Δ* is the band gap. All energies are in units of $|\beta|$. Parentheses are used to indicate an accidental degeneracy.

	G	π configuration	Γ_{HOMO}	Γ_{LUMO}	$\varepsilon_{\text{HOMO}}$	$\varepsilon_{\text{LUMO}}$	*Δ*
C_{44}	*T*	$a^2t^6t^6e^4t^6a^2t^6(a+e)^6t^6$	*t*	*t*	−0.540	−0.134	0.406
C_{56}	T_d	$a_1^2t_2^6t_2^6e^4a_1^2t_1^6t_2^6(t_1+t_2)^{12}e^4t_2^6a_1^2$	a_1	t_1	−0.414	−0.182	0.232
C_{68}	*T*	$a^2t^6t^6e^4a^2t^6t^6t^6e^4t^6a^2t^6t^6e^4a^2$	*a*	*t*	−0.310	−0.157	0.153
C_{84}	T_d	$a_1^2t_2^6e^4t_2^6t_1^6t_2^6a_1^2t_1^6t_2^6(a_1+e)^6(e+t_2)^{10}t_1^6t_2^6a_2^2t_1^6e^4$	*e*	t_2	−0.572	+0.124	0.696
C_{92}	*T*	$a^2t^6e^4t^6t^6t^6a^2t^6e^4a^2t^6t^6t^6e^4t^6e^4a^2t^6a^2t^6$	*t*	*t*	−0.150	−0.523	0.373
C_{92}	T_d	$a_1^2t_2^6t_2^6e^4a_1^2t_1^6t_2^6t_2^6e^4t_1^6a_1^2e^4t_2^6(t_1+t_2)^{12}t_1^6a_1^2a_2^2t_2^6e^4$	*e*	t_2	−0.449	−0.176	0.272

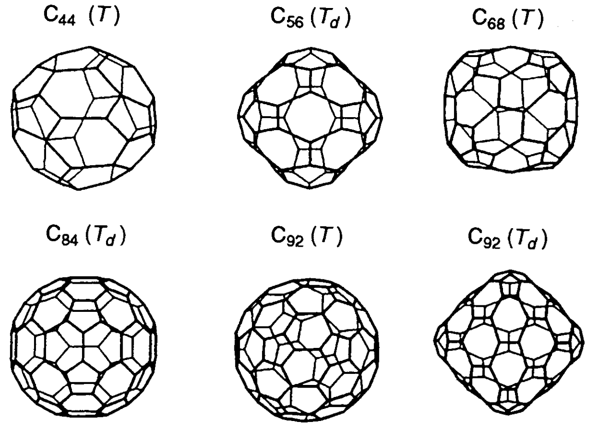

Fig. 1 Fullerene structures with (maximal) tetrahedral symmetry

total energy of 4220 kJ mol^{-1} (MNDO) and a gap of 5.020 eV between the HOMO and the LUMO (both of *t* symmetry) was found. A force constant calculation at this geometry gave a Hessian matrix with three negative eigenvalues corresponding to a triply degenerate imaginary frequency of 1514*i* cm^{-1}. Relaxation of symmetry constraints and reoptimisation in the D_2 sub-group produced a structure with a lower total energy of 4180 kJ mol^{-1} (MNDO) with an almost unaltered HOMO–LUMO gap of 5.016 eV (the barycentres of HOMO and LUMO are both lowered) and a splitting of the HOMO level into $b_1 + b_2 + b_3$ components. The Hessian matrix at this new stationary point is positive-definite with a lowest frequency of 301 cm^{-1}. Similar D_2 structures are minima in the AM1 and PM3 approximations, with energies lower by 17 and 15 kJ mol^{-1} than the respective tetrahedral stationary points. Further exploration of other distortions of the *T* structure led to the discovery of a structure of C_2 symmetry of still lower energy (4154 kJ mol^{-1}, MNDO). Again the structure was a true minimum (Hessian positive-definite, lowest frequency 302 cm^{-1}). The band gap increased to 5.616 eV with both an increase in the energy of the LUMO and a decrease in that of the HOMO.

As HOMO and LUMO are already equisymmetric in the tetrahedral point group, the distortion $T \longrightarrow D_2 \longrightarrow C_2$ is not driven by the classical second-order Jahn–Teller mechanism.[17] However, the loss of symmetry allows the *t* HOMO and LUMO levels to split and the resulting repulsion of components gives a lower HOMO barycentre in the structure of D_2 symmetry even though the band gap itself is hardly changed. The further symmetry reduction to C_2 allows further repulsion between HOMO and LUMO resulting in a significant increase of the band gap.

The net change in shape is small; at the C_2 minimum the structure has moments of inertia ($I/10^{-43}$ kg m^2) 0.553, 0.642 and 0.642 compared with the unique moment of 0.553 in tetrahedral symmetry. Bond lengths that are equal by symmetry in the tetrahedral molecule are split by at most 6% in the C_2 structure.

C_{56}.—Optimisation in full tetrahedral (T_d) symmetry gave a structure for this fullerene with a total energy of 4855 kJ mol^{-1} (MNDO) and a gap of 4.27 eV between the HOMO (*e*) and the LUMO (*t*). Force constant calculations were poorly converged but indicated a Hessian with several negative eigenvalues for the T_d structure. Perturbation of the geometry and complete relaxation of the symmetry constraints gave a structure with what proved to be S_4 symmetry. This was confirmed by repeating the calculation within S_4, D_2 and D_{2d} symmetry constraints; in both D_2 and D_{2d} symmetry the perturbed molecular geometry returned to T_d. In S_4 a structure with a total energy of 4747 kJ mol^{-1} (MNDO) and a band gap of 4.77 eV was found; it was shown to be a potential-energy minimum by calculation of the Hessian at the new optimal structure (lowest vibrational frequency 257 cm^{-1}). Similar results were given by the AM1 and PM3 parametrisations, with respective stabilisations of 92 and 95 kJ mol^{-1} on dropping from T_d to S_4 symmetry. In S_4 both HOMO and LUMO are of symmetry *a*. The unique moment of inertia for the T_d structure (0.880) changes in the S_4 structure to the values 0.894, 0.894 and 0.905 × 10^{-43} kg m^2.

C_{68}.—Optimisation of the C_{68} cage with *T* constraints gave a structure with energy 5212 kJ mol^{-1} (MNDO) and a gap of 3.83 eV between the HOMO (*e*) and LUMO (*t*) levels. The Hessian was not calculated but when the symmetry was relaxed to D_2, the energy fell to 5068 kJ mol^{-1}, the HOMO–LUMO gap widened to 4.90 eV and all degeneracies in orbital energies were lifted. Repeated asymmetrical perturbation of the Cartesian coordinates of the nuclei and reoptimisation without imposition of symmetry constraints regenerated a structure very close to D_2 and never of lower energy. We conclude that the D_2 structure represents a minimum on the potential-energy surface whilst the *T* structure does not. Repeating the calculations using the PM3 method gave essentially the same result: an energy stabilisation of 101 kJ mol^{-1} and an increase in band gap of 0.64 eV. Use of the AM1 Hamiltonian with D_2 constraints regenerated the structure in *T* symmetry. The unique moment of inertia in *T* of 1.318 changes to 1.316, 1.318 and 1.325 × 10^{-43} kg m^2 in D_2.

C_{84}.—Optimisation in T_d symmetry gave an energy of 4371 kJ mol^{-1} and a band gap of 6.22 eV (MNDO) between HOMO and LUMO which are both of symmetry *e*. Several calculations were carried out in Cartesian coordinates without symmetry constraints; no structure of lower energy was found. This closed-shell fullerene shows no tendency to distort to a less than maximal symmetry.

C_{92} (T_d).—For the isomer of T_d symmetry generated from the tessellation algorithm,[19] optimisation with T_d constraints gave a structure with energy 5960 kJ mol^{-1} (MNDO) and a gap of 4.23 eV between the triply degenerate HOMO and LUMO levels. With D_2 constraints a stationary point on the potential-energy surface was found with an energy of 5921 kJ mol^{-1}, with a slightly larger HOMO–LUMO gap of 4.31 eV. However, the application of S_4 constraints resulted in a further lowering of the energy of 5899 kJ mol^{-1} and a widening of the band gap to 4.71 eV. Repeated random perturbations of these three structures, followed by reoptimisation in cartesian coordinates yielded no structure with a lower energy. The PM3 method again gave a corresponding picture with energies T_d: 5614; D_2: 5598; S_4: 5574 kJ mol^{-1} and band gaps $D_2 \approx T_d < S_4$. In T_d the HOMO is of *e* symmetry and the LUMO of t_2 symmetry; in S_4 the HOMO and the LUMO has *e* symmetry. The unique moment of inertia in T_d changes from 2.406 to 2.400, 2.411, 2.411 × 10^{-43} kg m^2 in S_4. Convergence using the AM1 Hamiltonian proved difficult to achieve.

C_{92} (*T*).—This isomer, like the leap-frog C_{84} considered earlier, has isolated pentagonal rings. Unlike the C_{84} fullerene, it has only a pseudo-closed shell in Hückel theory. It is however, *much more stable* than the other pseudo-closed members of the tetrahedral series because of its lack of fused pentagon triples. In maximal symmetry an energy of 4735 kJ mol^{-1} (MNDO) was obtained with a band gap of 4.00 eV between the triply degenerate HOMO and LUMO levels. With D_2 constraints the energy dropped to 4655 kJ mol^{-1} with all degeneracies in orbital energies lifted and the band gap increased to 4.54 eV. Optimisation in randomly perturbed Cartesian coordinates with all constraints lifted failed to find any structure of lower energy. Use of the PM3 Hamiltonian gave a very similar picture: an energy decrease of 89 kJ mol^{-1} and a band gap wider by 0.50 eV. The unique moment of inertia in *T* of 2.408 splits to 2.400, 2.412, 2.421 × 10^{-43} kg m^2 in D_2. Use of the AM1 Hamiltonian was not attempted.

Discussion

The calculations reported in this paper confirm the predictions of qualitative molecular orbital theory. At the semiempirical level, the fullerene cages that Hückel theory picks out as pseudo-closed are unstable in tetrahedral symmetry and distort to structures with lower symmetry. Qualitative theory explains this as a second-order Jahn–Teller effect. The semi-empirical calculations also point to an interesting effect that may drive the distortion: in all isomers the charges on the atoms are reduced when the high symmetry is lost. Fig. 2 shows the components of the HOMO for C_{44} before and after distortion first to D_2 and then to C_2. In the tetrahedral structure charge is concentrated on the apical atoms at the junctions of three pentagons, but on distortion the charge distribution becomes more even. Hückel theory predicts inequalities of charge in these tetrahedral fullerenes and so gives warning of the likely distortion. For example, in C_{44} the π charges vary from 1.135 for the apical atoms common to three pentagonal rings to 0.982 for the atoms at the junctions of three hexagons. In the MNDO calculations on this molecule, the total atomic charges span a range of −0.25 to 0.14 in the *T* structure, and this falls to −0.06 to 0.04 in D_2 and −0.06 to 0.03 in C_2.

A second prediction of qualitative theory is that fullerenes with properly closed shells, since they have larger band gaps, should not distort. In the tetrahedral series the T_d isolated-pentagon isomer of C_{84} is the first with an electronic configuration of this type, and indeed it is found to retain full symmetry in semiempirical and SCF calculations.

The present calculations suggest that a 'small' HOMO–LUMO gap in maximal symmetry may be interpreted as one of *ca.* 5 eV or less in a semiempirical calculation, or $\leq 0.4|\beta|$ in a simple Hückel calculation and a gap of this order may be taken as an indicator of geometric instability. In the two cases where an 'intermediate' structure was discovered, C_{44}, $T \longrightarrow D_2$ and C_{92}, $T_d \longrightarrow D_2$, it may be noted that this structure, although of lower energy, had an almost unchanged HOMO–LUMO band-gap compared with that in high symmetry. In all cases, the structure of lowest energy has a band gap wider by 0.5–0.6 eV than that in the tetrahedral starting point. The geometric changes are not very large in the present cases but the energetic changes *are* significant and could affect predictions of isomer preference. The stabilisations of up to 150 kJ mol^{-1} found here can be compared with the range of 72 kJ mol^{-1} spanning the five isolated-pentagon isomers of C_{78};[7] changes of this order could easily change the predicted isomer preference.

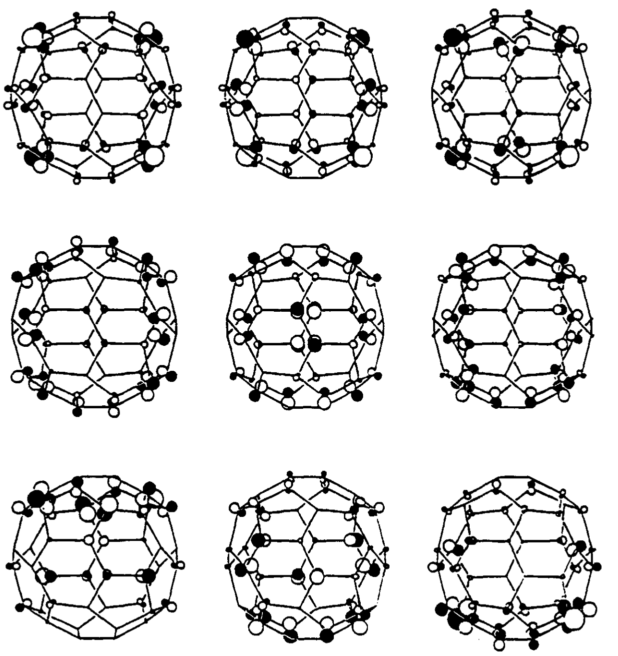

Fig. 2 Frontier orbitals of C_{44}. The rows (top to bottom) depict the three occupied orbitals of highest energy for *T*, D_2 and C_2 structures of C_{44} respectively. In the *T* geometry all three orbitals are degenerate, in D_2 and C_2 structures the orbital binding energy increases left to right. Note that in this particular presentation of the triply degenerate HOMO set in *T* symmetry, the largest coefficients occur on the four 'apical' atoms (those at the centres of the fused pentagon triples) in all three orbitals, and atoms near the middle of the diagram have negligible coefficients. On distortion to D_2, the distribution of the coefficients, and hence of atomic charges, is smoothed out. Less obviously, the distortion $T \longrightarrow C_2$ also smooths out this distribution; an apical atom has a large coefficient in only one of the three frontier orbitals and central atoms have significant coefficients in two. The total atomic charge is computed from a sum of squared coefficients taken over all occupied molecular orbitals.

As noted earlier, reduced symmetry has potential experimental consequences. In C_2 symmetry the particular isomer of C_{44} under discussion would have not five but 22 ^{13}C NMR peaks and vibrational modes spanning the reducible representation 31A + 29B (all IR- and Raman-active). In S_4 symmetry the C_{56} isomer would have 14 rather than nine ^{13}C NMR peaks and 81 IR-active and 122 Raman-active vibrational modes. Likewise C_{68} would give 17 ^{13}C peaks in its more stable D_2 symmetry rather than seven. For C_{92} (*T*) the number of ^{13}C resonances increases from nine to 23; for C_{92} (T_d) from seven to 23.

It is also worth noting that these symmetry changes would probably not be predictable by molecular mechanics calculations. Whether the starting structure in the case of C_{44} has *T*, D_2 or C_2 symmetry, the final structures obtained by such a process are identical. This has obvious implications when carrying out single-point *ab initio* calculations at a geometry obtained by, for example, the MM3 package.[7] Although the

Hamiltonian within a molecular mechanics package includes 'electronic effects' in the broad sense, clearly such calculations are not capable of reproducing effects such as Jahn–Teller distortion that depend upon electronic state.

None of the C_{44}, C_{56}, C_{68} or C_{92} (T_d) isomers considered here is expected to be a particularly stable fullerene, as all have fused triples of contiguous pentagons. However, they share the characteristic of a pseudo-closed-shell electronic structure with many more stable isomers such as C_{92} (T) where the symmetry-breaking effect is also observed. Second-order Jahn–Teller distortion may be the explanation of symmetry-breaking in previous calculations,[10,13] and may be widespread in the fullerene series. The possibility of this deviation from maximal symmetry should be borne in mind when predicting spectral signatures of fullerene isomers and when assigning experimental spectra.

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