PERKIN 2

Stabilisation of pentagon adjacencies in the lower fullerenes by functionalisation

Patrick W. Fowler[a] **and Thomas Heine**[b]

[a] *University of Exeter, School of Chemistry, Stocker Road, Exeter, UK EX4 4QD*
[b] *Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland*

Received (in Cambridge, UK) 22nd November 2000, Accepted 9th February 2001
First published as an Advance Article on the web 12th March 2001

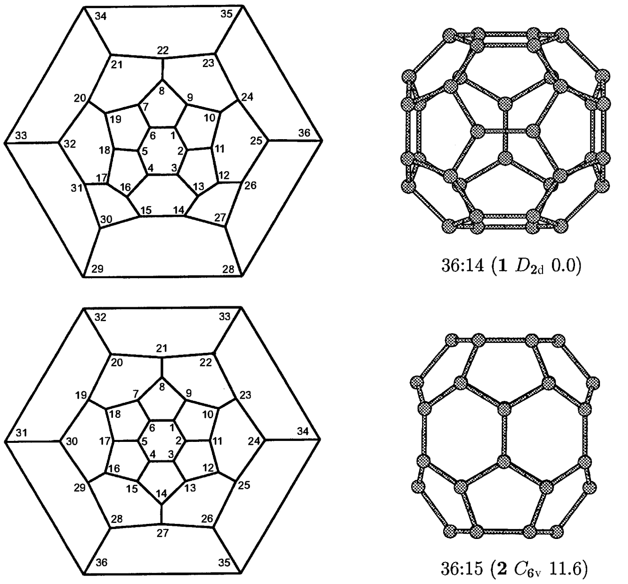
Relative stabilities are calculated with the density-functional based tight-binding method for all isomers $C_{36}H_{2x}$ ($x = 1, 2, 3$) based on the two C_{36} classical fullerenes with minimal pentagon adjacencies. Preferential addition at pentagon junctions leads to low-energy candidates for $C_{36}H_4$ and $C_{36}H_6$ based on the sixfold-symmetric cylindrical C_{36} fullerene cage, 36 : 15.

1 Introduction

The possibility of stable fullerene forms of carbon with fewer than 60 atoms per molecular unit has been the subject of some debate since the initial experiments by Piskoti *et al.*[1] on a C_{36} solid. The identification of the unit in this material as a particular C_{36} fullerene monomer, the cylindrical D_{6h} cage with 12 pentagon adjacencies (isomer 36 : 15[2]), was based on evidence from mass spectra, electron microscopy and a solid-state ^{13}C NMR spectrum. A band gap was later measured for thin films deposited on gold substrates, using STS.[3] The evidence has some ambiguities: the mass spectrum shows a peak at $C_{36}H_6$ rather than C_{36}, the diffraction pattern and ~ 0.8 eV band gaps are compatible with several possible solids, and the NMR spectrum lacks the sp^3 peaks expected for a covalently bound polymeric solid,[4] but the initial experiments have stimulated a number of parallel theoretical and experimental investigations.

C_{36} has 15 conceivable classical (pentagon + hexagon) fullerene isomers;[2] different theoretical approaches are agreed in predicting lowest energy for the two with fewest pentagon adjacencies (36 : 14 and 36 : 15), though the separation between these near-isoenergetic isomers is sensitive to the method of calculation. The nominally D_{6h}-symmetric isomer 36 : 15 is predicted to be subject to Jahn–Teller distortion[4] and to have strongly radicaloid character,[5] leading to a large dimerisation energy and a propensity to form polymeric solids. Ions of C_{36},[6,7] less stable alternative cages with squares or heptagonal rings,[4,8–10] and a number of hypothetical network solids based on C_{36} units[4,9,11–15] have also been studied.

The radicaloid character of 36 : 15 is also consistent with predictions of a facile addition chemistry. Particular reactivity of 1,4 sites in equatorial hexagons suggests a stable D_{3h} $C_{36}X_6$ pattern,[4,16] and Ito *et al.*[17] have predicted energetics of a selection of candidate structures for $C_{36}H_2$, $C_{36}H_4$, and $C_{36}H_6$ based on 1,4 addition to the 36 : 15 cage. Recently, Koshio *et al.*,[18,19] have reported a new synthesis of C_{36}-related species: ($C_{36}H_4$, $C_{36}H_6$, $C_{36}H_4O$ and $C_{36}H_6O$) which leads to milligram quantities of $C_{36}H_6$. In the light of this new work, it seems timely to make a systematic investigation of the likely structures of C_{36} hydrides and to identify factors affecting their stability. The present paper reports a complete study of possible hydrides $C_{36}H_{2x}$ ($x = 1, 2, 3$) based on the low-energy fullerene cages. Saturation of sites at pentagon adjacencies is seen to be a major stabilising factor in the relative energetics of the derivatives.



36:14 (**1** D_{2d} 0.0)

36:15 (**2** C_{6v} 11.6)

Fig. 1 C_{36} isomers 36 : 14 and 36 : 15 in Schlegel and conventional 3D representations. The point group and the relative energy (in kJ mol^{-1}, DFTB method) are given in brackets. 36 : 15 has a maximum possible symmetry of D_{6h} which falls to C_{6v} in optimisation as a result of Jahn–Teller distortion.

2 Methods

2.1 Generation of isomers

The two fullerene cage isomers selected from the 15 possibilities on energy grounds[4] are shown as polyhedral cages and Schlegel diagrams in Fig. 1. Vertices were labelled in spiral order and addition patterns $C_{36}H_{2x}$ for each cage were constructed as the

$$\binom{36}{2x}$$

binary sequences with 0 for a bare carbon and 1 for a hydrogenated centre. Symmetry operations of the parent D_{2d} and D_{6h} groups, expressed as vertex permutations, were then used to reduce the set to single representatives of symmetry-distinct isomers. Distinct isomers are conveniently labelled by listing the set of functionalised positions in the vertex spiral order from Fig. 1.

DOI: 10.1039/b009370j

Table 1 Number of isomers generated by exhaustion (total), subsequent symmetry reduction (distinct), and removal of intrinsic radicals (non-radical) for decorated cages $C_{36}H_x$

	36 : 14			36 : 15		
x	Total	Distinct	Non-radical	Total	Distinct	Non-radical
2	630	90	90	630	41	41
4	58 905	7 461	7 317	58 905	2 608	2 553
6	1 947 793	243 985	221 665	1 947 793	82 123	74 549

Intrinsically radical structures (those where the hydrogenation pattern leads to isolated bare carbon atoms or allylic fragments and hence to an open-shell configuration in a simple Hückel picture) were removed from the set. Table 1 gives the numbers of the candidate isomers of each set.

2.2 Geometry optimisations and energy calculations

Energies were calculated using the parameterised DFTB ('Density-Functional based Tight-Binding') method[20,21] which has been applied extensively to the prediction of relative energies in fullerenes[4,22–25] and their addition compounds.[16,26] Optimal bare-cage structures available from previous work[4] were decorated with radial 1.1 Å C–H bonds and then each isomeric candidate $C_{36}H_{2x}$ was fully optimised in Cartesian coordinates using BFGS[27] update and a P-RFO[28] step; tight convergence was generally reached within 50 steps, and the few recalcitrant isomers were reoptimised from the starting geometry using the BERNY technique.[29] One optimisation takes about 40 s on an IBM 375 MHz POWER/3 processor; ~300000 calculations were performed with SP/2 supercomputer facilities in Exeter and Geneva.

3 Results and discussion

3.1 Fullerene cages

Reported calculations on the relative stabilities of C_{36} carbon cages include treatments of all 15 classical isomers[2] and several more general trivalent polyhedral cages.[4,8–10] Two members of the classical set are distinguished graph theoretically by having the lowest achievable number of 12 pentagon adjacencies,[2] which is known indicator of stability in fullerene isomers.[24] The different methods (semi-empirical,[4,8] Hartree–Fock,[8,9] hybrid[9,10] and DFT[4,30]) find the isomer 36 : 14 to be of lowest energy. This structure has a 'tennis-ball' topology with eight hexagons arranged in orthogonal tetracene strips of four and the twelve pentagons forming the 'seam'. Its nearest competitor in energy is 36 : 15, with two polar hexagons, two cycles of pentagons, and an equatorial belt of six hexagons arranged in maximal D_{6h} symmetry. The energy separation between 36 : 14 and 36 : 15 is small in density-functional based calculations (18 kJ mol^{-1} LDA,[4] 0.0 eV GGA,[30] 14 kJ mol^{-1} hybrid,[9] 12 kJ mol^{-1} DFTB[4]) and much larger in Hartree–Fock like calculations (124 kJ mol^{-1} HF,[9] 134 kJ mol^{-1} SAM1,[8] 108 kJ mol^{-1} AM1,[4] 158 kJ mol^{-1} QCFF-PI[4]). Isomer 36 : 15 has a small gap in D_{6h} symmetry and undergoes second-order Jahn–Teller distortion to C_{6v}[4] or lower[9] symmetry; open-shell states are competitive with the closed-shell singlet, and even favoured over it in some calculations.[31] The next classical fullerene isomer 36 : 9 has 13 pentagon adjacencies and is predicted by several methods to lie 30–40 kJ mol^{-1} above 36 : 14.[4,8,9] Only the Hartree–Fock calculations in a 4-31G basis give a lower relative energy[9] of 16 kJ mol^{-1}, which may well be underestimated because of the small basis and the neglect of correlation.

All non-classical fullerenes appear to be much less stable than 36 : 14 and 36 : 15. Support for the restriction of further considerations to the two fullerene cages is given by calculated thermal distributions,[9] which are dominated by 36 : 14 and 36 : 15 for temperatures below 500 K, and still show these two isomers as constituting 60% of the mixture at 5000 K.

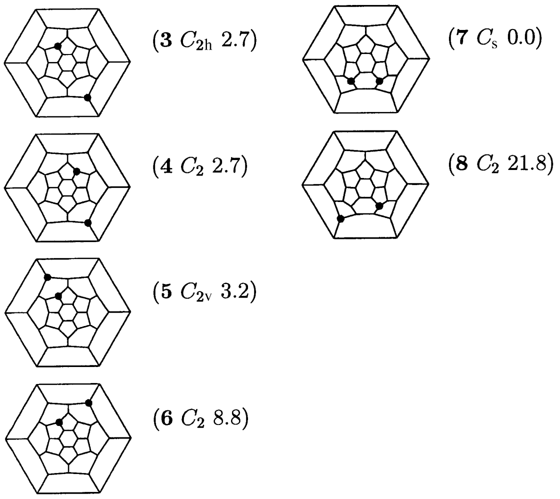


Fig. 2 Schlegel diagrams of the most stable $C_{36}H_2$ isomers within 30 kJ mol^{-1} of the most stable isomer 36 : 14H_2 : 7,21, labelled by point group and relative energy (in kJ mol^{-1}).

3.2 $C_{36}H_2$

Isomers of $C_{36}H_2$ span ranges of 224 and 251 kJ mol^{-1} for derivatives based on 36 : 14 and 36 : 15, respectively, according to the DFTB model. The most stable $C_{36}H_2$ isomers identified in the calculations are listed in Schlegel diagram form in Fig. 2. In terms of absolute internal energy, the most stable dihydro derivative is a C_s structure (**7**), constructed by 1,4 addition to 36 : 14. This is followed by a group of functionalised 36 : 15 cages with addition at pentagon–pentagon–hexagon (PPH) sites, all within 10 kJ mol^{-1} according to DFTB. All isomers based on 36 : 14 within the first 64 kJ mol^{-1} and on 36 : 15 within 83 kJ mol^{-1} have this PPH pattern of functionalisation.

3.3 $C_{36}H_4$

For $C_{36}H_4$ isomers the energy ranges are 382 and 444 kJ mol^{-1} for derivatives of 36 : 14 and 36 : 15, respectively, and the two molecules of lowest absolute internal energy now correspond to repeated 1,4 additions to 36 : 15, with C_{2v} and D_{2h} symmetry (Fig. 3). Both contain favoured $C_{36}H_2$ patterns. The best pattern for addition of 4 hydrogens to 36 : 14 is predicted to be a C_2 isomer with 1,4 hydrogenation of hexagons from the two distinct tetracene chains.

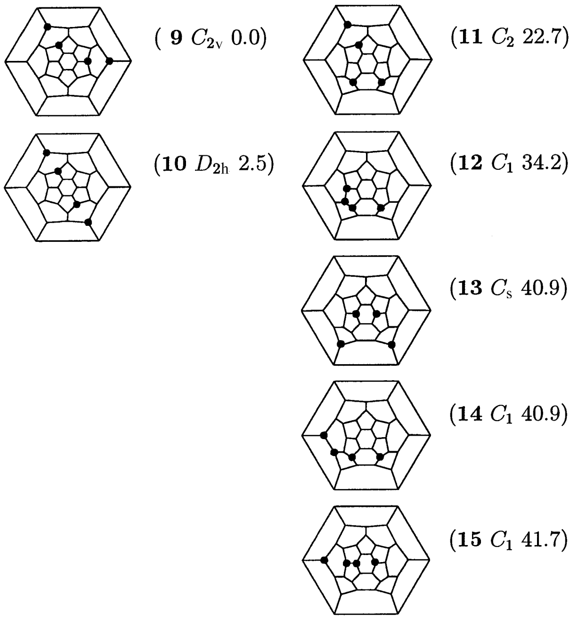
3.4 $C_{36}H_6$

For $C_{36}H_6$ isomers the energy ranges are again larger (650 kJ mol^{-1} for 36 : 14, 557 kJ mol^{-1} for 36 : 15), and the energy differences between the best isomers in each set is about twice that of $C_{36}H_4$. The lowest energy is found for the D_{3h} isomer based on 36 : 15 (Fig. 4), with triple 1,4 addition, which has been discussed extensively in previous work as an indication of both the addition chemistry[4,16,17] of C_{36} and the likely coordination of the C_{36} monomer in 'super-graphite' and another hexagonal infinite lattice.[13] Six is less clearly an obvious 'valence' of the D_{2d} C_{36} cage 36 : 14, and the isomer of lowest energy based on this cage is of only C_1 symmetry. Histograms of energy distributions for $C_{36}H_4$ and $C_{36}H_6$ (Fig. 5) show that once several hydrogen atoms have been added, both isomer sets are settling into the expected Gaussian-like pattern. The energy ranges (Fig. 6) suggest a trend in which the best derivatives of the more symmetrical 36 : 15 cage provide the globally best $C_{36}H_{2x}$ candidates. This trend apparently survives in the limit of full hydrogenation: optimisations of the 15 fullerenes $C_{36}H_{36}$ show a much flatter distribution of energy than for the fullerenes themselves with D_{6h} $C_{36}H_{36}$ stabilised by 13 kJ mol^{-1} with respect to the D_{2d} isomer based on 36 : 14 (Table 2).

3.5 Stabilisation of pentagon adjacencies

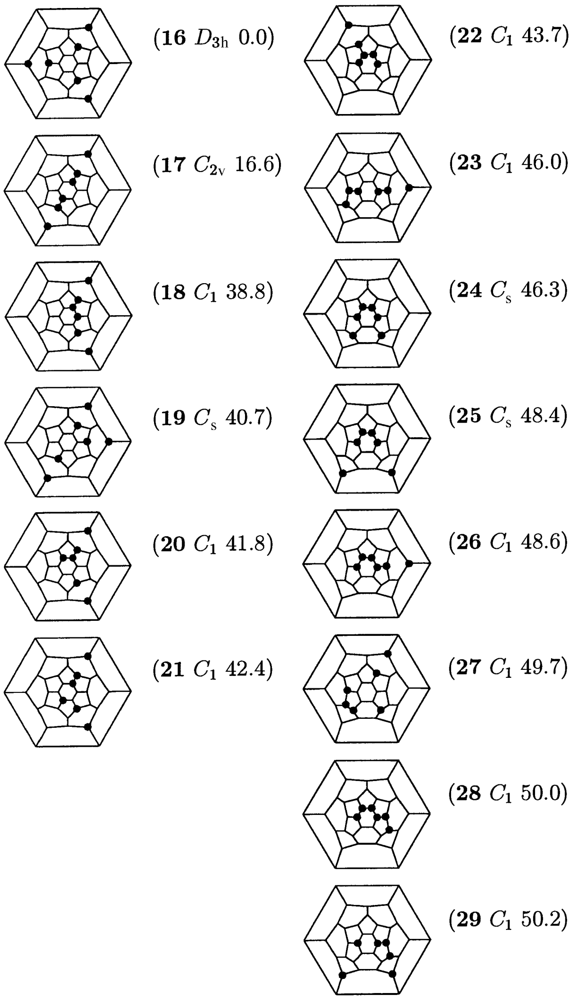
When the results of this study are taken in conjunction with a previous survey of all possible addition patterns $C_{24}H_{2x}$ ($x = 1$–12) on the smallest hexagon-containing fullerene, a simple rule of thumb for addition to lower fullerenes can be proposed: addition to a given lower fullerene will give the greatest energy lowering if sites are occupied in the order PPP > PPH > PHH > HHH, where the symbols denote the set of three rings fused at a given site.

Lower fullerenes necessarily contain pentagon adjacencies, which are sites of maximum strain, each pentagon–pentagon bond introducing an energy penalty[24] of ~ 70 kJ mol^{-1}. The most stable isomers of a lower fullerene will have minimum number of adjacencies; in higher fullerenes C_{60}, C_n ($n \geqslant 70$), this leads to the well-known isolated-pentagon rule. Triples of fused pentagons are even more destabilising.[32] Not only do PPP and PPH sites act as points of instability in the fullerene, but they are also sterically prepared for pyramidal sp^3 hybridisation in localised C–H bonds. The four PPP sites of T_d C_{28} provide an extreme example, accounting for the 'tetravalence' of this



(**9** C_{2v} 0.0)
(**10** D_{2h} 2.5)
(**11** C_2 22.7)
(**12** C_1 34.2)
(**13** C_s 40.9)
(**14** C_1 40.9)
(**15** C_1 41.7)

Fig. 3 Schlegel diagrams of the most stable $C_{36}H_4$ isomers. The point group and the relative energy (in kJ mol^{-1}) with respect to the isomer of $C_{36}H_4$ based on 36 : 15 with addends in positions 7,11,20,24 are given in brackets.



(**16** D_{3h} 0.0)
(**17** C_{2v} 16.6)
(**18** C_1 38.8)
(**19** C_s 40.7)
(**20** C_1 41.8)
(**21** C_1 42.4)
(**22** C_1 43.7)
(**23** C_1 46.0)
(**24** C_s 46.3)
(**25** C_s 48.4)
(**26** C_1 48.6)
(**27** C_1 49.7)
(**28** C_1 50.0)
(**29** C_1 50.2)

Fig. 4 Schlegel diagrams of the most stable $C_{36}H_6$ isomers. The point group and the relative energy (in kJ mol^{-1}) with respect to the isomer of $C_{36}H_6$ based on 36 : 15 with addends in positions 7,11,15,20,24,28 are given in brackets.

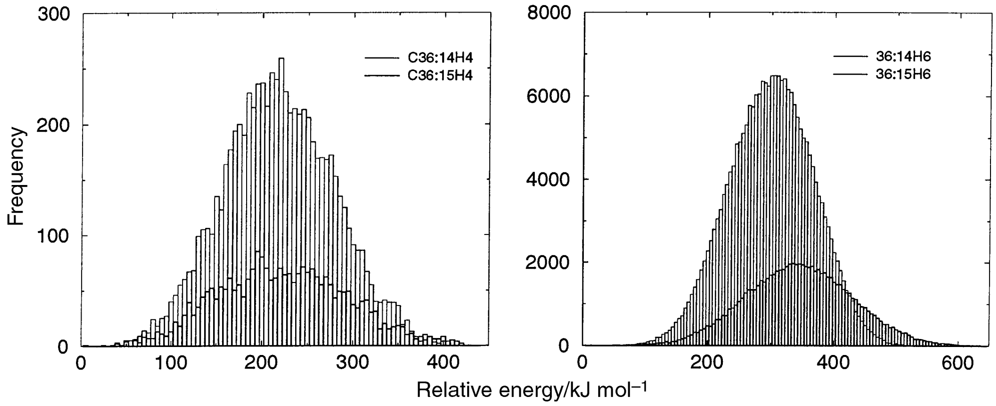


Fig. 5 Histograms of $C_{36}H_4$ (left) and $C_{36}H_6$ isomers. The number of isomers in each window of 5 kJ mol^{-1} is plotted.

Table 2 Calculated energies of 15 conventional bare C_{36} cages 36 : *N* (left) and the corresponding fully hydrogenated $C_{36}H_{36}$ molecules (labelled by *N*). Energy values are in kJ mol^{-1} and reported relative to the most stable isomer within each set of molecules

C_{36}		$C_{36}H_{36}$	
N	*E*	*N*	*E*
14	0.0	15	0.0
15	11.6	14	13.3
12	41.8	9	14.6
9	43.3	6	15.8
11	72.7	12	17.8
8	118.4	11	18.2
6	153.6	13	19.8
7	166.8	8	20.3
13	173.1	1	20.5
10	204.8	3	24.3
3	248.3	2	36.6
1	330.1	7	37.7
4	332.3	4	42.6
5	415.1	10	57.1
2	467.0	5	116.2

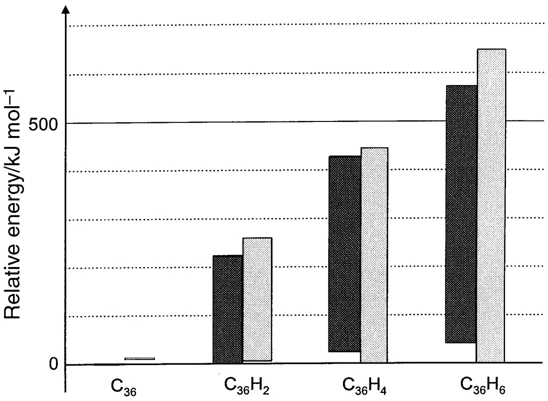


Fig. 6 Comparison of energy ranges of isomers based on 36 : 14 (dark) and 36 : 15 (light) fullerene cages. Energies are given in kJ mol^{-1} relative to the most stable isomer of each set, as calculated within the DFTB model.

fullerene 'superatom',[33–35] but the same trend is discernible in the results for C_{24}.[26] In the two isomers of C_{36}, PPP sites are absent and addition takes place at PPH. Although energies alone cannot be taken to imply a mechanism, the 'nesting' property in which stable $C_{36}H_2$ patterns appear as subsets of stable $C_{36}H_4$ patterns, which in turn are present within the best $C_{36}H_6$, is at least suggestive of a low-energy pathway for multiple hydrogenation. Finally, we note that these calculations have provided candidates for $C_{36}H_{2x}$ structures formed by hydrogenation of pre-existing C_{36} fullerene cages. Their symmetry properties in particular should aid in the assignment of the recently produced C_{36} fullerene hydrides.

Acknowledgements

The TMR Network project USEFULL CT97-0126 is thanked for support. Part of the work was performed under Project 20-55459.98 of the Swiss National Science Foundation. EPSRC is thanked for provision of the CERES Computing facility at Exeter University.

References

1 C. Piskoti, J. Yarger and A. Zettl, *Nature*, 1998, **393**, 771.
2 P. W. Fowler and D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.
3 P. G. Collins, J. C. Grossman, M. Côté, M. Ishigami, C. Piskoti, S. G. Louie, M. L. Cohen and A. Zettl, *Phys. Rev. Lett.*, 1999, **82**, 165.
4 P. W. Fowler, T. Heine, K. M. Rogers, J. P. B. Sandall, G. Seifert and F. Zerbetto, *Chem. Phys. Lett.*, 1999, **300**, 369.
5 P. W. Fowler, D. Mitchell and F. Zerbetto, *J. Am. Chem. Soc.*, 1999, **121**, 3218.
6 K. Yoshizawa, M. Tachibana and T. Yamabe, *J. Chem. Phys.*, 1999, **111**, 10088.
7 A. Ito, T. Monobe, T. Yoshii and K. Tanaka, *Chem. Phys. Lett.*, 1999, **315**, 348.
8 Z. Slanina, X. Zhao and E. Ōsawa, *J. Chem. Phys.*, 1998, **290**, 311.
9 Z. Slanina, F. Uhlík, X. Zhao and E. Ōsawa, *J. Chem. Phys.*, 2000, **113**, 4933.
10 L. F. Yuan, J. L. Yang, K. Deng and Q. S. Zhu, *J. Phys. Chem. A*, 2000, **104**, 6666.
11 M. Menon and E. Richter, *Phys. Rev. B*, 1999, **60**, 13322.
12 Y. H. Huang, Y. M. Chen and R. Z. Liu, *J. Phys. Chem. Solids*, 2000, **61**, 1475.
13 T. Heine, P. W. Fowler and G. Seifert, *Solid State Commun.*, 1999, **111**, 19.
14 M. Côté, J. C. Grossman, M. L. Cohen and S. G. Louie, *Phys. Rev. Lett.*, 1998, **81**, 697.
15 J. C. Grossman, S. G. Louie and M. L. Cohen, *Phys. Rev. B*, 1999, **60**, R6941.
16 T. Heine, P. W. Fowler, K. M. Rogers and G. Seifert, *J. Chem. Soc., Perkin Trans. 2*, 1999, 707.
17 A. Ito, T. Monobe, T. Yoshii and K. Tanaka, *Chem. Phys. Lett.*, 2000, **328**, 32.
18 A. Koshio, M. Inakuma, T. Sugai and H. Shinohara, *J. Am. Chem. Soc.*, 2000, **122**, 398.
19 A. Koshio, M. Inakuma, Z. W. Wang, T. Sugai and H. Shinohara, *J. Phys. Chem. B*, 2000, **104**, 7908.
20 G. Seifert, D. Porezag and T. Frauenheim, *Int. J. Quantum Chem.*, 1996, **58**, 185.
21 D. Porezag, T. Frauenheim, T. Köhler, G. Seifert and R. Kaschner, *Phys. Rev. B*, 1995, **51**, 12947.
22 P. W. Fowler, T. Heine, D. E. Manolopoulos, D. Mitchell, G. Orlandi, R. Schmidt, G. Seifert and F. Zerbetto, *J. Phys. Chem.*, 1996, **100**, 6984.
23 P. W. Fowler, T. Heine, D. Mitchell, G. Orlandi, R. Schmidt, G. Seifert and F. Zerbetto, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 1996.
24 E. Albertazzi, C. Domene, P. W. Fowler, T. Heine, G. Seifert, C. Van Alsenoy and F. Zerbetto, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2913.
25 T. Heine, M. Bühl, P. W. Fowler and G. Seifert, *Chem. Phys. Lett.*, 2000, **316**, 373.
26 P. W. Fowler, T. Heine and A. Troisi, *Chem. Phys. Lett.*, 1999, **312**, 77.
27 R. Fletcher, *Practical Methods of Optimization*, John Wiley, New York, 1980, vol. 1, p. 43.
28 A. Banerjee, N. Adams, J. Simons and R. Shepard, *J. Phys. Chem.*, 1985, **89**, 52; J. Baker, *J. Comput. Chem.*, 1986, **7**, 385.
29 H. B. Schlegel, *Adv. Chem. Phys.*, 1987, **67**, 249.
30 J. C. Grossman, M. Côté, S. G. Louie and M. L. Cohen, *Chem. Phys. Lett.*, 1998, **284**, 344.
31 M. N. Jagadeesh and J. Chandrasekhar, *Chem. Phys. Lett.*, 1999, **305**, 298.
32 S. J. Austin, P. W. Fowler, D. E. Manolopoulos, G. Orlandi and F. Zerbetto, *J. Phys. Chem.*, 1995, **99**, 8076.
33 P. W. Fowler, S. J. Austin and J. P. B. Sandall, *J. Chem. Soc., Perkin Trans. 2*, 1993, 795.
34 C. Milani, C. Giambelli, H. E. Roman, F. Alasia, G. Benedek, R. A. Broglia, S. Sanguinetti and K. Yabana, *Chem. Phys. Lett.*, 1996, **258**, 554.
35 H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, 1993, **214**, 353.