

## FARADAY COMMUNICATIONS

An End to the Search for the Ground State of  $C_{84}$ ?

David E. Manolopoulos

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK

Patrick W. Fowler

Department of Chemistry, University of Exeter, Exeter EX4 4QD, UK

Roger Taylor, Harold W. Kroto and David R. M. Walton

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Application of a simple symmetry rule for fullerene isomer distributions reveals that the  $^{13}\text{C}$  NMR pattern of  $C_{84}$  is uniquely consistent with a 2 : 1 thermodynamic mixture of isoenergetic  $D_2$  and  $D_{2d}$  symmetry isomers.

The search for the ground state structure of the fullerene  $C_{84}$  has not been altogether straightforward. On the experimental side, an initial report of 4 dominant  $^{13}\text{C}$  NMR lines in the  $C_{84}$  spectrum<sup>1</sup> soon gave way to a report of 25 lines,<sup>2</sup> and this has since been superseded by a reproducible count of 32.<sup>3,4</sup> On the theoretical side, an initial proposal of  $T_d$ ,  $D_{6h}$  and  $D_2$  symmetry candidate structures for  $C_{84}$  was based primarily on  $\pi$ -electronic stability.<sup>5</sup> It has since become apparent that the stability of fullerenes is a delicate balance between  $\pi$ -electronic and  $\sigma$ -bonding strain effects,<sup>6,7</sup> and semi-empirical calculations have found these initial candidate structures to be more strained than several others.<sup>8,9</sup> Developments such as these may seem surprising, since the initial structural proposals for  $C_{60}$ ,<sup>10</sup>  $C_{70}$ ,<sup>11</sup> and  $C_{76}$ <sup>12</sup> were all confirmed by spectroscopic (IR and NMR) evidence as soon as the experiments became possible.<sup>13–15</sup> However, because the number of potentially stable  $C_n$  isomers increases rapidly with  $n$ ,<sup>7</sup> the ground-state structures of higher fullerenes such as  $C_{84}$  are more difficult to determine.

The current theoretical situation can be summarised as follows. Stable higher fullerenes are expected to have isolated pentagons, because this both decreases the  $\sigma$ -bonding strain energy<sup>16</sup> and increases the  $\pi$ -bonding delocalisation.<sup>17</sup> A complete tabulation of the 24 topologically distinct isolated-pentagon fullerene isomers of  $C_{84}$  has been given by Manolopoulos and Fowler.<sup>7</sup> This tabulation has been exploited by Zhang *et al.*<sup>8</sup> who have performed semi-empirical calculations on all 24 isomers using a tight-binding Hamiltonian fit to the experimental properties of bulk carbon. These calculations suggest that two essentially isoenergetic isomers, with  $D_2$  and  $D_{2d}$  symmetry, should be significantly (*ca.* 23 kJ mol<sup>-1</sup>) more stable than any others. A similar conclusion has been reached independently by Raghavachari,<sup>9</sup> who has performed semi-empirical (MNDO) calculations on a subset of the 24 isomers. The particularly stable  $D_2$  and  $D_{2d}$  symmetry isomers are numbered 22 and 23 in the general tabulation,<sup>7</sup> and are shown again here in Fig. 1.

A simple topological explanation for the special stability of these  $D_2$  and  $D_{2d}$  isomers has also been proposed by Raghavachari.<sup>9</sup> According to his argument, the steric stability of a fullerene cage is maximised when the hexagonal faces have equal numbers of adjacent hexagonal neighbours. Thus  $C_{60}$  has an ideal distribution of steric strain because each of its 20 hexagons has the same number (3) of hexagonal neighbours, all of which have equivalent local environments. Such an ideal situation cannot be realised by  $C_{84}$ , the most uniform neighbour distribution for which has 28 hexagons with 4 hexagonal neighbours and 4 hexagons with 5 neighbours.<sup>9</sup> This

optimum distribution is only realised by one  $D_{2d}$  (23) and two  $D_2$  (21 and 22) structures in the complete list of  $C_{84}$  possibilities.<sup>7</sup> Moreover the four hexagons with five hexagonal neighbours are more evenly distributed on the surface of the fullerene in structures 22 and 23 than they are in structure 21, implying a secondary reduction in steric strain.<sup>9</sup> Thus an elementary consideration of steric strain points uniquely to the special stability of the  $D_2$  (22) and  $D_{2d}$  (23) isomers.

The current experimental situation is no less clear-cut. The  $^{13}\text{C}$  NMR spectrum of isolated  $C_{84}$  is dominated by 31 strong resonance lines and one additional line of half the intensity.<sup>3</sup> In contrast to the case of  $C_{78}$ , for which a number of quite different NMR spectra have been observed in different laboratories,<sup>3,18,19</sup> this  $C_{84}$  NMR pattern has now been reproduced by several independent groups.<sup>4,20,21</sup> Since different fullerene generation and chromatographic separation conditions were used in these various studies, the 32 line spectrum would appear to be an intrinsic property of the ground state of  $C_{84}$ . The  $^{13}\text{C}$  NMR spectrum of chromatographically separated  $C_{84}$  obtained by the Sussex group is shown here in Fig. 2,<sup>4</sup> and is essentially identical to those reported elsewhere.<sup>3,20</sup>

The  $D_2$  symmetry  $C_{84}$  structure in Fig. 1(a) has 21 sets of four equivalent carbon atoms. The  $D_{2d}$  symmetry  $C_{84}$  structure in Fig. 1(b) has 10 sets of eight equivalent carbon atoms, and one set of four. A 2 : 1 mixture of the two isomers is therefore consistent with the observed  $^{13}\text{C}$  NMR pattern. However, since there are three other possible  $D_2$  symmetry isolated-pentagon  $C_{84}$  isomers which also have 21 sets of four equivalent carbon atoms,<sup>7</sup> this interpretation of the spectrum is not unique. In order to provide stronger evidence for the assignment, we must also explain why the precise 2 : 1 ratio of  $D_2$  and  $D_{2d}$  symmetry isomers is obtained.<sup>3,4</sup>

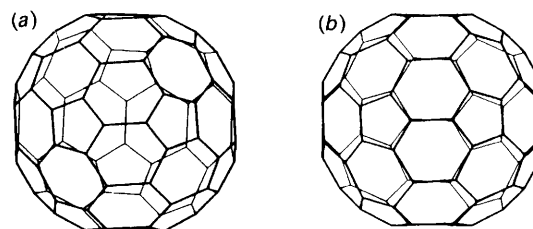


Fig. 1 Favoured  $C_{84}$  isomers with  $D_2$  and  $D_{2d}$  symmetry.<sup>8,9</sup> (a) A view down the principal axis that passes through two symmetry-equivalent pyracylene patches in the  $D_2$  isomer. (b) Rotation of the central bond of either patch produces the  $D_{2d}$  isomer

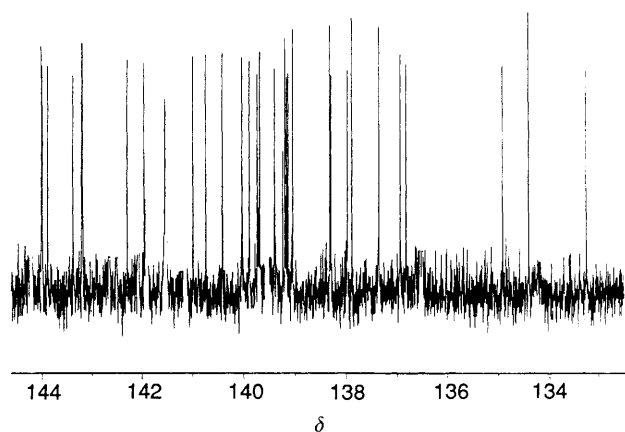


Fig. 2  $^{13}\text{C}$  NMR spectrum of  $\text{C}_{84}$ , obtained relative to  $\text{CDCl}_3$  as lock signal. Additional lines due to other minor isomer components have been deleted for clarity of presentation, and the full spectrum will be discussed in ref. 4. The pattern of 31 strong lines and one line at half the intensity is consistent with the observations of Kikuchi *et al.*<sup>3</sup> Diederich and Whetten have reported 31 of the 32 lines seen here,<sup>20</sup> and have since also assigned the 32nd line<sup>25</sup>

Assuming that the semi-empirical calculations are correct,<sup>8,9</sup> so that the  $D_2$  and  $D_{2d}$  symmetry structures in Fig. 1 are essentially isoenergetic, the anticipated thermodynamic isomer distribution is given by a simple rule: The equilibrium mole fraction of each molecule in a set of isoenergetic and interconverting  $\text{C}_n$  isomers is inversely proportional to the order of its molecular point group.<sup>22</sup> This rule has recently been derived<sup>22</sup> for the general case of an arbitrary number of isoenergetic  $\text{C}_n$  fullerene isomers interconverting under the Stone–Wales<sup>23</sup> pyracylene transformation, but we shall now re-derive it for clarity in the context of  $\text{C}_{84}$ .

One interesting feature of the  $D_2$  and  $D_{2d}$  symmetry fullerenes in Fig. 1 is that they are directly related by the Stone–Wales transformation.<sup>24</sup> Such a direct transformation is not actually required by the general argument,<sup>22</sup> but it does make the present analysis easier. The transforming pyracylene patch of two hexagons and two pentagons has site symmetry  $C_2$  in both isomers,<sup>24</sup> with the consequence that two equivalent patches in the  $D_2$  isomer can transform to give the  $D_{2d}$  isomer and four equivalent patches in the  $D_{2d}$  isomer can transform back to give  $D_2$ . [ $2 (= 4/2)$  is the ratio of the orders of the  $D_2$  and  $C_2$  point groups, whereas  $4 (= 8/2)$  is the ratio of the orders of  $D_{2d}$  and  $C_2$ ]. More detailed considerations reveal that two pyracylene patches in the  $D_{2d}$  isomer transform to give the left enantiomer, and two the right enantiomer, of the  $D_2$  isomer.<sup>22</sup>

According to the principle of microscopic reversibility the equilibrium concentrations of the  $D_2$  and  $D_{2d}$  isomers are related by  $K_c = [D_2]/[D_{2d}] = k_1/k_{-1}$ , where  $k_1$  and  $k_{-1}$  are the total forward ( $D_{2d} \rightarrow D_2$ ) and reverse ( $D_2 \rightarrow D_{2d}$ ) reaction rate constants. Since the two isomers are assumed isoenergetic these total rate constants are simply  $k_1 = 4k$  and  $k_{-1} = 2k$ , where  $k$  is the generic rate constant of a single ( $D_{2d} \rightarrow D_2$  or  $D_2 \rightarrow D_{2d}$ ) pyracylene transformation. Hence  $[D_2]/[D_{2d}] = 2/1$  at equilibrium as required. On a more detailed level the equilibrium consists of equal proportions of the  $D_{2d}$  isomer and the left and right enantiomers of  $D_2$ .<sup>22</sup> However, since the left and right  $D_2$  enantiomers have identical  $^{13}\text{C}$  NMR patterns, the observed result is simply a 2 : 1 mixture of  $D_2$  and  $D_{2d}$ .

When combined with the semi-empirical calculations described above, this elementary derivation of an entropic 2 : 1 isomer distribution suggests an unequivocal assignment of the  $\text{C}_{84}$  NMR pattern in Fig. 2 to the (almost) isoenergetic  $D_2$  and  $D_{2d}$  symmetry ground-state isomers in Fig. 1. More-

over the fact that the same NMR spectrum is obtained in several laboratories suggests that the experimental  $\text{C}_{84}$  product is determined by thermodynamic considerations and is insensitive to the detailed kinetics of the formation process.

The  $\text{C}_{84}$  result may also have important implications for other higher fullerenes. In general, since the number of potentially stable  $\text{C}_n$  isomers increases rapidly with  $n$ , one might expect entropic distributions of several essentially isoenergetic isomers to become the rule beyond  $\text{C}_{84}$ . Such distributions will be characterised by large numbers of  $^{13}\text{C}$  NMR lines of more or less equal intensity (because, in competition with the above symmetry rule for the isomer distribution, the average number of equivalent atoms in a molecule increases in proportion to its point-group order). But perhaps the most important conclusion we can draw from the  $\text{C}_{84}$  story is that scattered pieces of experimental,<sup>2–4,20,25</sup> theoretical<sup>7,22</sup> and semi-empirical<sup>8,9</sup> evidence have all contributed fruitfully to the solution of the structural puzzle.

It is a pleasure to acknowledge a very useful discussion with Prof. Martyn Poliakoff concerning this work.

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Communication 2/04142A; Received 31st July, 1992