Stability and IR spectra of isomers of $C_{60}F_{48}$

Sarah J. Austin,[a] **Patrick W. Fowler,**[a] **John P. B. Sandall**[a] **and Francesco Zerbetto**[b]

[a] *Department of Chemistry, University of Exeter, Stocker Road, Exeter, UK EX4 4QD*
[b] *Dipartimento di Chimica, 'G. Ciamician', Universitá di Bologna, via F. Selmi 2, 40126 Bologna, Italy*

Structural optimisations at the MNDO level for all nine isomers compatible with the published eight-line ^{19}F NMR spectrum of $C_{60}F_{48}$ favour a chiral structure of D_3 symmetry and its isoenergetic *meso* form by a margin of at least 175 kJ mol^{-1}; both low-energy isomers would have 10-line ^{13}C NMR signatures if fully ^{19}F-decoupled, and their IR spectra are predicted to be closely similar.

The preparation and characterisation of fullerene derivatives is bedevilled by the isomer problem; addition of m ligands to a fullerene cage C_n ($m \sim n$) could in principle result in an astronomical number of isomers[1-3] (*e.g.*, 11 661 527 055 for $C_{60}X_{48}$, of which 11 661 270 420 have a D and an L form[1]), and often an intractable mixture will be produced. In favourable cases, experiment produces a single, well characterised, homogeneous product, as when the C_{60} cage is saturated by six organometallic moieties[4] or 24 bromine atoms,[5] but in other cases, even when the product is dominated by a single isomer, the available experimental evidence must be supplemented by theoretical input if precise characterisation is to be achieved.[6,7]

Direct fluorination of C_{60}–NaF mixtures under appropriate conditions produces a fluorofullerene species in high yield, of which at least 60% is a single structure.[8] 1D ^{19}F NMR spectroscopy shows this product species to have eight sets of six equivalent fluorine atoms, in two clusters of four signals. 2D ^{19}F–^{19}F COSY spectra can be interpreted as consistent with a particular isomeric $C_{60}F_{48}$ structure, though in order to make the assignment a number of assumptions must be made; in particular, some four-bond ^{19}F–^{19}F coupling constants (which can vary from 0 to, say, 15 Hz in small organic molecules[9]) must be assumed to vanish.

In the present paper a semi-empirical quantum mechanical method is used to predict the most stable isomer of $C_{60}F_{48}$; the search is confined to the complete set of structures compatible with the observed 1D ^{19}F NMR spectrum, *i.e.*, to the set of structures with eight sets of six sp^3 sites (and in which no sp^2 site is isolated) on the C_{60} football. It turns out that two isomers, one of which is that assigned in ref. 8 on the basis of the COSY experiment, are essentially isoenergetic and more stable than all other competitors by some 175 kJ mol^{-1}.

In ref. 8 the 14 structures (including five D/L pairs) meeting the requirement that the CF groups should fall into eight sets of six were identified by exhaustive computer search of over 20 million possibilities. A simple group-theoretical argument produces the same structures much more compactly, as follows.

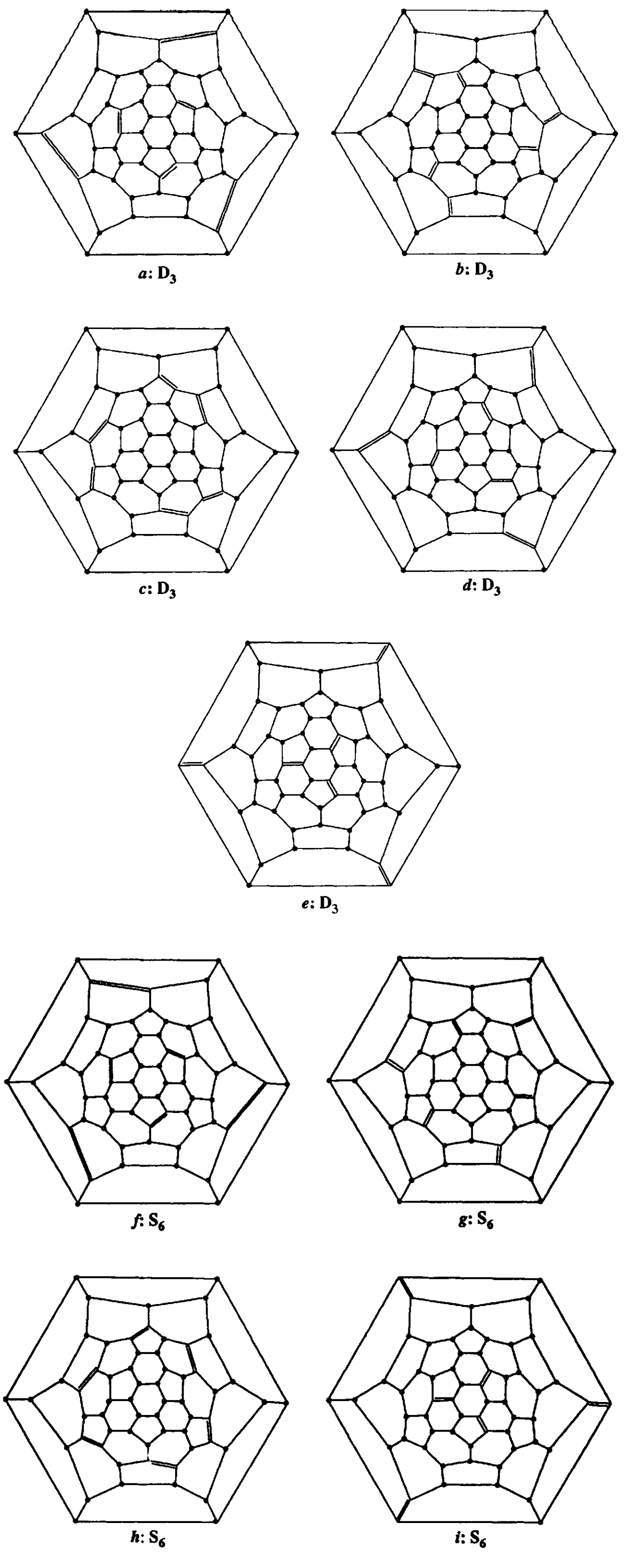
On the assumption that the connectivity of the underlying carbon framework is undisturbed, any fullerene derivative $C_{60}F_{48}$ must belong to a subgroup of the icosahedral point group I_h. Orbits (sets of equivalent sites) of size six derived from the originally fully equivalent 60 sites are possible in several subgroups,[10] but the groups in which eight or more sets of six can be present without implying a higher symmetry and therefore more extensive equivalence are just D_3 and S_6. In each of these groups, the 60 atoms of C_{60} fall into 10 orbits of six, $10O_6$. Construction of feasible $C_{60}F_{48}$ isomers proceeds as follows: take eight sets O_6 from the 10 available, avoiding choices that would imply a higher symmetry (as, for example, when the atoms of the eight O_6 sets coincide with those of the four O_{12} sets of D_{3d}), or would leave isolated sp^2 carbons surrounded by three sp^3 CF sites (which would presumably lead to radicals subject to Jahn–Teller distortion to some lower symmetry group). Case-by-case consideration of the 90 possible markings of the Schlegel diagrams for each of the two groups lead straightforwardly to just five distinct D_3 and four distinct S_6 isomers as the only possibilities. By construction, all isomers would give equal numbers of peaks in the ^{19}F NMR spectrum. The fact that all isomers are of D_3 or S_6 symmetry has the further implication that in principle the ^{13}C NMR spectral signatures would also be identical, with 10 peaks of equal intensity predicted for every isomer. Production of this spectrum in this simplified form would involve the difficult experiment of complete ^{19}F-decoupling. The nine distinct isomers are shown in Fig. 1.

Table 1 Relative stabilities of $C_{60}F_{48}$ isomers. The labels *a* to *i* refer to the structures in Fig. 1, *G* is the point group symmetry and *E* is the calculated energy (kJ mol^{-1}) expressed relative to the most stable isomer (*a*), for which the MNDO method gives a standard heat of formation of −4981.0 kJ mol^{-1}. Isomers *f*, *g*, *h* and *i* are the *meso* forms of the chiral *a*, *b*, *c* and *e*, respectively. ε_H and ε_L are the calculated HOMO and LUMO energies (eV)

Isomer	*G*	*E*	ε_H	ε_L
a	D_3	0	−14.48	−4.46
b	D_3	514.7	−13.95	−5.04
c	D_3	666.6	−13.89	−4.96
d	D_3	176.7	−14.46	−4.33
e	D_3	601.2	−14.44	−4.50
f	S_6	2.0	−14.47	−4.44
g	S_6	264.1	−14.44	−4.43
h	S_6	748.6	−14.18	−4.49
i	S_6	588.5	−14.45	−4.51

The geometries of all nine isomers satisfying the requirements of the 1D ^{19}F NMR spectrum were optimised using the semi-empirical MNDO method as implemented in MOPAC version 6.00,[11] and force fields calculated with the MNDO routines of GAUSSIAN92/DFT Revision G.1.[12] Internal coordinates were chosen to explore the relevant point-group symmetry, and eigenvector following was used to achieve well converged energies and gradients. The resulting energies are listed in Table 1, from which it can be seen that isomer *a*, the chiral structure assigned to the major experimental product on the basis of 1D and 2D NMR spectra in ref. 8, has the lowest calculated energy but lies only 2 kJ mol^{-1} below its *meso* form *f*. Given the size of the molecular system and the intrinsic uncertainties of the semi-empirical method, isomers *a* and *f* must be deemed to be essentially isoenergetic.

The two most stable isomers have isolated double bonds,



a: D_3 *b*: D_3 *c*: D_3 *d*: D_3 *e*: D_3 *f*: S_6 *g*: S_6 *h*: S_6 *i*: S_6

Fig. 1 Schlegel representations of the addition patterns in the nine distinct isomers of $C_{60}F_{48}$ that are compatible with an eight-line ^{19}F NMR spectrum. Black dots mark CF sites.

each lying on a pentagon–hexagon fusion of the C_{60} framework, and arranged in two *sym*-trivinyl patterns radiating from perfluorocyclohexane caps. Isomer *d* has the same trivinyl caps but now with the double bonds on hexagon–hexagon fusions, an arrangement that is less stable by some ~ 175 kJ mol^{-1}. Conjugation is strongly disfavoured, presumably because it increases the number of F–C–C–F eclipsed repulsive contacts: the only candidates (*b* and *c*) to have conjugated π bonds (arranged as three equatorial butadienoid fragments) lie over 500 kJ mol^{-1} above *a* and *f* (Table 1).

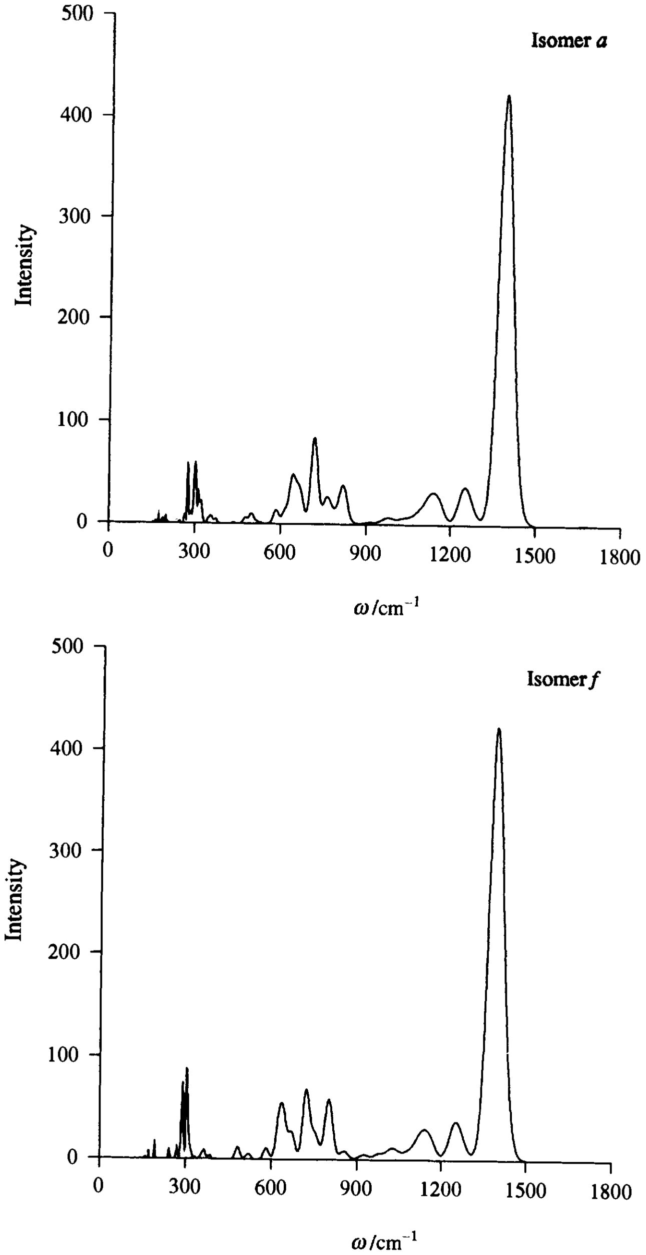


Fig. 2 Simulated IR spectra of the two low-energy isomers of $C_{60}F_{48}$. Frequencies and intensities are derived from the results of MNDO calculations as described in the text. The intensity is plotted in arbitrary units.

Isomers *a* and *f* are indistinguishable on energetic grounds, and have equal numbers of peaks in both idealised 1D ^{19}F and ^{13}C NMR spectra. Very similar electrochemical behaviour would also be expected of both isomers in view of their almost identical calculated HOMO and LUMO energies (Table 1); the stabilisation of the LUMO by 1.9 eV with respect to that of C_{60} calculated in the same semi-empirical approach is qualitatively consistent with the observation[13] that the reduction potential of $C_{60}F_{48}$ is more positive by 1.38 eV than that of the first reduction wave of the parent molecule.

One technique that might in principle distinguish between these closely similar isomers is IR spectroscopy, since all five distinct D_3 isomers have vibrational signature $\Gamma_{\text{vib}} = 54A_1 + 5A_2 + 106E$, giving 158 IR-active, 160 Raman-active and 106 coincident fundamentals, whereas all four S_6 isomers have $\Gamma_{\text{vib}} = 53A_g + 53E_g + 53A_u + 53E_u$, giving 106 IR-active, 106 Raman-active fundamentals obeying a rule of mutual exclusion.

Simulated IR spectra for the normal (^{12}C, ^{19}F) isotopomers of structures *a* and *f* are shown in Fig. 2; the spectra were constructed using MNDO vibrational frequencies and dipole-moment derivatives calculated for the optimised geometries. For display purposes, a Gaussian lineshape function was applied to broaden the computed stick spectrum, the calculated frequencies were scaled by a factor of 0.9 to counteract the known tendency of MNDO to overestimate force constants, and the intensities were scaled by the density-of-states formula[14] used in previous work on fullerene IR spectra. The linewidth function of $1 + 2 \ln \rho$ for each fundamental was calculated from the density of states ρ at that frequency. The two spectra are extremely similar, with an intense peak in the C–F stretching region and some structure in the C–C stretching region. Even allowing for some underestimation of intensities of cage modes in MNDO calculations on fullerenes, it is unlikely that IR spectroscopy could distinguish between these isomers of $C_{60}F_{48}$, but the spectra in Fig. 2 give a clear prediction of what is to be expected for isomers *a*, *f* or any mixture of the two.

Cage *a* and its *meso* form, *f*, are of course expected to be similar in energy and in many properties, because they are composed of essentially the same half-cage units differing only in the mode of their assembly. However, one cage is chiral and the other is not. One experimental technique that would probe directly this essential difference is that of circular dichroism (CD). CD spectra have been recorded for a number of fullerene derivatives. The calculation of theoretical CD spectra for fullerenes and related compounds is in its infancy, though the first results[15] are encouraging.

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