Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Role of Four-membered Rings in C_{32} Fullerene Stability and Mechanisms of Generalized Stone-Wales Transformation: A Density Functional Theory Investigation

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Electronic Supplementary Information

Contents

Table S1 Heat of formation of 364 C_{32} fullerenes obtained at AM1 level. [a]

label[b]:*sym*	Ring Index[c] (n_4, n_5, n_6)	PA [d]	$\triangle H_f$	$\lvert\beta\rvert$
32:D_{4d}	(2, 8, 8)	8	0	0.6458
1:D_3	(0, 12, 6)	15	19.4	0.3639
5:C_s	(1, 10, 7)	12	21.8	0.3792
33:C_s	(1, 10, 7)	11	39.5	0.3879
6:C_2	(0, 12, 6)	16	46.5	0.2527
59:C_s	(3, 6, 9)	4	46.8	0.6165
9:C_2	(2, 8, 8)	9	53.5	0.2524
12:C_s	(2, 8, 8)	8	54.6	0.4374
2:C_1	(1, 10, 7)	11	60.6	0.2313
15:C_1	(2, 8, 8)	6	62.9	0.4900
18:C_2	(2, 8, 8)	6	63.9	0.4305
41:C_s	(2, 8, 8)	7	72.3	0.2055
17:C_1	(2, 8, 8)	7	73.3	0.5031
105:C_{2v}	(1, 10, 7)	10	73.8	0.1981
34:C_1	(1, 10, 7)	12	74.2	0.2485
27:C_2	(2, 8, 8)	7	78.0	0.4373
58:C_1	(3, 6, 9)	5	79.1	0.3916
36:C_s	(1, 10, 7)	12	79.5	0.1811
16:C_1	(2, 8, 8)	7	81.6	0.3656
20:C_1	(2, 8, 8)	8	82.0	0.3390
23:C_1	(2, 8, 8)	9	82.5	0.1824
37:C_1	(1, 10, 7)	12	82.7	0.2937
3:C_1	(1, 10, 7)	11	83.3	0.1989
31:C_{2v}	(1, 10, 7)	14	84.5	0.0147
29:C_1	(2, 8, 8)	9	85.9	0.0417
4:C_2	(0, 12, 6)	17	86.8	0.0117
13:C_s	(1, 10, 7)	12	87.2	0.0183
25:C_1	(2, 8, 8)	9	88.2	0.1457
96:C_{2v}	(2, 8, 8)	11	89.2	0.3579
89:C_1	(3, 6, 9)	6	90.9	0.4566
99:C_1	(2, 8, 8)	7	94.3	0.3806
26:C_1	(1, 10, 7)	12	94.4	0.0445
94:D_{2h}	(0, 12, 6)	18	96.6	0.0000
57:C_1	(3, 6, 9)	6	98.5	0.1450
126:C_{2v}	(4, 4, 10)	0	100.1	0.3531
179:C_2	(4, 4, 10)	5	100.2	0.4299
100:C_1	(2, 8, 8)	7	100.2	0.3356
107:D_{3h}	(0, 12, 6)	18	101.1	0.3943
14:C_2	(2, 8, 8)	7	102.1	0.1379
65:C_3	(3, 6, 9)	3	104.3	0.6603
78:C_s	(3, 6, 9)	6	107.9	0.0930
85:C_1	(3, 6, 9)	5	109.9	0.3193
7:C_1	(1, 10, 7)	11	110	0.0419
55:C_s	(2, 8, 8)	6	110.1	0.1951
93:C_2	(4, 4, 10)	1	110.3	0.2484
70:C_1	(3, 6, 9)	4	111.2	0.1665
64:C_1	(3, 6, 9)	4	111.5	0.0954
22:C_1	(2, 8, 8)	10	111.7	0.1759
11:C_1	(2, 8, 8)	7	112.6	0.0518
30:D_2	(0, 12, 6)	18	113.6	0.0000
66:C_1	(3, 6, 9)	5	114.1	0.2965
52:C_1	(2, 8, 8)	6	115.1	0.1272
71:C_1	(3, 6, 9)	3	115.4	0.2610
43:C_1	(2, 8, 8)	6	115.5	0.0169
177:C_1	(2, 8, 8)	8	116.1	0.5059
98:C_1	(2, 8, 8)	8	116.3	0.0713
67:C_1	(3, 6, 9)	4	116.4	0.0705
35:C_1	(1, 10, 7)	13	117.5	0.0526
54:C_1	(2, 8, 8)	7	117.8	0.2228
88:C_1	(3, 6, 9)	3	118.6	0.3082
91:C_2	(2, 8, 8)	4	120.7	0.1514
77:C_1	(3, 6, 9)	7	120.8	0.1618
72:C_1	(3, 6, 9)	3	120.8	0.2224
68:C_1	(2, 8, 8)	8	121.5	0.0519
8:C_1	(1, 10, 7)	12	123.2	0.1131
76:C_1	(3, 6, 9)	7	123.4	0.058
95:C_1	(1, 10, 7)	11	123.8	0.2301
130:C_2	(2, 8, 8)	5	125.2	0.1609
116:D_2	(2, 8, 8)	9	125.8	0.0443
62:C_1	(3, 6, 9)	5	126.1	0.2354
74:C_1	(3, 6, 9)	2	126.3	0.3222
46:C_1	(3, 6, 9)	3	126.5	0.1585
10:C_2	(2, 8, 8)	8	127.3	0.1529
87:C_1	(4, 4, 10)	3	128.3	0.2483
136:C_1	(3, 6, 9)	4	128.6	0.3174
61:D_2	(2, 8, 8)	8	128.7	0.0518
19:C_1	(2, 8, 8)	8	128.7	0.0504
44:C_1	(2, 8, 8)	5	129.2	0.2759
49:C_1	(1, 10, 7)	12	129.4	0.0334
90:C_1	(2, 8, 8)	9	130.0	0.178
146:C_1	(3, 6, 9)	3	131.0	0.1392
40:C_1	(2, 8, 8)	6	131.1	0.0923
60:C_1	(3, 6, 9)	4	131.3	0.1936
215:C_s	(3, 6, 9)	2	135.5	0.2419

102:C_1	(2, 8, 8)	7	135.8	0.1442
144:C_1	(3, 6, 9)	4	136.5	0.2136
51:C_1	(3, 6, 9)	4	136.5	0.2481
21:C_1	(2, 8, 8)	10	137.6	0.0847
56:C_1	(3, 6, 9)	5	137.6	0.0778
47:C_1	(3, 6, 9)	3	137.9	0.1536
160:C_1	(3, 6, 9)	4	138.7	0.3507
223:C_1	(4, 4, 10)	1	138.8	0.2429
84:C_1	(4, 4, 10)	2	138.8	0.2326
81:C_1	(2, 8, 8)	10	138.9	0.0816
169:C_s	(2, 8, 8)	9	139	0.0319
171:D_2	(4, 4, 10)	2	140.4	0.2811
83:C_1	(3, 6, 9)	5	140.5	0.0718
28:C_2	(2, 8, 8)	6	140.7	0.0373
153:C_1	(2, 8, 8)	7	141.0	0.1836
92:C_2	(2, 8, 8)	9	141.5	0.1563
63:C_1	(3, 6, 9)	3	141.5	0.1788
79:C_1	(3, 6, 9)	5	141.7	0.0715
148:C_2	(2, 8, 8)	5	143.5	0.0478
180:C_1	(4, 4, 10)	1	143.6	0.2814
119:C_2	(3, 6, 9)	2	143.8	0.2619
111:C_1	(2, 8, 8)	7	144	0.1798
145:C_1	(2, 8, 8)	8	144.2	0.1082
210:C_1	(2, 8, 8)	7	144.3	0.0795
168:C_1	(3, 6, 9)	4	145.8	0.2159
73:C_s	(3, 6, 9)	2	146.8	0.1233
141:C_s	(1, 10, 7)	13	146.9	0.0936
24:C_2	(2, 8, 8)	8	147.1	0.1299
173:C_1	(4, 4, 10)	3	148.0	0.2652
178:C_1	(3, 6, 9)	2	148.1	0.1672
45:C_1	(2, 8, 8)	7	148.7	0.0497
114:C_1	(3, 6, 9)	4	148.8	0.2402
53:C_s	(2, 8, 8)	8	149.2	0.0987
82:C_1	(4, 4, 10)	2	149.3	0.0893
104:C_1	(2, 8, 8)	9	149.8	0.0593
147:C_1	(2, 8, 8)	7	149.9	0.1747
200:C_1	(4, 4, 10)	3	149.9	0.3559
38:C_1	(1, 10, 7)	13	150.3	0.0982
39:C_1	(2, 8, 8)	7	150.8	0.0961
167:C_1	(3, 6, 9)	3	151.5	0.2082
124:C_1	(2, 8, 8)	5	152.6	0.121
157:C_1	(4, 4, 10)	1	152.7	0.3232
125:C_1	(3, 6, 9)	2	152.7	0.3456
217:C_1	(3, 6, 9)	2	152.9	0.3276

159:C_1	(4, 4, 10)	1	154.3	0.2142
113:C_1	(3, 6, 9)	5	154.5	0.2458
241:C_1	(3, 6, 9)	5	154.7	0.3385
183:C_1	(2, 8, 8)	8	156.9	0.1995
97:C_1	(2, 8, 8)	9	157.4	0.0878
158:C_1	(4, 4, 10)	1	157.5	0.3006
239:C_1	(2, 8, 8)	8	157.7	0.2788
184:C_1	(3, 6, 9)	4	158.4	0.2331
112:C_1	(2, 8, 8)	6	158.9	0.053
109:C_1	(2, 8, 8)	8	159.7	0.1609
174:C_1	(3, 6, 9)	3	160.6	0.2353
120:C_1	(2, 8, 8)	5	160.8	0.1096
154:C_1	(3, 6, 9)	3	160.9	0.1802
101:C_1	(3, 6, 9)	6	161.4	0.0962
142:C_2	(2, 8, 8)	6	161.6	0.1017
150:C_s	(3, 6, 9)	3	161.7	0.0301
240:C_s	(3, 6, 9)	3	163.4	0.2266
364:C_s	(5, 2, 11)	0	163.5	0.3152
118:C_1	(2, 8, 8)	6	163.6	0.1465
357:C_s	(5, 2, 11)	0	163.9	0.3945
163:C_1	(4, 4, 10)	1	164.5	0.1667
86:C_1	(3, 6, 9)	4	165	0.1727
123:C_s	(2, 8, 8)	8	165.1	0.2624
356:C_3	(6, 0, 12)	0	165.1	0.0000
42:C_s	(1, 10, 7)	13	167.0	0.0312
189:C_1	(3, 6, 9)	3	167.1	0.2956
363:C_1	(5, 2, 11)	0	167.1	0.0405
138:C_1	(4, 4, 10)	1	167.7	0.0834
151:C_1	(3, 6, 9)	3	167.9	0.0756
108:C_1	(2, 8, 8)	11	168.5	0.0976
110:C_1	(2, 8, 8)	6	168.6	0.165
134:C_1	(3, 6, 9)	3	169.2	0.2479
164:C_1	(4, 4, 10)	1	169.3	0.1342
172:C_1	(4, 4, 10)	2	169.3	0.1318
191:C_s	(3, 6, 9)	5	169.9	0.0576
106:C_1	(2, 8, 8)	8	170.0	0.0861
133:C_1	(3, 6, 9)	3	170.4	0.1034
208:C_2	(2, 8, 8)	7	171.1	0.005
251:D_2	(4, 4, 10)	0	171.9	0.1376
75:C_1	(4, 4, 10)	3	172.0	0.3393
132:C_1	(2, 8, 8)	7	173.4	0.1201
69:C_2	(4, 4, 10)	2	173.8	0.4168
155:C_1	(3, 6, 9)	2	173.8	0.1924
245:C_1	(4, 4, 10)	0	173.8	0.2348

234:C_1	(4, 4, 10)	2	173.9	0.1993
190:C_1	(3, 6, 9)	5	173.9	0.2466
209:C_1	(3, 6, 9)	4	174.9	0.4143
203:C_1	(2, 8, 8)	7	174.9	0.2568
161:C_2	(4, 4, 10)	0	175.2	0.1070
201:C_1	(2, 8, 8)	6	175.3	0.1400
170:D_2	(4, 4, 10)	2	175.6	0.2528
103:C_2	(2, 8, 8)	10	175.7	0.0504
122:C_1	(3, 6, 9)	5	176.6	0.1763
50:C_2	(2, 8, 8)	7	176.8	0.0999
181:C_1	(2, 8, 8)	6	176.8	0.2432
218:C_1	(3, 6, 9)	3	176.9	0.2046
196:C_1	(4, 4, 10)	3	177.3	0.1637
253:D_2	(4, 4, 10)	0	177.3	0.3783
211:C_1	(3, 6, 9)	5	178.4	0.2301
355:C_1	(5, 2, 11)	0	178.5	0.0000
185:C_1	(3, 6, 9)	3	179.0	0.1619
360:C_s	(5, 2, 11)	0	179.2	0.1679
214:C_1	(2, 8, 8)	9	180.2	0.1146
162:C_s	(3, 6, 9)	5	181.6	0.1967
311:C_{2h}	(4, 4, 10)	0	182.0	0.2947
224:C_1	(3, 6, 9)	5	182.0	0.2711
131:C_1	(3, 6, 9)	2	182.6	0.2278
186:C_1	(3, 6, 9)	3	183.7	0.0874
166:C_1	(4, 4, 10)	2	183.9	0.1201
143:C_1	(3, 6, 9)	3	185.3	0.029
139:C_s	(1, 10, 7)	13	185.4	0.0728
235:C_s	(2, 8, 8)	10	185.7	0.2391
259:C_2	(4, 4, 10)	1	186.0	0.3843
176:C_1	(3, 6, 9)	3	186.0	0.2275
275:C_1	(3, 6, 9)	5	186.2	0.1527
216:C_s	(3, 6, 9)	4	187.2	0.0586
229:C_s	(2, 8, 8)	5	187.2	0.1146
354:C_2	(5, 2, 11)	0	188.8	0.2454
140:C_2	(2, 8, 8)	11	189.9	0.0066
278:D_2	(4, 4, 10)	0	190.1	0.1531
121:D_2	(2, 8, 8)	6	190.5	0.1796
187:C_1	(4, 4, 10)	2	190.6	0.3605
249:C_1	(4, 4, 10)	1	191.0	0.2364
231:C_1	(3, 6, 9)	6	191.1	0.0928
252:C_2	(4, 4, 10)	1	191.3	0.1785
222:C_1	(3, 6, 9)	3	191.5	0.0169
48:C_1	(3, 6, 9)	5	191.8	0.1021
256:C_1	(3, 6, 9)	4	192.1	0.0273

238:C_2	(2, 8, 8)	7	193.0	0.0397
197:C_1	(4, 4, 10)	2	193.9	0.0957
213:C_1	(3, 6, 9)	4	194.2	0.1415
207:C_1	(2, 8, 8)	6	194.2	0.0309
274:C_2	(2, 8, 8)	8	194.3	0.1296
281:C_1	(3, 6, 9)	3	195	0.3391
165:C_1	(3, 6, 9)	4	195.2	0.1989
226:C_1	(2, 8, 8)	6	195.3	0.0594
199:C_s	(3, 6, 9)	5	195.5	0.3157
182:D_2	(4, 4, 10)	0	196.1	0.1563
128:C_1	(3, 6, 9)	4	196.5	0.0011
353:C_s	(5, 2, 11)	0	197.3	0.4207
271:C_1	(4, 4, 10)	2	197.6	0.3692
313:D_2	(4, 4, 10)	1	198.1	0.0527
292:C_1	(4, 4, 10)	1	198.1	0.1097
289:C_2	(4, 4, 10)	2	198.9	0.3046
248:C_1	(4, 4, 10)	1	199.3	0.3051
127:C_1	(3, 6, 9)	4	200.6	0.0284
129:C_s	(3, 6, 9)	4	200.8	0.0542
220:C_1	(3, 6, 9)	4	201.5	0.1257
243:C_1	(3, 6, 9)	3	201.6	0.2373
193:C_s	(3, 6, 9)	9	201.7	0.1453
225:C_2	(4, 4, 10)	0	201.7	0.3637
117:C_1	(3, 6, 9)	3	202.2	0.1936
293:C_s	(4, 4, 10)	0	203.3	0.1125
230:C_1	(3, 6, 9)	6	203.4	0.0683
194:C_1	(3, 6, 9)	6	204.3	0.0699
250:C_2	(4, 4, 10)	0	204.4	0.0914
137:C_1	(4, 4, 10)	1	204.5	0.2693
192:C_1	(3, 6, 9)	4	204.6	0.0622
242:C_1	(3, 6, 9)	4	205.5	0.0282
156:C_2	(4, 4, 10)	1	206.2	0.3983
115:C_1	(3, 6, 9)	4	206.9	0.0293
237:C_1	(3, 6, 9)	4	206.9	0.1695
254:C_{2h}	(4, 4, 10)	0	207.1	0.1452
301:C_1	(3, 6, 9)	5	207.3	0.1062
303:C_2	(2, 8, 8)	9	208.8	0.1816
227:C_1	(3, 6, 9)	3	209.2	0.1614
272:C_s	(3, 6, 9)	2	210.3	0.254
273:C_1	(3, 6, 9)	4	211.3	0.2292
221:C_1	(2, 8, 8)	6	211.6	0.0527
206:C_1	(3, 6, 9)	5	212.4	0.1775
291:C_s	(3, 6, 9)	4	216.6	0.0971
228:C_1	(3, 6, 9)	5	217.6	0.2271

204:C_1	(3, 6, 9)	4	217.6	0.0808
255:C_1	(4, 4, 10)	2	218.1	0.2174
80:C_2	(4, 4, 10)	3	218.2	0.0921
280:C_s	(3, 6, 9)	4	218.5	0.1588
359:C_s	(5, 2, 11)	0	218.7	0.3861
263:C_s	(3, 6, 9)	4	218.8	0.0905
205:C_1	(3, 6, 9)	3	219.3	0.2384
202:C_1	(2, 8, 8)	7	219.4	0.1277
135:C_1	(3, 6, 9)	3	220.2	0.2036
188:C_1	(4, 4, 10)	2	220.3	0.3108
257:C_s	(4, 4, 10)	1	221.1	0.3739
270:C_1	(3, 6, 9)	6	221.4	0.0205
236:C_{2h}	(2, 8, 8)	8	222.3	0.1232
279:C_1	(4, 4, 10)	2	225.1	0.0386
244:C_1	(3, 6, 9)	4	225.2	0.0557
232:C_1	(3, 6, 9)	4	225.8	0.1280
152:C_{2v}	(3, 6, 9)	2	226.0	0.0096
195:C_1	(3, 6, 9)	5	226.5	0.0555
294:C_1	(3, 6, 9)	4	226.6	0.1323
269:C_1	(3, 6, 9)	4	228.3	0.1392
219:C_1	(4, 4, 10)	1	228.5	0.0521
268:C_1	(4, 4, 10)	1	229.3	0.1486
246:C_1	(4, 4, 10)	2	229.9	0.2147
175:D_2	(4, 4, 10)	2	231.7	0.1788
342:C_s	(5, 2, 11)	0	232.1	0.0000
276:C_s	(3, 6, 9)	5	234.3	0.2091
288:C_1	(4, 4, 10)	2	234.7	0.2232
282:C_1	(3, 6, 9)	3	234.9	0.1606
286:C_1	(3, 6, 9)	7	235.5	0.1983
362:C_s	(5, 2, 11)	0	235.5	0.061
309:C_1	(3, 6, 9)	4	237.2	0.2158
295:C_s	(4, 4, 10)	2	237.9	0.0887
267:C_1	(4, 4, 10)	2	237.9	0.0937
247:C_3	(3, 6, 9)	3	238.3	0.3872
297:C_2	(4, 4, 10)	0	240.6	0.294
287:C_1	(4, 4, 10)	2	242.7	0.2107
283:C_1	(3, 6, 9)	4	246.9	0.194
277:C_1	(2, 8, 8)	8	247.2	0.1294
149:C_2	(4, 4, 10)	2	248.1	0.3693
312:C_1	(3, 6, 9)	5	248.1	0.1707
260:C_1	(3, 6, 9)	3	251.4	0.3315
233:C_2	(4, 4, 10)	2	253.4	0.0827
302:D_2	(2, 8, 8)	10	254.6	0.1512
198:C_1	(4, 4, 10)	2	255.7	0.0683

304:C_1	(3, 6, 9)	3	256.2	0.1834
212:C_1	(4, 4, 10)	2	256.4	0.1998
261:C_1	(4, 4, 10)	1	257.1	0.1120
308:C_1	(3, 6, 9)	3	259.2	0.2332
305:C_1	(3, 6, 9)	5	260.2	0.1705
322:C_s	(2, 8, 8)	12	260.6	0.1714
262:C_s	(3, 6, 9)	5	260.7	0.2412
264:C_1	(4, 4, 10)	3	260.9	0.1675
361:C_1	(5, 2, 11)	0	260.9	0.1221
285:D_2	(2, 8, 8)	6	266.0	0.0430
306:C_2	(4, 4, 10)	0	266.1	0.0429
258:C_2	(4, 4, 10)	2	267.1	0.3473
358:C_1	(5, 2, 11)	0	268.4	0.3113
284:D_2	(3, 6, 9)	4	273.2	0.2955
307:C_1	(4, 4, 10)	3	273.6	0.3033
310:C_1	(4, 4, 10)	1	274.1	0.1646
290:D_2	(4, 4, 10)	2	274.9	0.1815
343:C_s	(5, 2, 11)	0	277.7	0.0286
299:C_1	(4, 4, 10)	3	280.2	0.1857
315:C_1	(4, 4, 10)	5	280.2	0.0838
300:C_2	(4, 4, 10)	5	282.8	0.1125
327:C_1	(3, 6, 9)	5	283.3	0.1028
265:C_1	(4, 4, 10)	3	283.5	0.1332
316:C_1	(4, 4, 10)	0	283.5	0.2725
334:D_2	(2, 8, 8)	8	283.6	0.1885
298:C_1	(4, 4, 10)	3	284.3	0.2452
296:C_s	(4, 4, 10)	2	291.1	0.2862
317:C_1	(3, 6, 9)	5	294.9	0.1177
351:C_s	(5, 2, 11)	0	295.3	0.1942
319:C_1	(3, 6, 9)	5	295.4	0.2743
328:C_1	(4, 4, 10)	2	295.4	0.0329
314:C_2	(4, 4, 10)	2	296.8	0.3688
266:C_s	(4, 4, 10)	3	296.9	0.3336
344:C_1	(5, 2, 11)	0	298.2	0.2104
318:C_2	(4, 4, 10)	1	298.5	0.0286
348:C_1	(5, 2, 11)	0	298.7	0.208
337:C_2	(4, 4, 10)	2	299.9	0.0117
321:C_1	(4, 4, 10)	0	300.6	0.0361
331:C_s	(4, 4, 10)	2	301.9	0.0546
345:C_1	(5, 2, 11)	0	302.9	0.1762
329:C_1	(4, 4, 10)	1	303.8	0.0288
346:C_1	(5, 2, 11)	0	310.2	0.1086
332:C_s	(4, 4, 10)	3	315.5	0.0763
320:C_1	(3, 6, 9)	4	317.5	0.0896

325:C_1	(4, 4, 10)	2	317.8	0.1981
347:C_2	(6, 0, 12)	0	319.8	0.2489
336:C_2	(4, 4, 10)	2	321.4	0.3297
323:C_1	(3, 6, 9)	4	322.6	0.1485
324:C_1	(4, 4, 10)	1	326.6	0.1004
350:C_2	(6, 0, 12)	0	326.8	0.2585
335:C_1	(4, 4, 10)	0	328.9	0.2379
338:C_1	(4, 4, 10)	2	330.2	0.1475
330:C_1	(4, 4, 10)	1	331.9	0.1745
339:C_1	(4, 4, 10)	2	338.3	0.183
326:C_1	(4, 4, 10)	1	347.0	0.0792
349:C_1	(5, 2, 11)	0	352.8	0.3553
352:C_1	(5, 2, 11)	0	355.1	0.276
333:C_2	(4, 4, 10)	1	377.0	0.1124
341:C_{2h}	(4, 4, 10)	2	401.4	0.1618
340:C_2	(4, 4, 10)	2	405.0	0.1727

[a] Heat of formation obtained at AM1 level, units in kilocalories per mole; band gap calculated at the HMO level, in units of $|\beta|$, where β is the Hückel resonance integral. [b] Numbering convention of isomers recommended in ref 41. [c] Ring Index: number of four-, five-, and six- membered rings. [d] PA: number of pentagon adjacency.

Table S2 Relative energies of the most stable C_{32} fullerene isomers[a]

label:*sym*	B3LYP/6-31G(d)	B3LYP/6-311G(d, p)	PBE1PBE/6-311G(d, p)	HF/6-311G(d, p)
32:D_{4d}	**0**	**0**	**0**	**0**
1: D_3	4.17	2.93	2.42	11.11
5:C_s	10.21	9.63	9.54	16.24

[a] Relative energy units in kilocalories per mole.

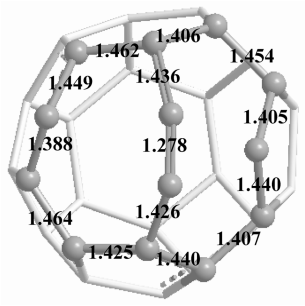


Fig. S1 Transition state of rearrangement between **32** and **5** (TS1-A). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

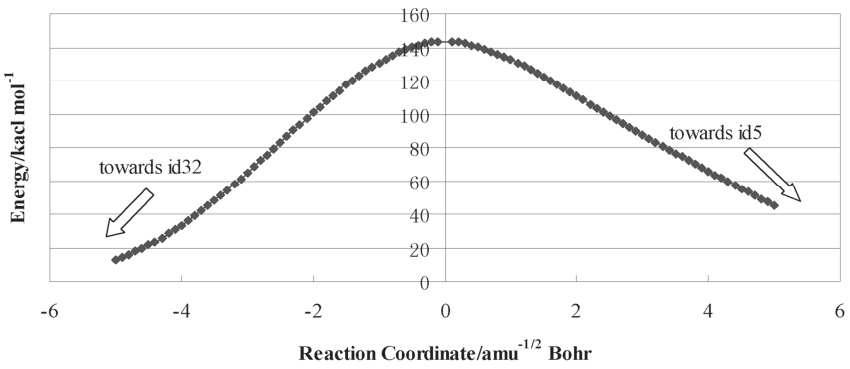
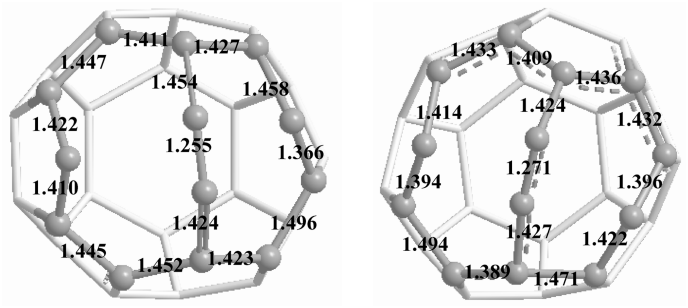
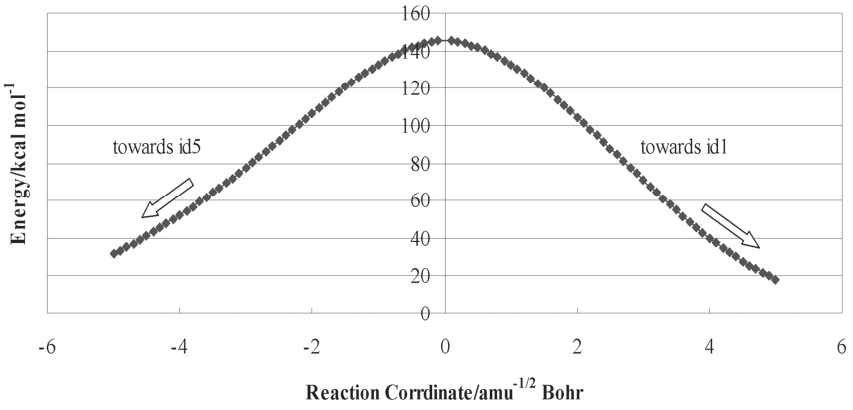


Fig. S2 Plot of the intrinsic reaction coordinate (in amu$^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS1-A as computed at the PBE1PBE/6-31G(d) level of theory.

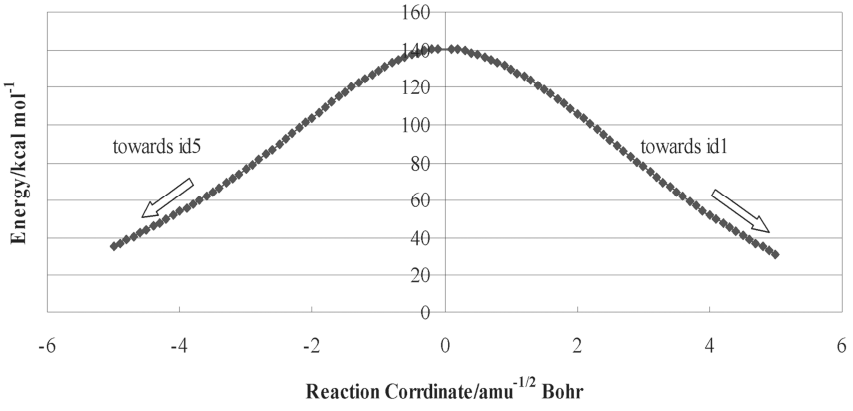


TS2-Aa TS2-Ab

Fig. S3 Transition states of rearrangement between **5** and **1** (TS2-Aa and TS2-Ab). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.



IRC starting from TS2-Aa



IRC starting from TS2-Ab

Fig. S4 Plot of the intrinsic reaction coordinate (in amu$^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS2-Aa and TS2-Ab as computed at the PBE1PBE/6-31G(d) level of theory.

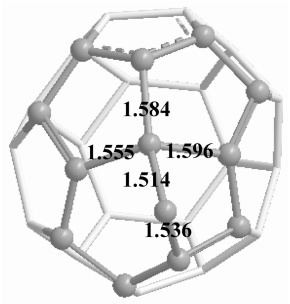


Fig. S5 Transition state of rearrangement between **32** and **5** (TS1-B1). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

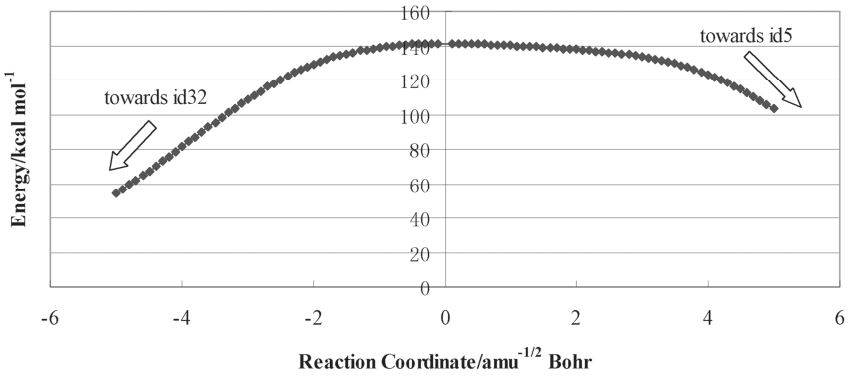


Fig. S6 Plot of the intrinsic reaction coordinate (in $amu^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS1-B1 as computed at the PBE1PBE/6-31G(d) level of theory.

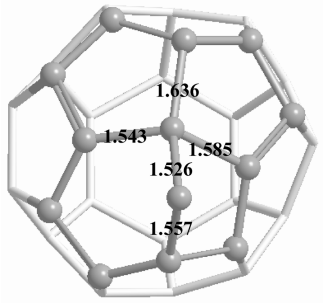


Fig. S7 Transition state of rearrangement between **5** and **1** (TS2-B1c). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

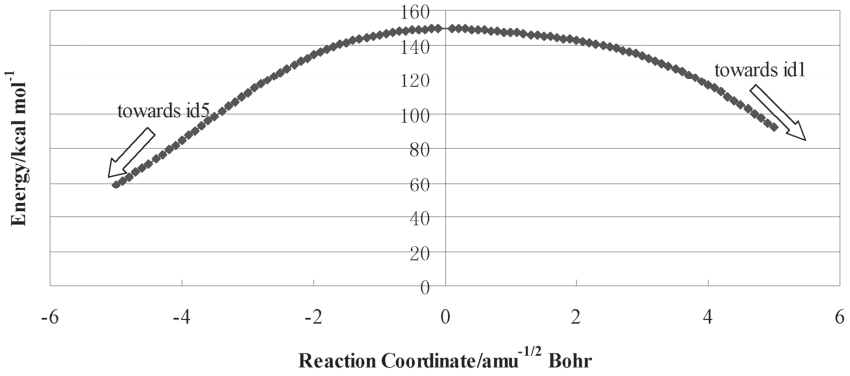


Fig. S8 Plot of the intrinsic reaction coordinate (in $amu^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS2-B1c as computed at the PBE1PBE/6-31G(d) level of theory.

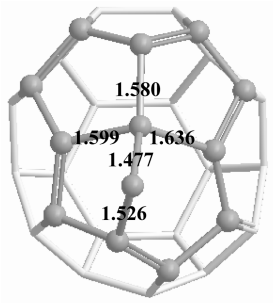


Fig. S9 Transition state of rearrangement between **5** and **1** (TS2-B1d). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

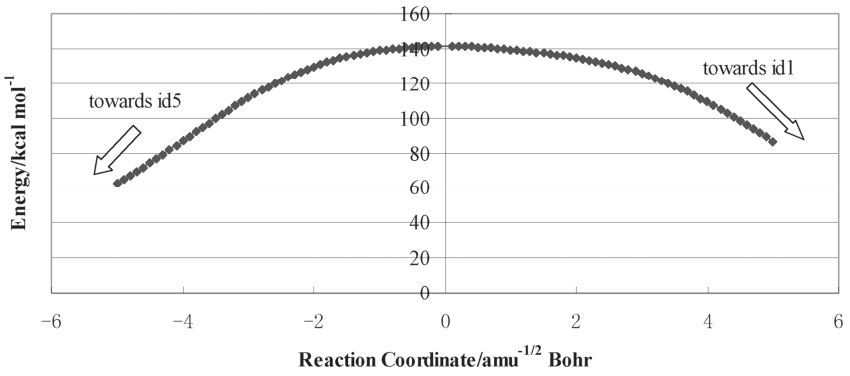


Fig. S10 Plot of the intrinsic reaction coordinate (in $amu^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS2-B1d as computed at the PBE1PBE/6-31G(d) level of theory.

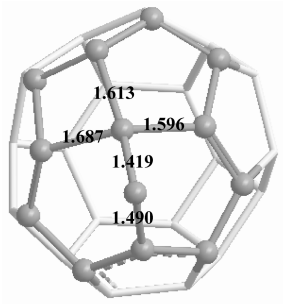


Fig. S11 Transition state of rearrangement between **32** and **5** (TS1-B2). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

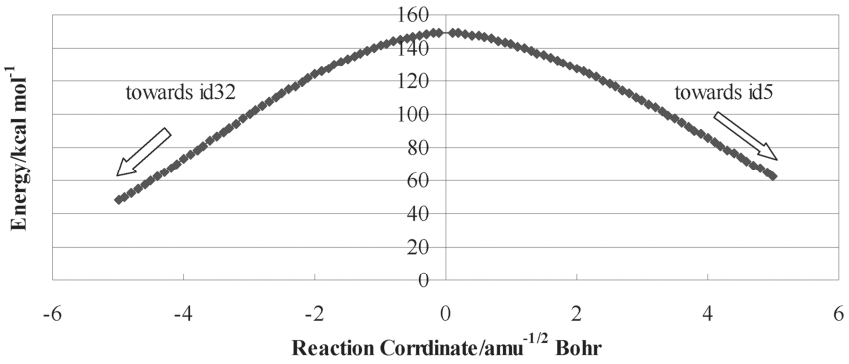


Fig. S12 Plot of the intrinsic reaction coordinate (in amu$^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS1-B2 as computed at the PBE1PBE/6-31G(d) level of theory.

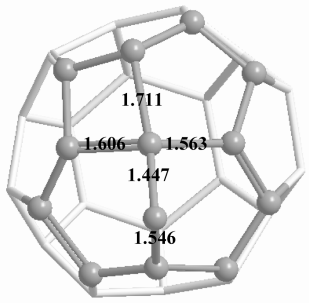


Fig. S13 Transition state of rearrangement between **5** and **1** (TS2-B2e). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

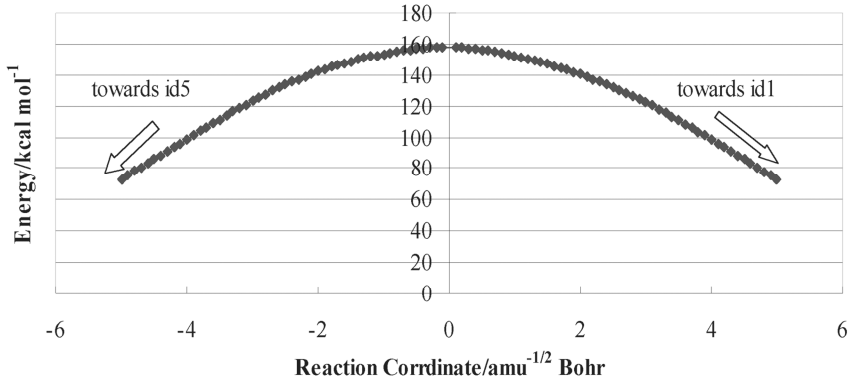


Fig. S14 Plot of the intrinsic reaction coordinate (in amu$^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS2-B2e as computed at the PBE1PBE/6-31G(d) level of theory.

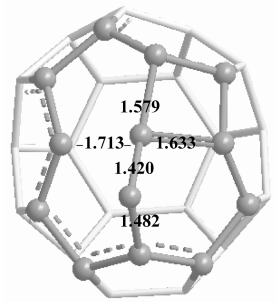


Fig. S15 Transition state of rearrangement between **5** and **1** (TS2-B2f). Bond lengths (in Å) obtained at PBE1PBE/6-31G(d) level of theory.

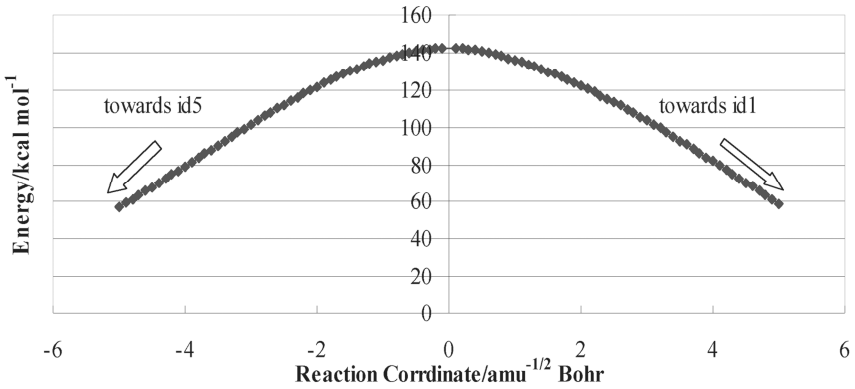
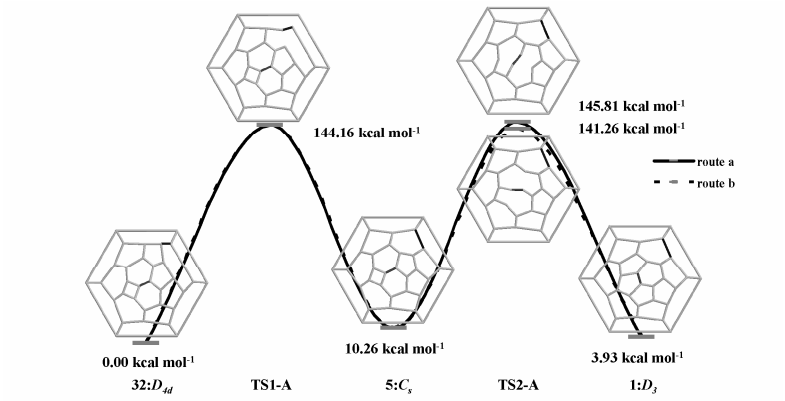
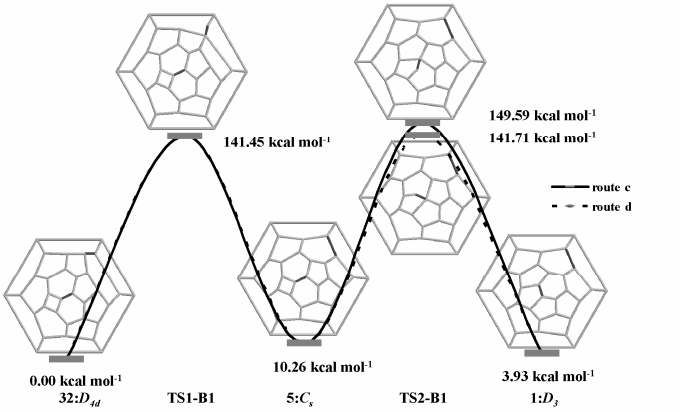


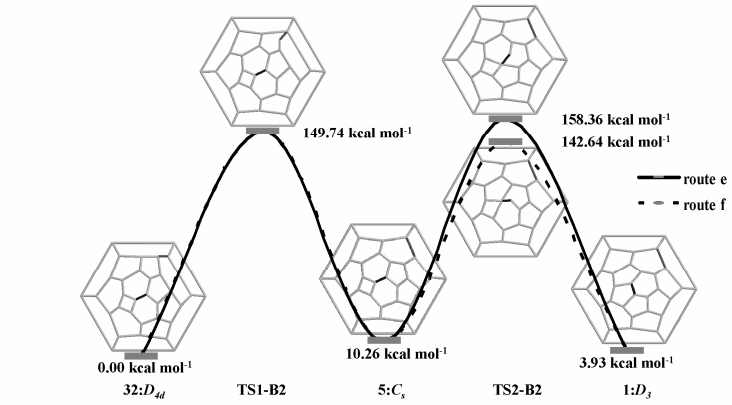
Fig. S16 Plot of the intrinsic reaction coordinate (in amu$^{-1/2}$ Bohr) versus energy (in kcal mol^{-1}, relative to **32**, starting from TS2-B2f as computed at the PBE1PBE/6-31G(d) level of theory.



Scheme S1. The GSWT relationship and transition states (TS1-A, TS2-Aa and TS2-Ab) between **32**:D_{4d}, **5**:C_s and **1**:D_3 of concerted reaction mechanism. Relative energies of structures (in kcal mol^{-1}) at PBE1PBE/6-31G(d) level of theory.



Scheme S2. The GSWT relationship and transition states (TS1-B1, TS2-B1c and TS2-B1d) between **32**:D_{4d}, **5**:C_s and **1**:D_3 of stepwise reaction mechanism. Relative energies of structures (in kcal mol^{-1}) obtained at PBE1PBE/6-31G(d) level of theory.



Scheme S3. The GSWT relationship and transition states (TS1-B2, TS2-B2e and TS2-B2f) between **32**:D_{4d}, **5**:C_s and **1**:D_3 of stepwise reaction mechanism. Relative energies of structures (in kcal mol^{-1}) obtained at PBE1PBE/6-31G(d) level of theory.