

Bond-stretch Isomerism and the Fullerenes

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It is argued that because many fullerene molecular graphs admit multiple totally symmetric Kekulé structures, the fullerene class of molecules may provide examples of bond-stretch isomerism (π -tautomerism). Calculations on the prototype D_2 isomer of C_{28} demonstrate the existence on the potential surface for 28 carbon atoms of at least three enantiomorphic pairs of fullerene minima of this symmetry, all with the same connectivity. The three patterns of long and short bonds in these isomers are 'orthogonal' in that any one CC bond is formally double in precisely one and formally single in precisely two of the structures.

The term 'bond-stretch isomerism' was introduced by Stohrer and Hoffmann¹ to describe cases in which a molecule has two or more stable conformations that are related by simple bond stretching but differ in their electronic configurations. Although the concept is straightforwardly defined, unambiguous experimental examples have proved elusive;² early reports of 'distortional isomers' of molybdenum oxo complexes³ are now thought to refer to mixtures of distinct chemical compounds,⁴ and claims for other bond-stretch pairs are regarded as non-proven.² In the present paper we argue that the new and as yet imperfectly explored class of fullerene molecules may yield examples of a specific form of bond-stretch isomerism. This line of reasoning is supported by calculations that show multiple minima for the D_2 fullerene C_{28} .

The central idea of the present paper can be simply stated. A Kekulé structure for a fullerene corresponds to a distribution of formal single and double bonds that implies a specific set of long and short bond lengths and hence an idealised geometric structure for the cage. If the Kekulé structure is totally symmetric, then that idealised geometry is compatible with the point group symmetry (deducible from the molecular graph⁵) and is a consistent guess for the molecular geometry. Our proposal is that any totally symmetric Kekulé structure could therefore conceivably correspond to a minimum on the potential surface and if two or more such Kekulé structures do in fact correspond to minima, then they should be examples of bond-stretch isomers (perhaps ' π -tautomers' would be a better term), because they would differ in idealised geometry and could differ in electronic configuration. Before exhibiting an explicit example where this prediction turns out to be true, at least at a semiempirical level, we summarise in the following sections the qualitative theory of fullerenes and show how symmetry factors influence the number of possible totally symmetric Kekulé structures.

Theoretical Background

A fullerene is a molecule in the form of a geometrically closed polyhedral cage C_n consisting of n carbon atoms arranged in 12 pentagonal and $(n/2 - 10)$ hexagonal rings. Each atom is connected to three neighbours by σ bonds, and participates in a surface π system to which it contributes one electron and a single radially directed valence orbital (a p or sp^x hybrid).⁶

The qualitative features of the electronic structure can be described by pictorial molecular orbital theory. Although all fullerenes are by definition geometrically closed, only a fraction of them have properly closed-shell electronic configurations.

Electronic closed shells are found⁵ for the well defined geometric structures that belong to the leapfrog⁷ and cylinder⁸ series and so occur at certain 'magic numbers' of carbon atoms [$60 + 6k$ ($k \neq 1$) for leapfrogs, $70 + 30k$ (all k) and $84 + 36k$ (all k) for cylinders]. C_{60} is the first leapfrog fullerene. Some properly closed-shell configurations exist outside these series for large numbers of atoms.

A localised valence bond picture based on Kekulé can also be used.⁹⁻¹¹ Fullerenes generally have many Kekulé structures (KS); icosahedral C_{60} has 12 500, for example.¹² However, the electronic structure of a given fullerene may be dominated by a relatively small number of these. It has been argued, for instance, that C_{60} is not aromatic in any traditional sense, and that its physical and chemical properties are compatible with the dominance of just one KS, the only one of the 12 500 to have the full I_h symmetry of the nuclear framework.¹³ C_{60} is therefore quite unlike an aromatic compound in which the wavefunction would typically consist of a mixture of several KSs, each with less than full symmetry (e.g. in benzene the D_{6h} ground-state wavefunction combines two D_{3h} KSs). If it turns out that other fullerenes also have more localised structures than at first expected, then the argument of this paper is that the prospects for finding bond-stretch isomerism in this class of molecules are good.

There is one class of fullerenes for which a totally symmetric Kekulé structure can always be found. A leapfrog cluster C_n is notionally derived by omnicaapping and dualising a smaller fullerene with one third the number of atoms;⁷ since fullerene isomers exist for $n = 20 + 2k$ ($k \neq 1$), leapfrogs exist for $n = 60 + 6k$ ($k \neq 1$). All leapfrogs have properly closed electronic shells,⁷ but more importantly for the present discussion all have at least one totally symmetric KS.¹¹ One third of the edges of a leapfrog fullerene correspond to 90° rotations of edges of the parent. Placing a double bond along each of these special edges gives a localised valence-bond structure with full molecular symmetry incorporating the greatest possible number ($n/3$) of benzenoid hexagons.¹¹ Additional totally symmetric KS may exist for a leapfrog isomer (Fig. 1).

Totally symmetric Kekulé structures are possible in many other cases. Any fullerene has at least three KS, because a fullerene is a trivalent polyhedral cage.¹⁴ The structures are mutually orthogonal in that each edge appears as a double bond in one and only one of the three. If the fullerene happens to have C_1 point group symmetry, then trivially all of its Kekulé structures are totally symmetric. As most fullerene isomers are in fact of C_1 symmetry,¹⁵ most fullerenes have at least three totally symmetric KS.

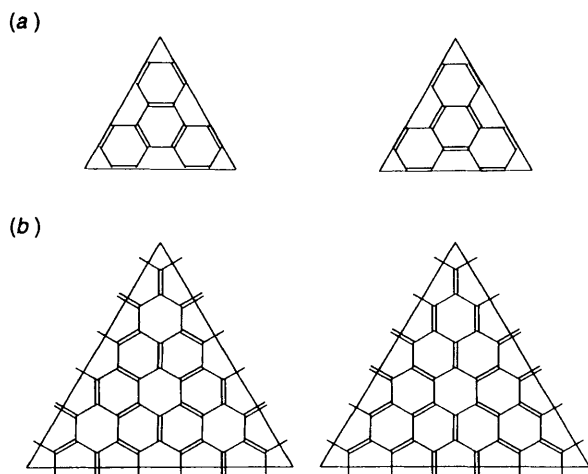


Fig. 1 Non-uniqueness of totally symmetric Kekulé structures. The benzenoid hexagons of the canonical totally symmetric KS of a leapfrog fullerene (see ref. 11 for a construction) are Clar sextets. Simultaneous exchange of single and double bonds in all members of an orbit of such hexagons may lead to a new totally symmetric KS. Examples where this happens in the icosahedral fullerenes are (a) C_{240} and (b) C_{720} . In each case the pattern is repeated on the 20 faces of an icosahedron to make the full cage, and the three corners of the master triangle are then pentagon centres in the full cage.

Symmetry Arguments

Some general group-theoretical criteria for the existence of totally symmetric KS can be stated. The basic concept needed is that of an orbit—a set of equivalent points or objects permuted amongst themselves by the operations of the point group. Members of an orbit share a characteristic site symmetry related to that of the molecule as a whole by (No. of points in orbit) \times (order of site symmetry group) = (order of full point group).¹⁶ If the molecule decorated with a particular KS is to remain totally symmetric, then that KS must treat all members of an orbit in the same way, *i.e.* all equivalent atoms, edges or faces must remain equivalent in the KS.

The atoms of a fullerene lie at sites of C_{3v} , C_3 , C_s or C_1 symmetry.⁵ If any atoms are in sites of C_{3v} or C_3 symmetry (*i.e.* if they lie on a C_3 axis), then a totally symmetric KS is impossible, because one of the three equivalent bonds linked to such an atom must be double and two must be single. A corollary is that no open-shell icosahedral fullerene (of I or I_h symmetry) can have a totally symmetric KS, since all such fullerenes have 20 atoms lying on C_3 axes; all other icosahedral fullerenes have no atom on a C_3 axis and are leapfrogs of the open-shell series,¹⁷ each with at least one totally symmetric KS. Again, orbit counting shows that although all fullerenes C_n of tetrahedral symmetry (T_h , T_d or T) consist of multiples of four atoms, only those where n is a multiple of 12 can have a totally symmetric KS; those with $n = 12k + 4$ or $12k + 8$ atoms have four and eight atoms on C_3 axes, respectively. Similarly, fullerenes of D_{3d} , D_{3h} or D_3 symmetry can have totally symmetric KS only if they have $6k$ and not $6k + 2$ atoms, and fullerenes of C_{3v} , C_{3h} or C_3 symmetry must have $3k$ atoms to have a totally symmetric KS. Leapfrogging preserves molecular symmetry but replaces atoms on C_3 axes by hexagons centred on the axis and multiplies the atom count by a factor of three, and so for all these groups produces a cage that satisfies the conditions for a totally symmetric KS. The existence of a totally symmetric KS for any leapfrog¹¹ is therefore understandable.

If an atom lies at a site of C_s symmetry (*i.e.* if it lies in a mirror plane but not on a C_3 axis) then its double bond is fixed in the totally symmetric KS and must lie in the local mirror plane. C_1 site symmetry for an atom places no limitation on the KS.

An edge of a fullerene can occupy a site of C_{2v} , C_s , C_2 or C_1 symmetry;⁵ an edge in a C_{2v} site must be a formal double bond in any totally symmetric KS that may exist, an edge in a C_s site must be double if wholly in the mirror plane, but may be single or double if perpendicular to the plane. In a totally symmetric KS any orbit of edges, of whatever site symmetry, in which members share common atoms is automatically made up of single bonds, and any two orbits of edges whose members share atoms are mutually exclusive in the double-bond list.

The edge orbits also determine the π electronic configuration corresponding to a totally symmetric KS, as follows. If a fullerene C_n belonging to a point group G of order $|G|$ has e_{2v} , e_2 , e_s and e_1 orbits of edges with C_{2v} , C_2 , C_s and C_1 site symmetry, respectively, then summation of edges gives eqn. (1),

$$|G| \left(\frac{e_{2v}}{4} + \frac{e_2}{2} + \frac{e_s}{2} + e_1 \right) = \frac{3n}{2} \quad (1)$$

and if d_{2v} , d_2 , d_s and d_1 are the numbers of orbits of double bonds, summation gives eqn. (2), where $d_{2v} = e_{2v}$. Now, any

$$|G| \left(\frac{d_{2v}}{4} + \frac{d_2}{2} + \frac{d_s}{2} + d_1 \right) = \frac{n}{2} \quad (2)$$

orbit has a permutation representation Γ_σ within the point group of the molecule and so the total reducible representation of the formal double bonds (*i.e.* the symmetries spanned by the doubly occupied π orbitals) in a particular totally symmetric KS is found by summing the Γ_σ for all $d_{2v} + d_2 + d_s + d_1$ edge orbits, taking into account the fact that distinct orbits with the same site symmetry but different Γ_σ values are possible in some groups.¹⁶ The total electronic configuration can be found by adding the reducible representations spanned by the $3n/2$ edge-precise single bonds and n $1s^2$ carbon cores. In every case, a given totally symmetric KS generates an electronic configuration with well defined occupation numbers in each symmetry. Different KSs may correspond to the same set of occupation numbers, as for example in C_1 fullerenes, where all KS are symmetric and all have the trivial π configuration $1a^2 \dots (n/2)a^2$.

This simple model is a way of supplying a reasonable guess for the electronic configuration if the geometric structure corresponds closely to that implied by a single totally symmetric KS. For example, the orbit of 30 equivalent double bonds in the unique totally symmetric KS of icosahedral C_{60} has a permutation representation shown in eqn. (3), implying precisely the π configuration found in molecular

$$\Gamma_\sigma = A_g + G_g + 2H_g + T_{1u} + T_{2u} + G_u + H_u \quad (3)$$

orbital calculations on this molecule.

When there is no totally symmetric KS the configuration is less easy to guess, as it must be a superposition of several resonance structures, and even when one or several totally symmetric KSs exist it is always possible that the ground-state electron configuration will be a superposition. An example of the latter case is C_{70} for which there are two totally symmetric KS, but the optimal structure predicted by an SCF calculation has benzenoid rings around its equator and a configuration that is an equal combination of two non-totally symmetric KS.¹⁸

Finally, the faces of a fullerene have site symmetries C_{5v} , C_5 , C_s or C_1 (pentagons) or C_{6v} , C_6 , C_{3v} , C_3 , C_{2v} , C_2 , C_s or C_1 (hexagons).⁵ Axes of high order (C_5 or C_6) passing through a face force all bonds within the ring to be single and bonds *exo* to the ring to be double in a totally symmetric KS. Local mirror planes passing through ring vertices also fix double bonds.

Explicit construction of all possible Kekulé structures

Table 1 Totally symmetric Kekulé structures of fullerene isomers C_n (n from 20–40). N_s is the number of totally symmetric and N_t is the total number of Kekulé structures. Each isomer is listed in canonical order as a ring spiral¹⁹ and assigned to its point group G as described in ref. 5. For chiral point groups the spiral represents a pair of enantiomers each with N_s totally symmetric and N_t general KS

n	Isomer	G	N_s	N_t	n	Isomer	G	N_s	N_t
20	5555555555	I_h	0	36	38	555656566656655655	C_{2v}	2	360
24	555556555555	D_{6d}	1	54	38	555656665565565555	C_2	16	386
26	555556565555	D_{3h}	0	63	38	555656665656555555	C_1	377	377
28	55555656655555	D_2	8	90	38	555656666556555555	C_{2v}	1	365
28	55565655555556	T_d	0	75	38	555666665555555566	C_{3v}	0	378
30	55555666655555	D_{5h}	1	151	38	556566565565665655	C_2	14	382
30	55555666665555	C_{2v}	3	117	40	555556666666665555	D_{5d}	1	701
30	55566566555555	C_{2v}	1	107	40	555556666666665555	C_2	31	493
32	5555565666565555	C_2	18	168	40	555556656666665555	D_2	8	596
32	5555566566565555	D_2	6	184	40	555566666556566555	C_1	508	508
32	5555666566565555	D_{3d}	0	180	40	555566666565665555	C_s	8	536
32	5556656655565655	C_2	19	151	40	555566666556565655	C_1	498	498
32	5556656656565655	D_{3h}	0	150	40	555566666566565655	C_s	20	528
32	5556656556565655	D_3	0	144	40	555566666566565655	C_{2v}	1	565
34	5555566666565555	C_2	12	212	40	555566566656665655	C_2	37	535
34	5555666665555556	C_s	5	219	40	555566566656665655	C_1	476	476
34	5555666665656555	C_s	4	196	40	555566566656665655	C_2	31	533
34	5556656665565655	C_2	11	229	40	555665666566565556	C_1	512	512
34	5556656665656555	C_2	12	204	40	555665666566565555	C_s	5	489
34	5556656665665655	C_{3v}	0	195	40	555666665556566555	C_s	7	507
36	555556566666565555	C_2	23	275	40	555666665565565655	C_2	34	542
36	5555665666665555	D_2	9	319	40	555666665565565655	C_2	34	582
36	5555666666565655	C_1	290	290	40	555666665565565655	C_1	540	540
36	5555666666565655	C_s	5	299	40	555666665566566555	C_2	36	560
36	5556656665665655	D_2	10	270	40	555666665655655655	C_2	34	524
36	5556656665665655	D_{2d}	1	283	40	555666665655655655	C_{3v}	0	432
36	5556665666565655	C_1	283	283	40	555666665665665655	C_2	30	454
36	5556665666566555	C_s	11	299	40	555666665665665655	C_1	474	474
36	5556666655555556	C_{2v}	2	312	40	555666665666566555	C_2	31	487
36	5556666656656555	C_2	26	266	40	555666665666565556	C_s	18	480
36	5556666656656555	C_2	23	269	40	555666665666565556	C_2	30	500
36	5556666656655556	C_2	23	289	40	555666665665555656	C_1	497	497
36	5556666656655656	D_{3h}	1	364	40	555666665665565656	C_2	30	496
36	5566665656555656	D_{2d}	4	288	40	555666665666566555	C_s	47	541
36	5566665656556656	D_{6h}	1	272	40	555666665665555656	C_2	34	494
38	555556566666565555	C_2	13	355	40	555666665665555656	C_3	0	483
38	555556665666566555	D_{3h}	0	456	40	555666665665565655	C_s	10	520
38	555566666656565555	C_1	353	353	40	555666665665565655	D_2	8	502
38	555566666656565555	C_1	402	402	40	555666665665565655	D_{2h}	1	541
38	555665666566565555	C_1	375	375	40	555666665665555655	C_1	494	494
38	555665666566565555	C_2	17	385	40	556566565656566655	C_2	31	493
38	555665666566565555	C_1	367	367	40	556566565656566655	C_2	31	473
38	555666666555565655	C_1	409	409	40	556566565656566655	C_{2v}	1	513
38	555666666556565655	D_3	0	468	40	556566565656566655	D_2	8	518
38	555656566566565655	C_2	17	355	40	556566565656566655	D_{5d}	2	562
38	555656566566565556	C_1	360	360	40	556665665656565655	T_d	0	576

compatible with a fullerene of a given point group is straightforward, and can be automated using the techniques described elsewhere;⁵ all that is required is an adjacency matrix (efficiently coded in most cases by the face spiral algorithm¹⁹). Symmetry assignment, orbit analysis and KS counting then follow. Table 1 lists all possible structural isomers of the fullerenes from C_{20} – C_{40} , gives the number of totally symmetric KS for each and compares it to the full Kekulé count. 68 of the 92 cases considered in Table 1 have multiple totally symmetric Kekulé structures and hence are candidates for bond-stretch isomerism. The smallest fullerene of this type is the D_2 isomer of C_{28} which is considered further in the following section.

Bond-length Isomers of C_{28}

C_{28} has three fullerene isomers (T_d 1, D_2 right- and left-handed 2 and 3) of which the most stable is predicted to be the tetrahedral form, with an open-shell 5A_2 ground state.²⁰ Nevertheless, there is at least one pair of enantiomeric minima for the D_2 isomers, and $D_2 C_{28}$ has been studied at both

ab initio and semiempirical levels as the prototype system for the Stone–Wales mechanism of fullerene isomerisation.²¹

The tetrahedral isomer of C_{28} has four isolated hexagonal rings and four of its atoms lie on C_3 axes, so there can be no totally symmetric KS. This isomer has 75 non-totally symmetric Kekulé structures. In the D_2 isomers the hexagons occur as two naphthalene-like patches which lie on a C_2 axis and are twisted with respect to one another by an angle of roughly 45°. The sense of this twist determines the enantiomer. As Table 1 shows, each enantiomer has eight totally symmetric Kekulé structures (out of a total of 90 KS). If the conjecture made in the present work is correct, then some or all of these KSs should correspond to D_2 minima. We already know that there is one such minimum;^{20,21} the possibility that there may be more is now tested by explicit calculation.

The totally symmetric structures of $D_2 C_{28}$ can be counted 'by hand' as follows. The 42 edges of the fullerene cage fall into 12 sets: nine sets of four and three of two (shown in Fig. 2). Each set of four equivalent bonds is an example of the regular orbit of D_2 , the orbit in which every edge is shifted by every symmetry operation apart from the identity and which therefore has

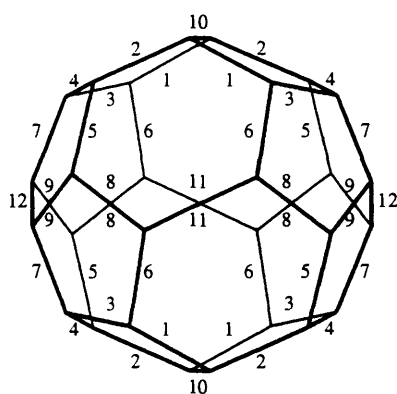


Fig. 2 Sets of equivalent edges in the D_2 isomer of C_{28}

a permutation representation equal to the regular representation* of the group [see eqn. (4)]. Each set of two equivalent

$$\Gamma_{\sigma}(O_4) = A + B_1 + B_2 + B_3 \quad (4)$$

bonds lies on one of the three independent C_2 rotational axes. The permutation representations of these three sets are shown in eqns. (5)–(7).

$$\Gamma_{\sigma}(O_{2x}) = A + B_3, \quad (5)$$

$$\Gamma_{\sigma}(O_{2y}) = A + B_2, \quad (6)$$

$$\Gamma_{\sigma}(O_{2z}) = A + B_1 \quad (7)$$

In a Kekulé structure 14 of the 42 edges are double, and if the KS is to be totally symmetric the double bonds must form complete orbits, so that the conceivable combinations are $3O_4 + O_{2x}$, $3O_4 + O_{2y}$, $3O_4 + O_{2z}$ and $2O_4 + O_{2x} + O_{2y} + O_{2z}$ with ideal (localised) π occupied orbitals spanning $4A + 3B_1 + 3B_2 + 4B_3$, $4A + 3B_1 + 4B_2 + 3B_3$, $4A + 4B_1 + 3B_2 + 3B_3$, $5A + 3B_1 + 3B_2 + 3B_3$, respectively. Of the 288 ways of selecting the O_4 orbitals to fit these combinations, the vast majority can be ruled out because they would place double bonds next to each other, and the only survivors are easily found to be the eight structures shown in Fig. 3. Only one of these (**K4**) has all three 2-orbits occupied by double bonds, three more (**K2**, **K7**, **K8**) have double bonds on the junctions of the hexagonal rings, and two each have double bonds on one of the other 2-orbits [(**K3**, **K5**) and (**K1**, **K6**)].

Each KS was used to generate a starting geometry with an appropriate pattern of long and short bonds, and then the structure was optimised by three different semiempirical methods (AM1, PM3 and MNDO) using the routines available in the MOPAC package. Optimisation was carried out in Cartesian coordinates. Each critical point was characterised by diagonalisation of the full Hessian matrix. All three Hamiltonians agree on the number and types of minimum found from the eight starting points (Tables 2 and 3), all predict the same D_2 structure (**K2**) to be optimal, and all give the same order of energies for the less stable structures. The eight starting geometries gave rise to three distinct D_2 minima. There are therefore at least three pairs of enantiomorphic D_2 minima on the potential surface, each mapping onto a single Kekulé

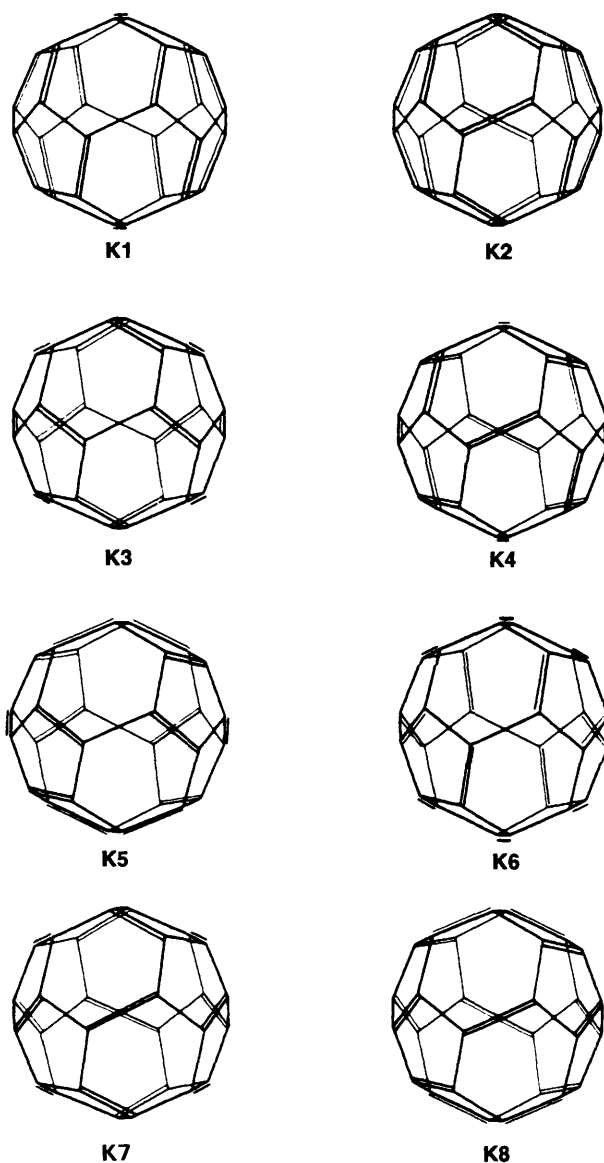


Fig. 3 The totally symmetric Kekulé structures of D_2 C_{28} . The structures **K1**–**K8** correspond to different choices of double bonds within the constraint of overall D_2 symmetry. In the notation of Fig. 2 the sets of double bonds in each structure are: 5, 6, 7, 10 (**K1**); 1, 5, 7, 11 (**K2**); 1, 4, 8, 10 (**K3**); 3, 5, 10, 11, 12 (**K4**); 2, 3, 8, 12 (**K5**); 4, 6, 9, 10 (**K6**); 1, 4, 9, 11 (**K7**) and 2, 3, 9, 11 (**K8**). Note that there are three orthogonal trios (**K1**, **K3**, **K8**), (**K1**, **K5**, **K7**) and (**K2**, **K5**, **K6**) that have the property that within a trio every edge in C_{28} is double in just one and single in just two of the Kekulé structures.

Table 2 Relative stability of D_2 minimum-energy structures of C_{28} . Each minimum is labelled by the starting Kekulé structure that it most resembles. Energies quoted in the Table (in kJ mol^{-1}) are heats of formation referred to the most stable D_2 structure calculated by each of the three semiempirical methods (PM1, AM1 and MNDO) available in the MOPAC program

	PM3	AM1	MNDO
K6	316	346	281
K5	141	150	135
K2	0	0	0

* The regular representation of a point group G has character $|G|$, the order of the group, under the identity, and zero under all other operations. It contains all irreducible representations of the group with weights equal to their degeneracies.

structure (that is to say, in each case the 14 shortest bonds in the optimised structure are the formal double bonds of the starting guess).

Table 3 Geometric structures of the three D_2 minima of C_{28} . The 12 distinct bond lengths (see Fig. 2) are quoted (in Å) for the MNDO Hamiltonian. A star denotes a formal double bond of the starting KS. Results for the PM3 and AM1 methods are similar and give the same pattern of near-single and near-double bonds. Note the delocalisation in the naphthalene patches of **K2** where the central formal double bond is surrounded by four long bonds, but the other six bonds of the patch are all short

Bond orbit	Multiplicity	K2	K5	K6
1	4	1.395*	1.451	1.474
2	4	1.430	1.385*	1.447
3	4	1.498	1.423*	1.502
4	4	1.519	1.517	1.422*
5	4	1.406*	1.460	1.482
6	4	1.475	1.492	1.404*
7	4	1.379*	1.449	1.480
8	4	1.477	1.422	1.515
9	4	1.519	1.520	1.407*
10	2	1.539	1.536	1.434*
11	2	1.414*	1.453	1.464
12	2	1.494	1.406*	1.515

A previous study²¹ has shown a close correspondence between *ab initio* SCF and PM3 semiempirical levels of theory in predictions of the number, type, symmetry and approximate geometry of critical points on the C_{28} potential surface, and so it seems reasonable to expect that all three of these minima would survive at an *ab initio* level of calculation. Structures **K2** and **K5** are known to remain true minima when an SCF calculation is carried out within the STO-3G minimal basis.

The comparative stability of structure **K2** is easily rationalised. The starting KS is the only Kekulé structure in which all four hexagons of the cage have alternating single and double bonds. In the optimised structure the alternation in bond length within the fused hexagon pairs is reduced. Although the electronic configuration $(a)^{46}(b_1)^{42}(b_2)^{40}(b_3)^{40}$ [corresponding to 28 $1s^2$ cores, 42 edge bonds and a π configuration $(a)^8(b_1)^8(b_2)^6(b_3)^6$] was predicted from the fully localised KS, in this particular case the symmetries of the occupied orbitals are not changed by delocalisation within the naphthalene-like fragments and so the configuration remains formally the same.

The survival of exactly three of the original eight KS as fully symmetric minima may be a consequence of the interlocking relationship between them. Inspection of Fig. 3 shows that the set of Kekulé structures **K2**, **K5** and **K6** is special in that every CC bond appears as a double bond in one and only one of the three. Each of these Kekulé structures corresponds to a choice of one distinct O_2 orbit from the three, and three distinct O_4 orbits from the nine, available; the choices are exclusive and together they exhaust the set of edges. As arguments based on the four-colour theorem show, it is always possible to find a set of three KS that exhausts the edges of any fullerene graph, but they are not always totally symmetric. In the present case, the 'orthogonality' of the structures makes it easier for the optimisation to be trapped in a local minimum, and hence to find the structures of higher energy. The two other orthogonal trios of Kekulé structures are (**K1**, **K3**, **K8**) and (**K1**, **K5**, **K7**), but neither of these contains the relatively stable **K2**.

The three surviving minima correspond to different electronic configurations, the different occupancies of the b -type orbitals reflecting the different symmetries of the π MOs and the different arrangement of long and short bonds. Since the orbital occupancies are different, transitions between them are likely to involve loss of elements of symmetry, and hence transition states of C_2 or C_1 symmetry; exploratory calculations with the PM3 Hamiltonian for the conversion of **K5** into **K2** indicate a C_2 transition state.

These calculations provide some support for our suggestion that the fullerene class may generate bond length isomers. Although the D_2 isomers of C_{28} are unlikely to be accessible experimentally because the T_d geometric isomer lies well below the most stable of them,²⁰ the evidence from Table 1 is that minima of this kind may grow in number for many of the larger fullerenes. It therefore seems reasonable to expect that for at least some of these cases the conditions for simultaneous stability of one or more bond length isomers will be fulfilled.

At a practical level, the present results also give a warning to those of us who perform *ab initio* calculations: a minimum with the expected symmetry and connectivity may be found in the course of an optimisation on the fullerene potential energy hypersurface, but it may not be the only or the lowest minimum of that type.

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