[Supporting Information]

Theoretical investigations of *sp*-*sp*^{2} hybridized zero-dimensional fullerenynes

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Methods

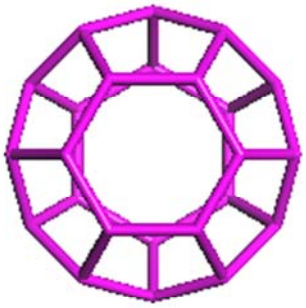
First-principles DFT calculations were performed within the generalized–gradient approximation (GGA) implemented in the DMol3 software. The Perdew, Burke, and Ernzerhof (PBE) exchange–correlation functional is used. All fullerenyne nanostructures are optimized without any symmetry constraints. Double numerical basis sets including polarization functions on all atoms (DNP) are used in the calculations.[1,2] The DNP basis set corresponds to a double–ζ quality basis set with a p–type polarization function added to hydrogen and d–type polarization functions added to heavier atoms. The global cutoff radius is set to be 3.7 Å. The convergence criteria applied during geometry optimization is 1.0×10^{-6} Hartree for energy. All atoms are relaxed until the force on each atom is less than 0.002 Ha/Å. Smearing of 0.0001 Ha is used for these systems to accelerate SCF convergence. For corroborating the stable structures, the vibrational frequency calculations have been performed, which further verify the true minima of the potential energy surface of all nanostructures. In addition, the binding energy per atom is calculated in order to analyze the relative stability of clusters with different structures.[3] We have defined the average binding energy (E_b) as the energy gained in assembling the fullerenyne nanocages from its isolated constituent atoms. Hence, the binding energies of fullerenynes are calculated by Equation:

$$E_b = \left(nE_C - E_{system} \right) \Big/ n \,,$$

where E_C is the sum of the energies of individual carbon atoms; E_t is the total energy of the system.

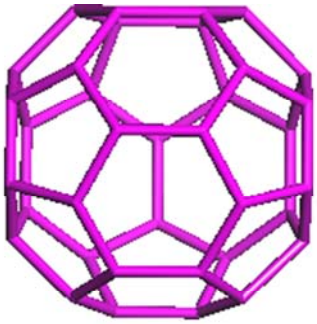
The molecular dynamics simulation (MD), with the simulation package GULP, was performed for C_{96} fullerene based on ReaxFF force field at temperatures 298K and 300-1100 K. All simulations were performed under constant temperature and constant volume (NVT) conditions. The semiclassical reactive force field (ReaxFF) method by van Duin and co-workers[4] is apparently computationally much more economical and enables the simulation on a nanosecond time scale. ReaxFF energetics of π-conjugated species are generally in good agreement with quantum chemical DFT benchmark data by virtue of the empirical parametrization.[5] C_{96} fullerene was allowed to equilibrate for 4000 ps with a time step of 1 fs. We simulated the C_{96} fullerene at 100 K intervals from 300 K to 1100 K. In addition, we calculated the production stage of MD simulation for 5000 ps in this study.

C_{24}

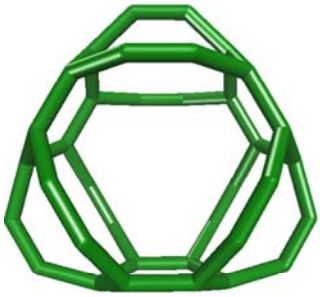


D_{3d} $E_b = 5.655$ eV

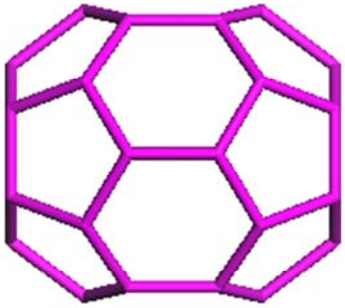
D_{6d} $E_b = 5.867$ eV



C_{36}



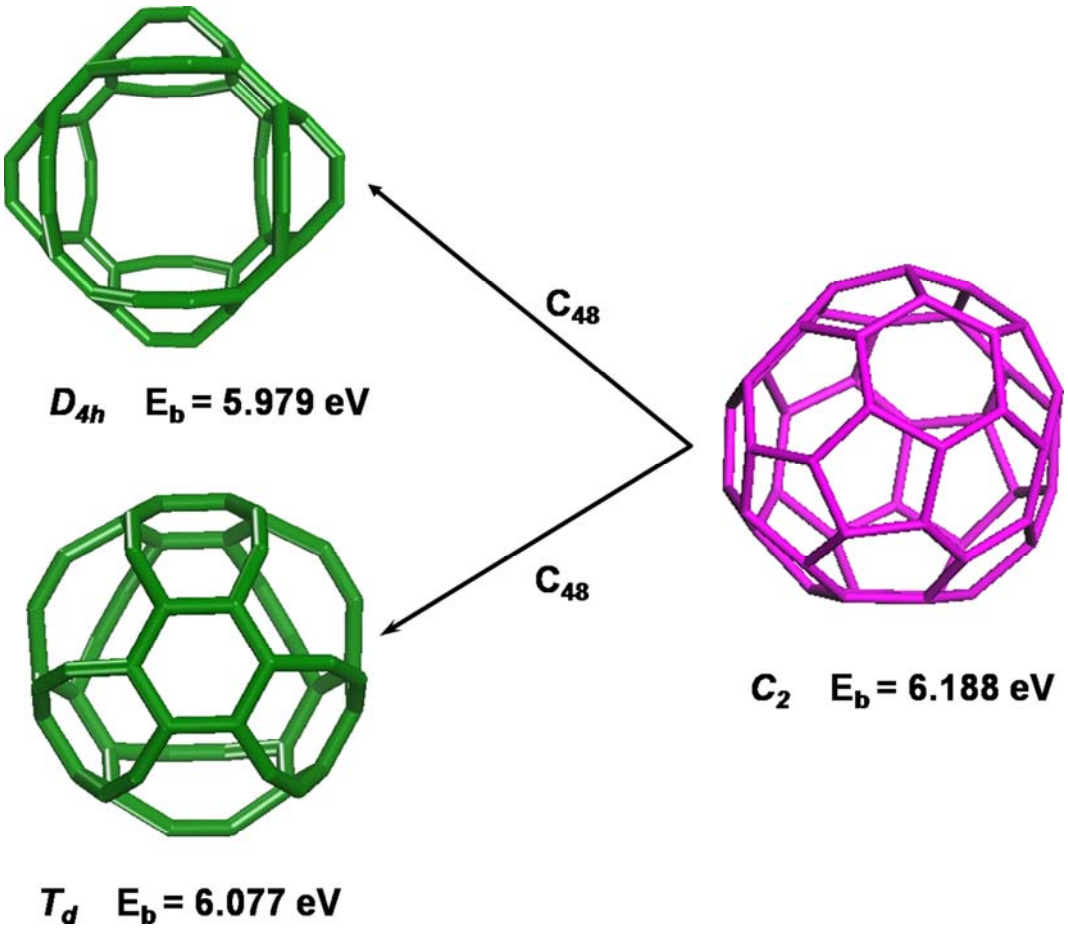
C_{36}

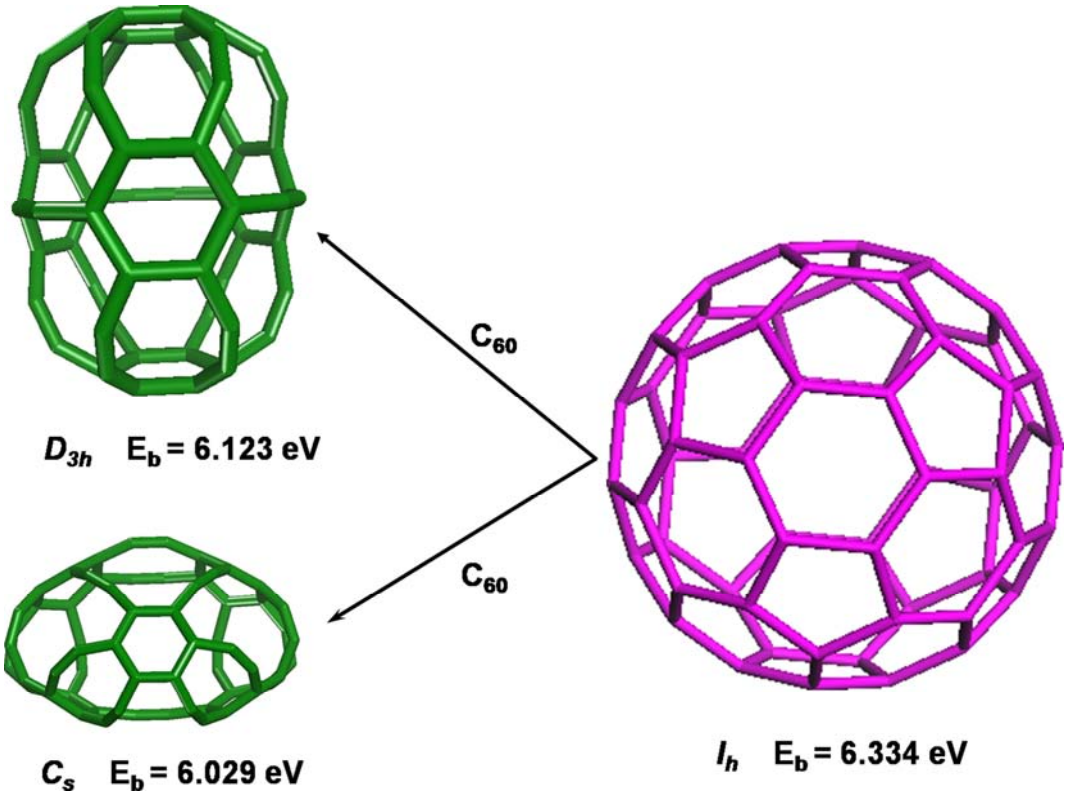


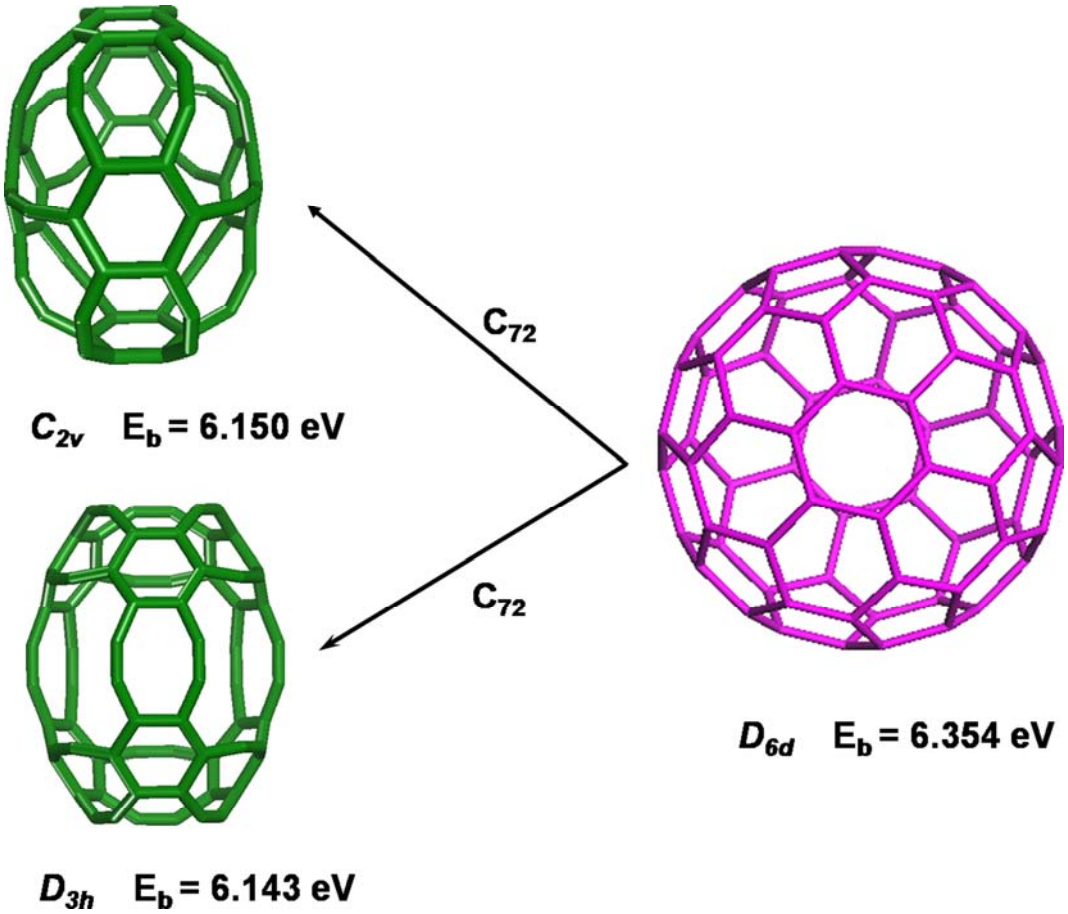
D_{2d} $E_b = 6.030$ eV

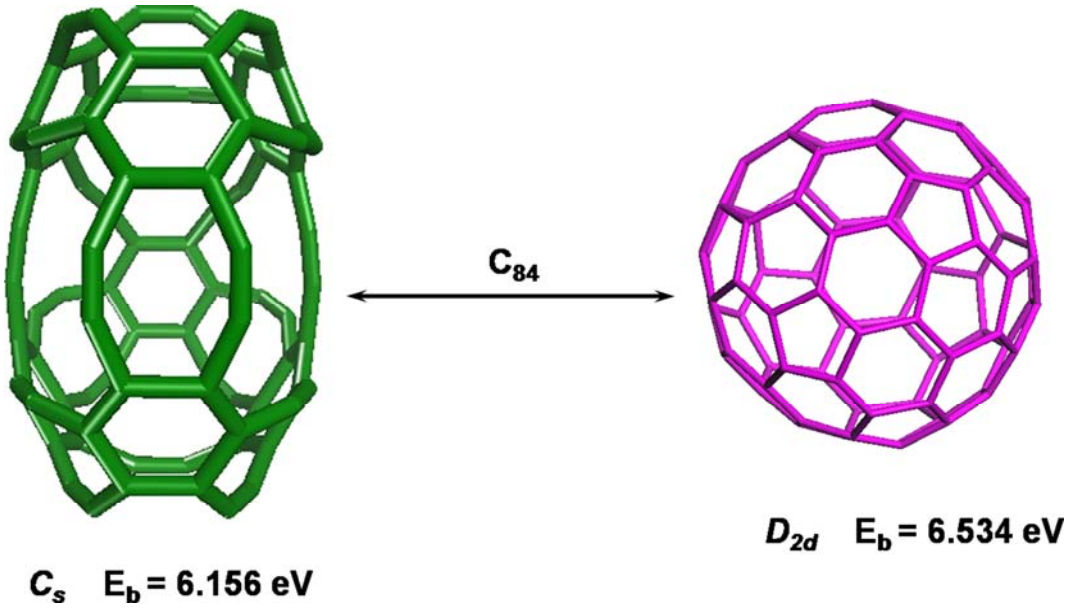
D_{3h} $E_b = 5.917$ eV

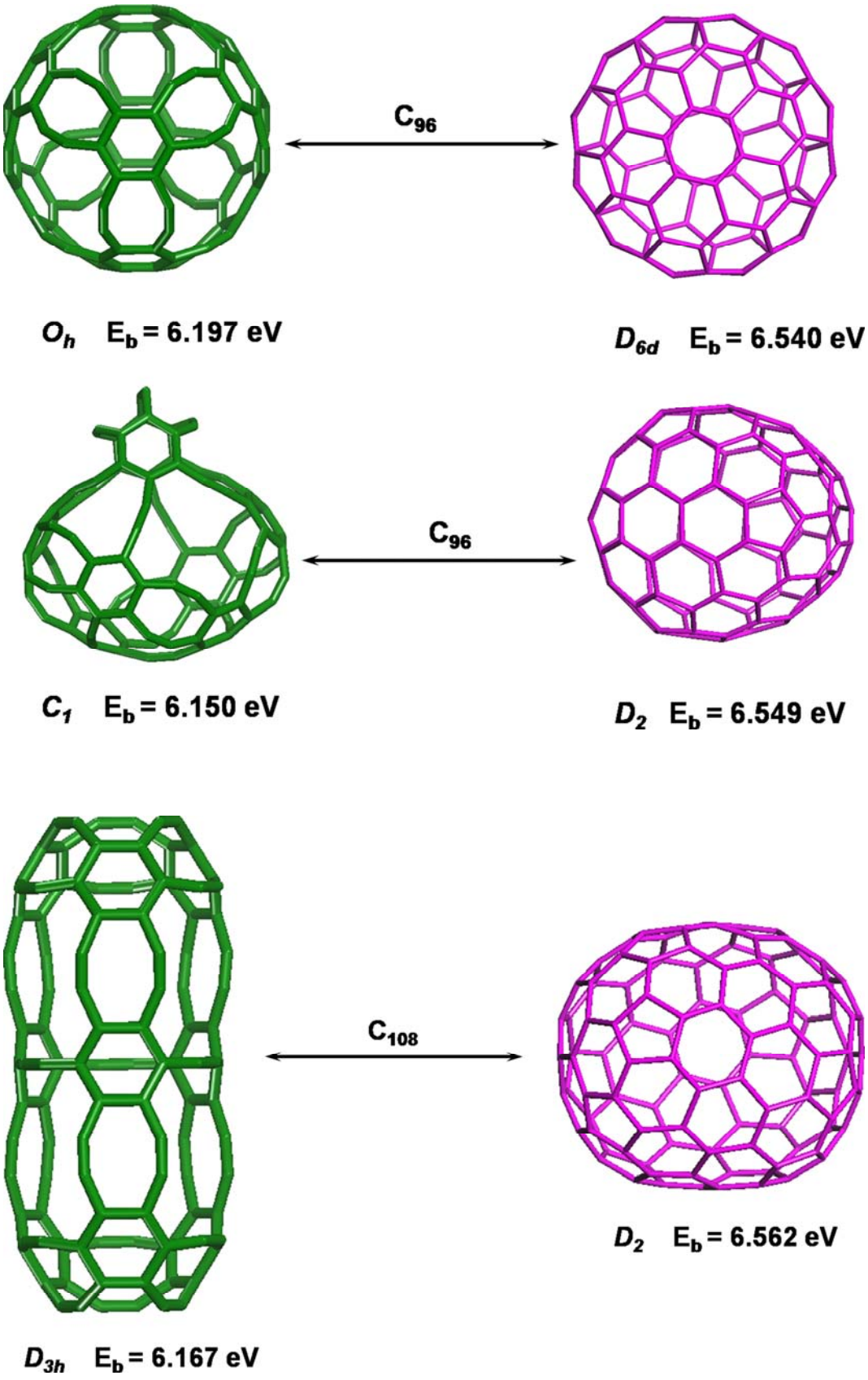
D_{6h} $E_b = 6.028$ eV











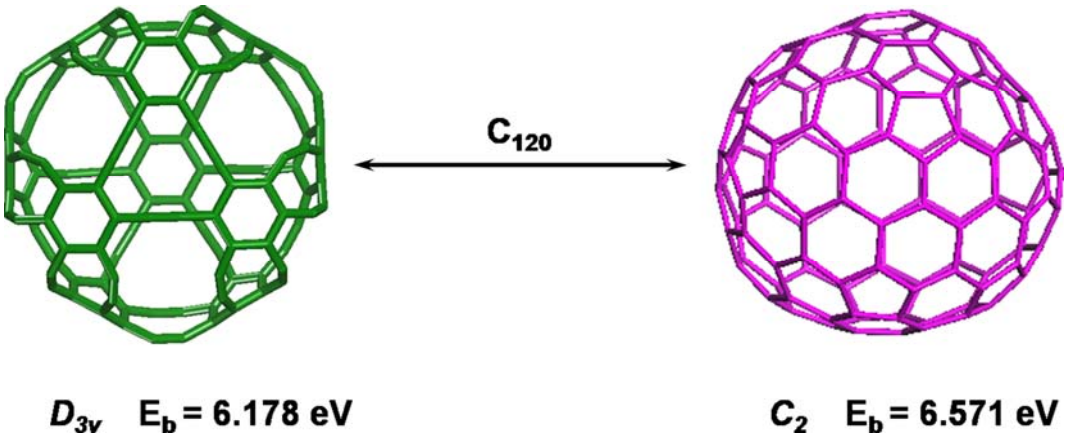


Fig. S1 All *sp*-*sp*^{2} hybridized fullerenyne models from C_{24} to C_{120} with different symmetry groups and binding energies, and the corresponding closest (in molecular weight) non-*sp*-*sp*^{2} hybridized fullerene structures. The green carbon models and pink carbon models present fullerenyne and fullerene, respectively. Herein, the corresponding closest non-*sp*-*sp*^{2} hybridized fullerene structures are very stable from the available reports[6,7].

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5 K. D. Nielson, A. C. T. van Duin, J. Oxgaard, W.Q. Deng and W. A. Goddard III, *J. Phys. Chem. A,* 2005, **109**, 493.

6 N. Shao, Y. Gao, S. Yoo, W. An and X. C. Zheng, *J. Phys. Chem. A,* 2006, **110**, 7672.

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Table S1. All the fullerenynes (C_n) with the corresponding symmetry groups and energy gaps (eV).

C_n	Symmetry group	Energy gap (eV)
C_{24}	D_{3d}	1.44
C_{36}	D_{3h}	0.52
C_{48}	D_{4h}	0.55
C_{48}	T_d	1.30
C_{60}	D_{3h}	1.30
C_{60}	C_s	0.48
C_{72}	C_{2v}	0.52
C_{72}	D_{3h}	0.85
C_{84}	C_s	0.76
C_{96}	O_h	0.74
C_{96}	C_1	0.51
C_{108}	D_{3h}	0.50
C_{120}	C_{3v}	0.50

The xyz coordinate of C_{96} fullernenyne with O_h symmetry group is presented.

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C_{96} O_h symmetry

C	-15.060636088	17.012519404	13.898834175
C	-16.910977158	15.159458108	13.735916054
C	-16.257024318	15.218795828	14.993930871
C	-16.885336736	12.902482620	15.592722534
C	-15.225681830	16.250529231	15.084824431
C	-14.221322835	16.154253664	16.060159889
C	-16.244497445	14.134348204	15.885266157
C	-15.198853354	14.037117219	16.902201426
C	-12.972603450	16.814766894	15.929229280
C	-14.208830631	15.027815269	16.989599727
C	-12.951350389	14.792571201	17.602123749
C	-15.016558985	12.732050222	17.425864901
C	-11.743260163	16.816826615	15.924795007
C	-11.722041929	14.794811313	17.594906480
C	-10.474780042	15.039071155	16.963730601
C	-9.647954008	12.748039387	17.383904669
C	-10.487952245	16.164771135	16.033075991
C	-9.502735071	16.267968682	15.039683342

C	-9.480393822	14.054525039	16.858402561
C	-8.456386629	14.158160544	15.820266617
C	-9.693252834	17.028632256	13.856535397
C	-8.466147467	15.243229694	14.929692335
C	-7.832280046	15.188187674	13.661902413
C	-7.813082748	12.930649760	15.515569793
C	-16.886179962	11.677394716	15.481161980
C	-16.899706080	9.816613510	13.228222804
C	-16.246807548	9.521264351	14.453066542
C	-15.039720308	7.978295735	13.034023094
C	-16.239694874	10.415312001	15.535507052
C	-15.194301971	10.320658439	16.552134909
C	-15.207934359	8.498881861	14.342535139
C	-14.205179080	8.407789569	15.320220368
C	-15.012266774	11.507462409	17.309030964
C	-14.197431084	9.339216540	16.444901554
C	-12.940757346	9.464119887	17.090600000
C	-12.952854958	7.789956525	15.069522661
C	-9.647018873	11.523290486	17.268228238
C	-11.711455258	9.465351586	17.084334811
C	-10.464045600	9.348775447	16.418310192
C	-11.723470442	7.792983105	15.063476265

C	-9.471975470	10.337050038	16.508228477
C	-8.448137780	10.440091964	15.470377295
C	-10.470396155	8.417321500	15.293046687
C	-9.485745560	8.514701905	14.297977125
C	-7.810480525	11.705480994	15.405042045
C	-8.453470768	9.545520000	14.388715557
C	-7.819773680	9.842878676	13.154441191
C	-9.668867323	7.991646411	12.992247306
C	-15.066113261	17.135093816	12.674792425
C	-16.915466363	15.283304813	12.511993605
C	-16.281646624	15.581296166	11.278017193
C	-16.927090168	13.423126406	10.259835315
C	-15.249179679	16.612002974	11.369200206
C	-14.265421423	16.710664191	10.373343517
C	-16.287836651	14.687762665	10.195533007
C	-15.264059952	14.791098451	9.157671654
C	-13.012430610	17.335506931	10.602238455
C	-14.272116005	15.779589288	9.247754124
C	-13.024745040	15.662617003	8.581737957
C	-15.087555646	13.604834726	8.398133166
C	-11.783122626	17.338049811	10.596407895
C	-11.795393640	15.664434829	8.575265128

C	-10.538643031	15.788862551	9.220916868
C	-9.724103000	13.620545966	8.356507050
C	-10.530809838	16.720180300	10.345742108
C	-9.528710594	16.628082392	11.323940782
C	-9.541833922	14.807439737	9.113350116
C	-8.496202555	14.712831074	10.129739048
C	-9.696602390	17.149065717	12.632223066
C	-8.489614042	15.605896339	11.212989071
C	-7.837104690	15.309150865	12.437729868
C	-7.849196730	13.450959147	10.183790545
C	-16.925042743	12.198085088	10.147873531
C	-16.904319239	9.943324642	12.004542469
C	-16.271029825	9.886581371	10.736555706
C	-15.045058962	8.100222429	11.809868575
C	-16.281342458	10.970434267	9.844439803
C	-15.256938889	11.073811340	8.806968896
C	-15.234301251	8.861938593	10.627262457
C	-14.248928235	8.964463157	9.633843988
C	-15.089919158	12.380230083	8.280953649
C	-14.261983839	10.089652932	8.702668497
C	-13.014245969	10.335720328	8.073016978
C	-12.993293801	8.313394418	9.744043018

C	-9.720161465	12.395920661	8.240544621
C	-11.784890870	10.335000635	8.064777694
C	-10.527268836	10.100035958	8.677473957
C	-11.764083480	8.315560749	9.740461020
C	-9.537226079	11.090959875	8.764227031
C	-8.491277693	10.993976932	9.780518971
C	-10.514822326	8.974744554	9.607519894
C	-9.510286139	8.878885176	10.582845732
C	-7.849863560	12.225879215	10.071777251
C	-8.478661216	9.910178599	10.672899994
C	-7.824844345	9.970567442	11.930944352
C	-9.675279603	8.116608547	11.768436437