An SCF-MO Study of the Dimerisation Reaction of Hemifullerene ($C_{30}H_{12}$) to the Potential Fullerene Precursor $C_{60}H_{24}$

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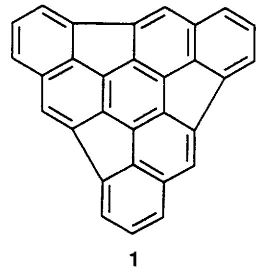
AM1 and PM3 SCF-MO calculations suggest the dimerisation of hemifullerene **1** to **2** by a mechanism involving six concurrent $_{\pi}2_s + {}_{\pi}4_s$ additions corresponds to a stationary point with six negative force constants; the first stepwise $_{\pi}2_s + {}_{\pi}4_s$ transition state is found to be highly unsymmetrical with a large barrier to reaction.

Whilst triindenotriphenylene **1** ($C_{30}H_{12}$) has attracted recent attention[1] as a rational synthetic precursor to the C_{60} fullerene skeleton, and the overall dimerisation to **2** ($C_{60}H_{24}$) is estimated to be thermoneutral,[2] no estimate of the dimerisation barrier and hence the feasibility of this reaction is available. This system also represents an unusual example of a multibond reaction involving potentially twelve bonds, where the timing of the bond formations is of some interest.[3] Whilst the simple $_{\pi}2_s + {}_{\pi}4_s$ cycloaddition of ethene and butadiene is thought to be synchronous,[4] both strain[5] and ring size[6] may induce asynchronous or even stepwise behaviour. We report here semi-empirical SCF-MO calculations at the closed shell AM1 and PM3 levels for the reaction of **1** and various model compounds, which suggest that the concerted $_{\pi}2_s + {}_{\pi}4_s$ dimerisation reaction may be both asynchronous and have a large barrier to reaction.

The transition state for the initial single $_{\pi}2_s + {}_{\pi}4_s$ cycloaddition of **1** (to its mirror image) proved unusually difficult to locate using conventional methods.† We adopted a stepwise strategy of combining **1** with smaller precursors such as ethene or **3**–**7** acting as the $_{\pi}2_s$ component or with butadiene acting as the $_{\pi}4_s$ component, and using the located transition states as the starting geometry for the next optimisation (Table 1). We did not attempt to calculate any of the subsequent five $_{\pi}2_s + {}_{\pi}4_s$ cycloadditions, and hence the first barrier establishes only a lower limit for the overall reaction rate-limiting step. The results reveal that the barriers to these reactions are significantly higher than for the simple reaction of ethene and butadiene (Table 1), due to both loss of aromaticity and strain. The increase in barrier derives more from **1** acting as a diene than as an alkene (Table 1).‡ We also note that for symmetrical $_{\pi}2_s + {}_{\pi}4_s$ reactions at least, the closed shell RHF approximation compares well with MCSCF results.[4] For the series **1** + **3**, **4**, **5**, **6**, **7** and finally **2** itself, the calculated asymmetry in the two forming bonds increases (Table 1).[5] Although both the AM1 and PM3 methods concur structurally with *ab initio* methods for the ethene + butadiene reaction,[4] asymmetric distortion due to strain has not hitherto been demonstrated at the *ab initio* level. The asymmetry for the $_{\pi}2_s + {}_{\pi}4_s$ cycloaddition of **1** + **1** also implies that significant biradical character may be present in the transition state, and that the reaction may be easily diverted from the full dimerisation pathway by radical or hydrogen elimination reactions. Although the closed shell SCF derived barrier for such an asynchronous and biradical-like reaction is certainly overestimated, that for the more symmetrical reaction of **1** + **3** is also high. The size of the system currently precludes a properly correlated calculation at an *ab initio* level.



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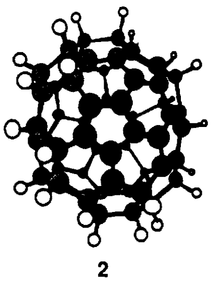

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Table 1 Calculated PM3 enthalpies for the reaction between **1** and **3**–**7** in kJ mol^{-1}

Structure	$\Delta H_{\text{Reactants}}$	ΔHts	$\Delta H^{\#}$	r_1, r_2 (Å)	ν_i (cm^{-1})
1 + ethene	1135	1309	174	2.06, 2.10	1066
1 + butadiene	1198	1357	159	2.10, 2.15	966
1 + **3**	1838	2108	270	1.99, 2.19	1017
1 + **4**	1898	2169	271	1.98, 2.21	1003
1 + **5**	2016	2295	279	1.97, 2.23	985
1 + **6**	2506	2778	272	1.99, 2.22	1003
1 + **7**	2558	2831	273	1.97, 2.25	975
1 + **1**[a]	2131	2388	257	1.69, 3.03	205
1 + **1**[b]	2441	2710	268	1.74, 2.91	497
1 + **1**[c]	2131	3754	1623	2.14, 2.10	[e]
1 + **1**[b,c]	2441	4120	1680	2.17, 2.10	[f]
[d]	202	312	110	2.14, 2.14	928

[a] Energies of intermediates corresponding to the product of successive $_{\pi}2_s + {}_{\pi}4_s$ additions; 2206, 2121, 2310, 2316, 2189 kJ mol^{-1}. [b] AM1 calculation. [c] Stationary point for six concurrent cycloadditions. [d] Reaction between ethene and butadiene. [e] Values of six imaginary modes, 1274*i*, 1189*i*, 1189*i*, 1060*i*, 1060*i*, 977*i* cm^{-1}. [f] Values of seven imaginary modes: 1199*i*, 1116*i*, 1116*i*, 982*i*, 982*i*, 904*i*, 78*i*.

The stationary point corresponding to concurrent sixfold $_{\pi}2_s + {}_{\pi}4_s$ cycloaddition was readily characterised, and was shown to have either 6 (PM3) or 7 (AM1) negative force constants, with a very high energy barrier (Table 1). The near degeneracy of the first six vibrations indicates that the genuine transition states are likely to correspond to six successive rather than to six concurrent $_{\pi}2_s + {}_{\pi}4_s$ additions. Our previous finding that metal ions as templates do not appear to enhance the dimerisation, coupled with the present findings that the first $_{\pi}2_s + {}_{\pi}4_s$ step may have a higher than normal barrier, indicate that high temperatures may still be necessary for attempts to form the C_{60} nucleus from **1**.

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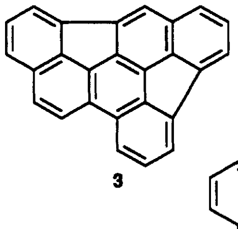

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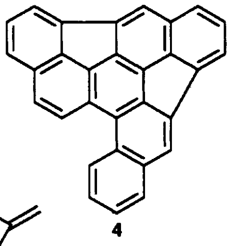

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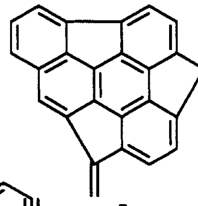

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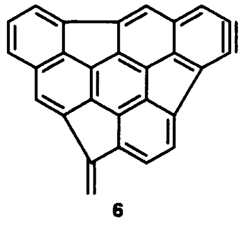

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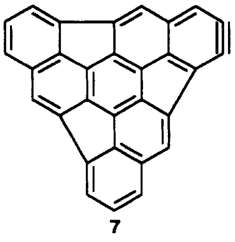

7

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Footnotes

† Theoretical calculations were carried out at the restricted Hartee–Fock level (RHF) AM1 or PM3 semi-empirical methods, as implemented in the MOPAC 93 program. All structures were optimised using the eigenvector following algorithm, followed by a vibrational analysis to characterise the stationary points.

‡ Computer readable files for Unix, Apple Macintosh or Microsoft Windows systems in MPEG video animation format illustrating the three-dimensional properties of these stationary points are available for general access using the world-wide-webb uniform resource locator http://www.ch.ic.ac.uk/rzepa/RSC/CC/4_02038C.html and from the Gopher+ server *gopher.ch.ic.ac.uk.* in the Scientific_publications/rzepa/Royal_Society_of_Chemistry/Chemical_communications/4_02038C directory, for a period of at least two years from the publication of this paper. A description of how to visualise such material, together with appropriate programs is available from the same sources.

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