

Supporting Information

Evidence for a ball-shaped cyclen cyclophane: an experimental and first principles study

Jonathan P. Hill, Roberto Scipioni, Mauro Boero, Yutaka Wakayama, Misaho Akada, Tsuyoshi

Miyazaki, and Katsuhiko Ariga

Contents

General procedures.

- Figure S1.** Proton NMR spectra of **1-1** in various solvents.
- Figure S2.** MALDI-TOF-MS spectrum of **1** using dithranol as matrix.
- Figure S3.** ^{13}C -NMR spectrum of **1-1**.
- Figure S4.** Expansions of the ^1H - ^1H COSY spectrum of **1** in $\text{DMSO-}d_6$.
- Figure S5.** Full ^1H - ^1H COSY spectrum of **1** in $\text{DMSO-}d_6$.
- Figure S6.** ^1H - ^1H COSY spectrum of **1** in pyridine- d_5 .
- Figure S7.** ^1H - ^1H NOESY spectrum of **1** in pyridine- d_5 .
- Figure S8.** Assignment of 1-D spectra of **1**.
- Figure S9.** Integrated difference spectrum of **1-1**.
- Figure S10.** Powder X-ray diffraction pattern of **1**.
- Figure S11.** Structure of the (A) HOMO and (B) LUMO for the box-like conformer **1-2**.

General Procedures.

Solvents and chemicals were obtained from Tokyo Kasei Chemical Co. Ltd., Wako Chemical Co. Ltd. or Nacalai Tesque Chemical Co. Ltd. and used without further purification. MALDI-TOF mass spectra were obtained using a Kratos-Shimadzu Axima CFR+ instrument employing dithranol as matrix. NMR spectra were collected using JEOL AL300BX spectrometer operating at 300.4 or 75 MHz for ^1H and ^{13}C , respectively. Variable-temperature measurements (VT- ^1H -NMR) were performed using the appropriate JEOL temperature control unit (temperature fluctuation ± 0.3 °C). Powder X-ray diffraction was performed using a Rigaku RINT III diffractometer with Cu K α radiation.

Figure S1. Proton NMR spectra of **1-1** in various solvents illustrating only slight changes caused by differing solvent polarities. Top: low field region; bottom: high field region, in solvents: (a) CDCl_3 ; (b) CD_2Cl_2 ; (c) $\text{DMSO}-d_6$; (d) CD_3CN ; (e) Pyridine- d_5 . Asterisk denotes residual solvents or HOD/ H_2O

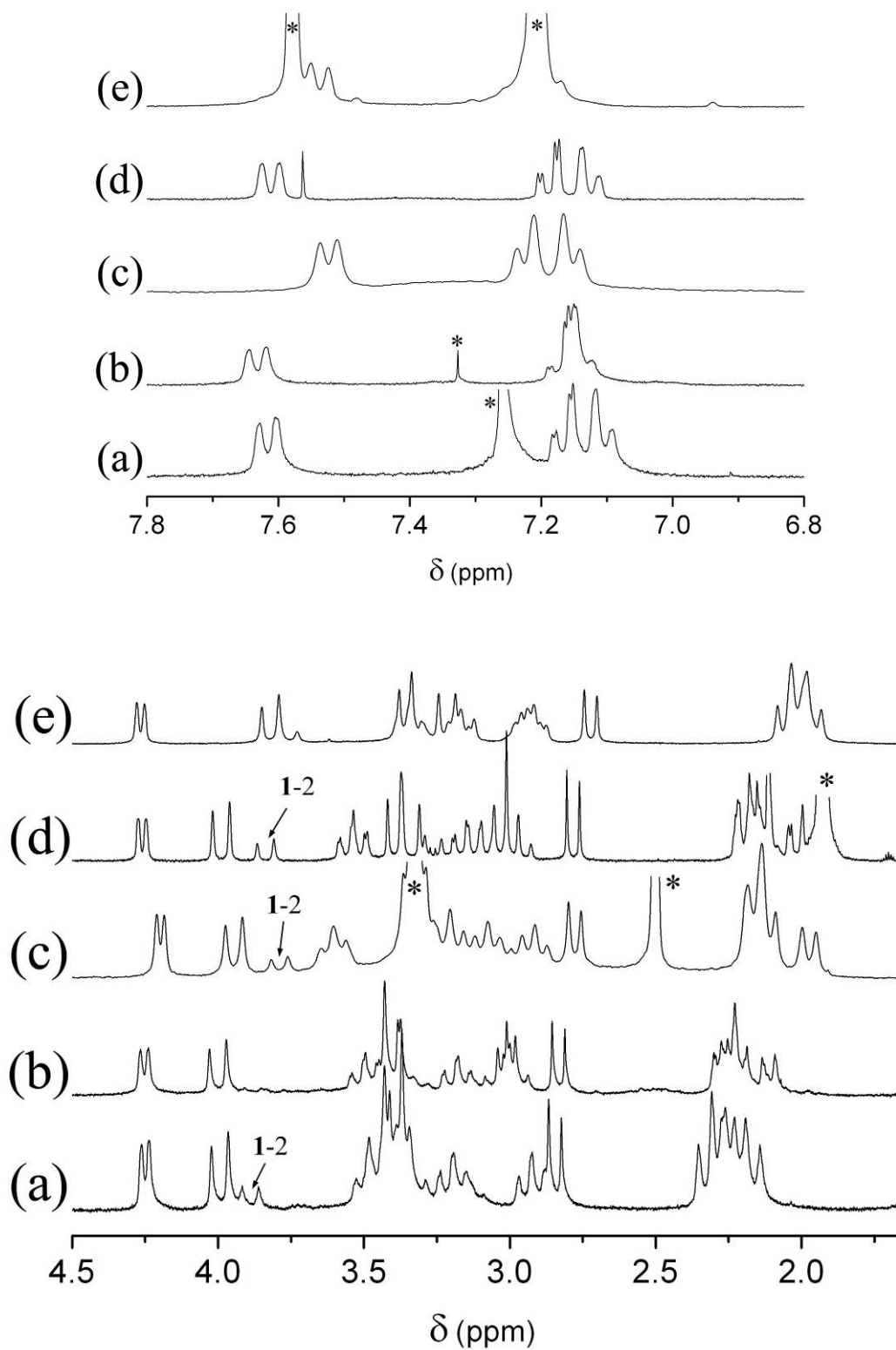


Figure S2. MALDI-TOF-MS spectrum of **1** using dithranol as matrix.

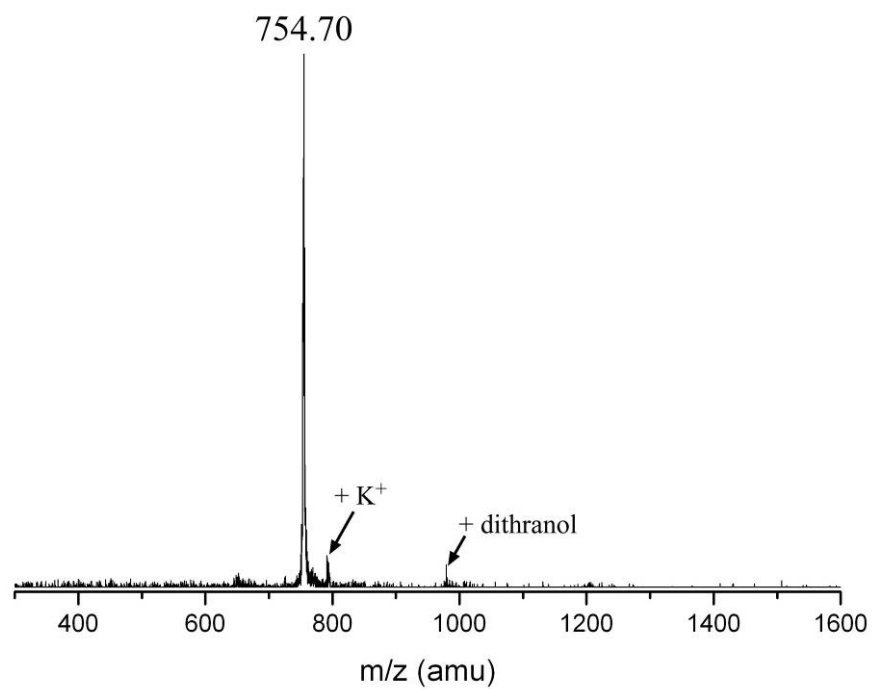


Figure S3. ^{13}C -NMR spectrum of **1**-1.

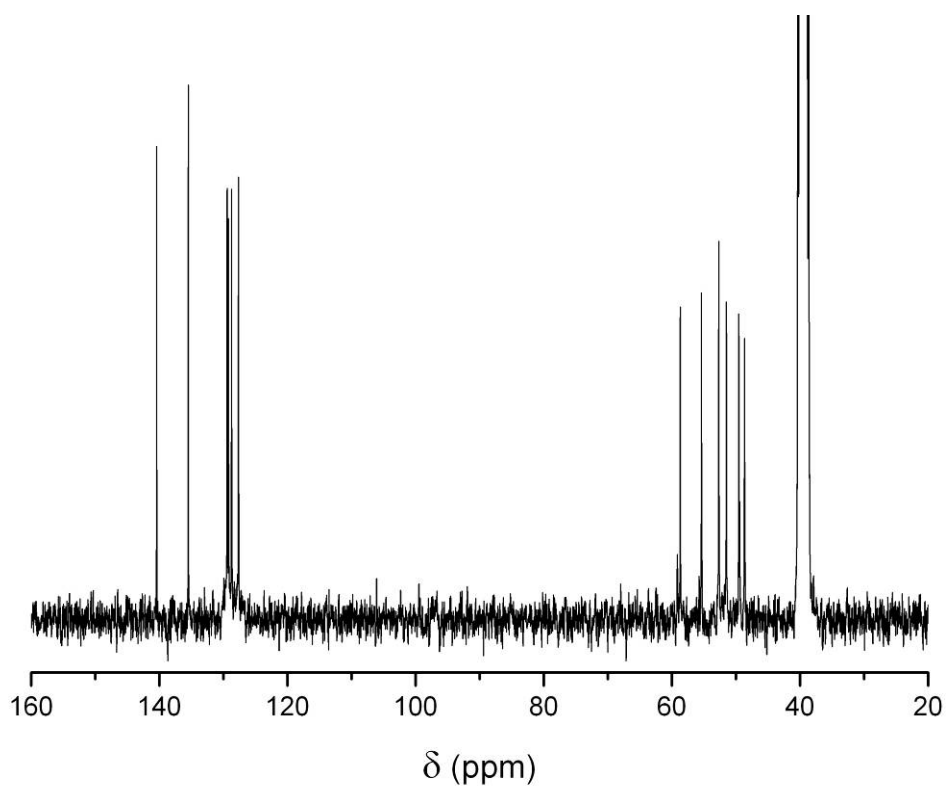


Figure S4. ^1H - ^1H COSY spectrum of **1** in $\text{DMSO-}d_6$. Top: aromatic region; bottom: highfield region (red crosses and green asterisks denote mutually coupled protons in two distinct ethylene groups. Scales are in ppm relative to tetramethylsilane (0 ppm). Asterisk signifies 4-bond (meta) couplings. Scales are in ppm relative to tetramethylsilane (0 ppm).

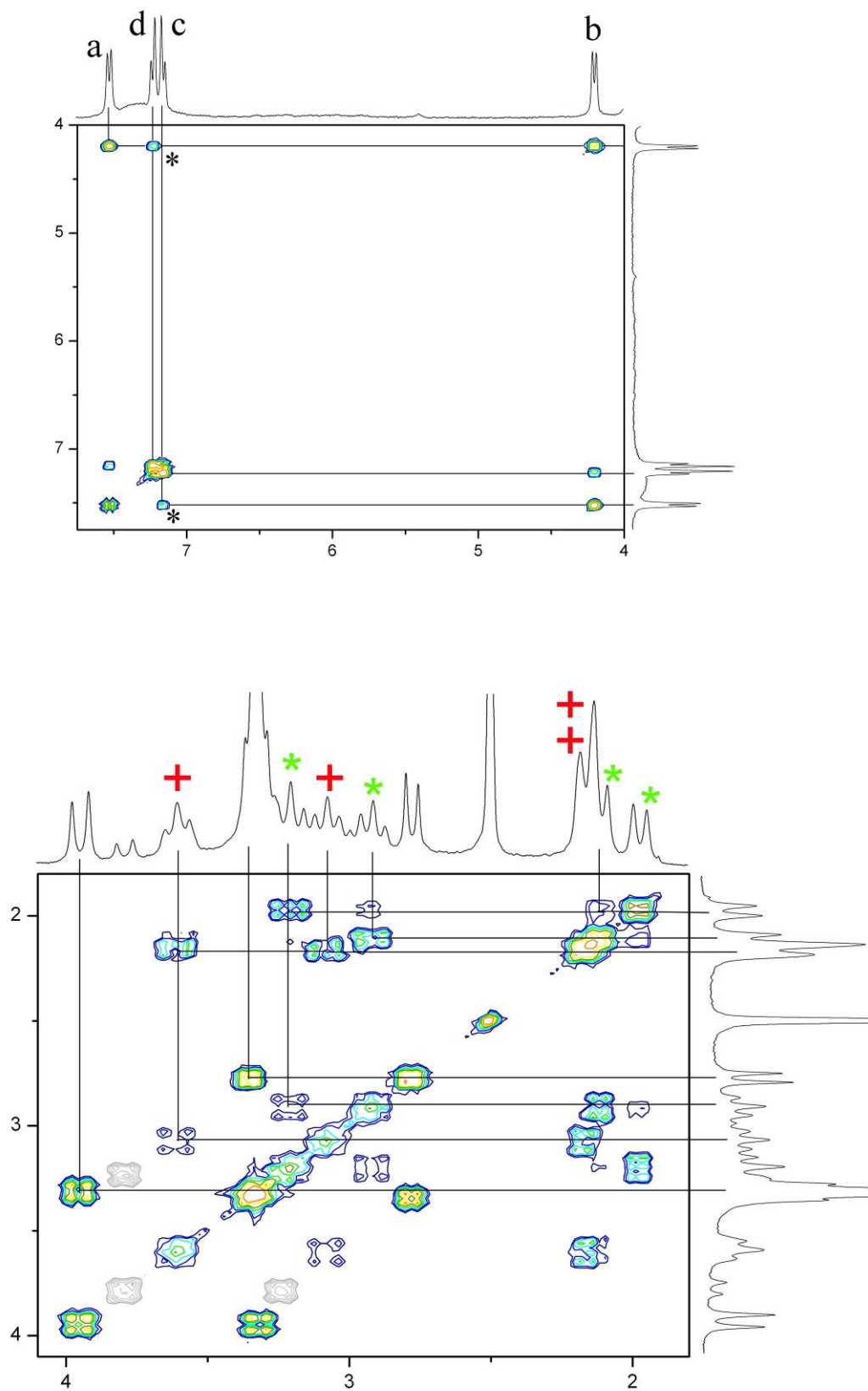


Figure S5. Full ^1H - ^1H COSY spectrum of **1** in $\text{DMSO}-d_6$ illustrating weak 4-bond couplings of protons a and c with one of the 1,4-xylyl methylene groups. Scales are in ppm relative to tetramethylsilane (0 ppm).

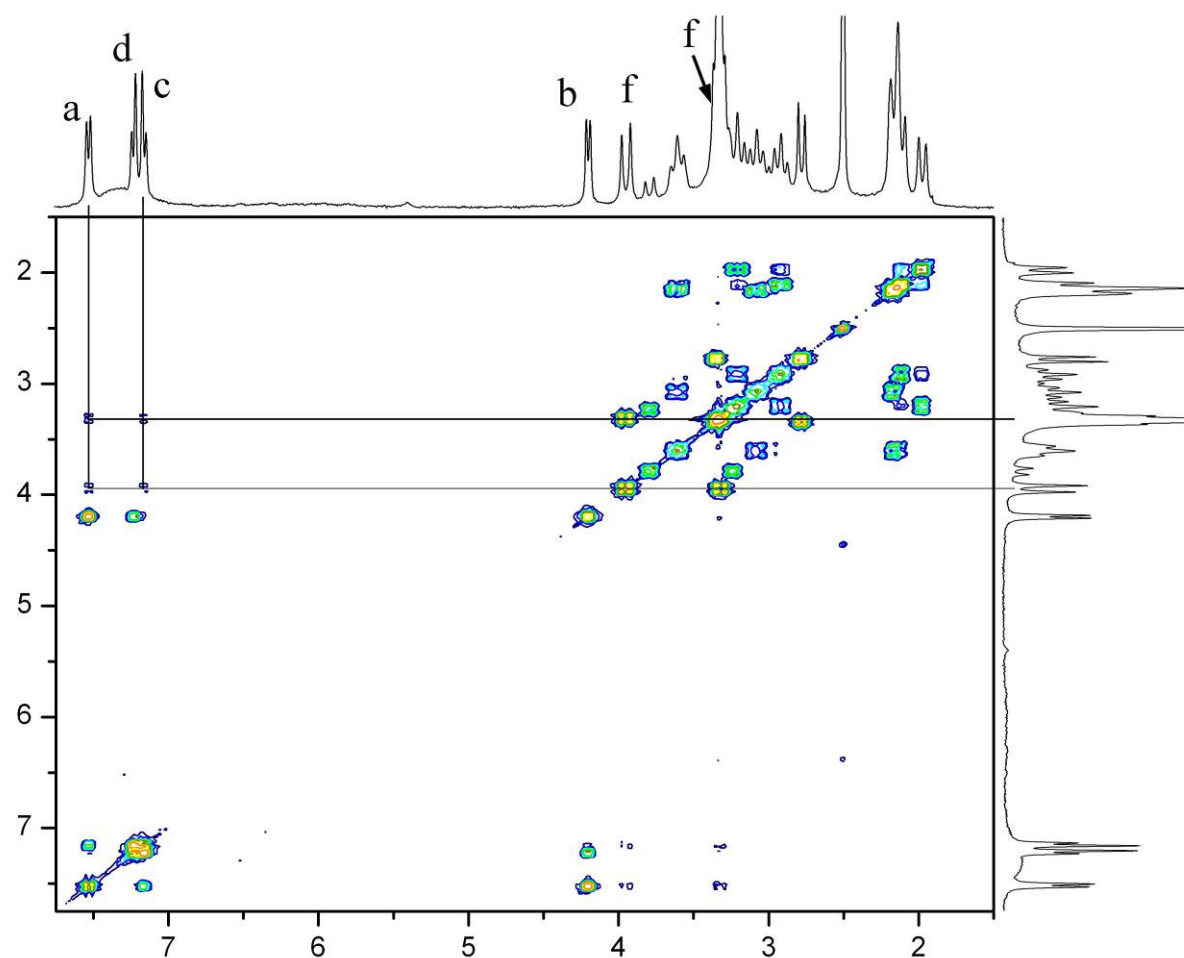


Figure S6. ^1H - ^1H COSY spectrum of **1** in pyridine- d_5 . Scales are in ppm relative to tetramethylsilane (0 ppm). (Gives similar data to the spectrum in DMSO- d_6 but without residual solvent and water peaks.)

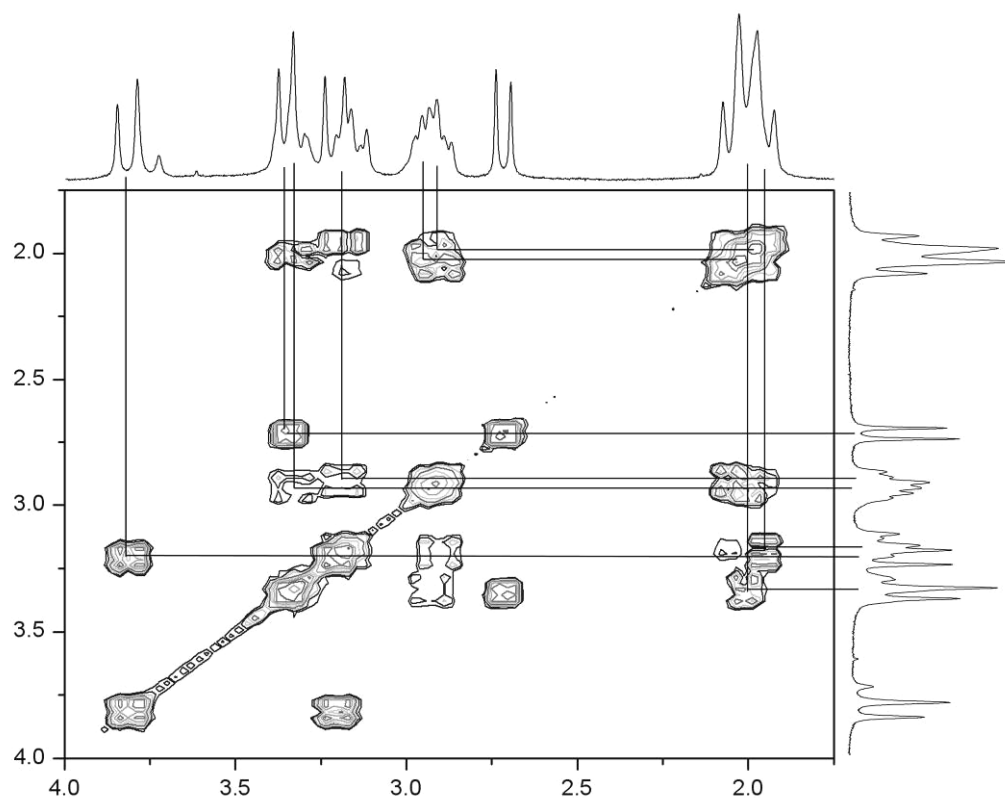


Figure S7. ^1H - ^1H NOESY spectrum of **1** in pyridine- d_5 . Scales are in ppm relative to tetramethylsilane (0 ppm).

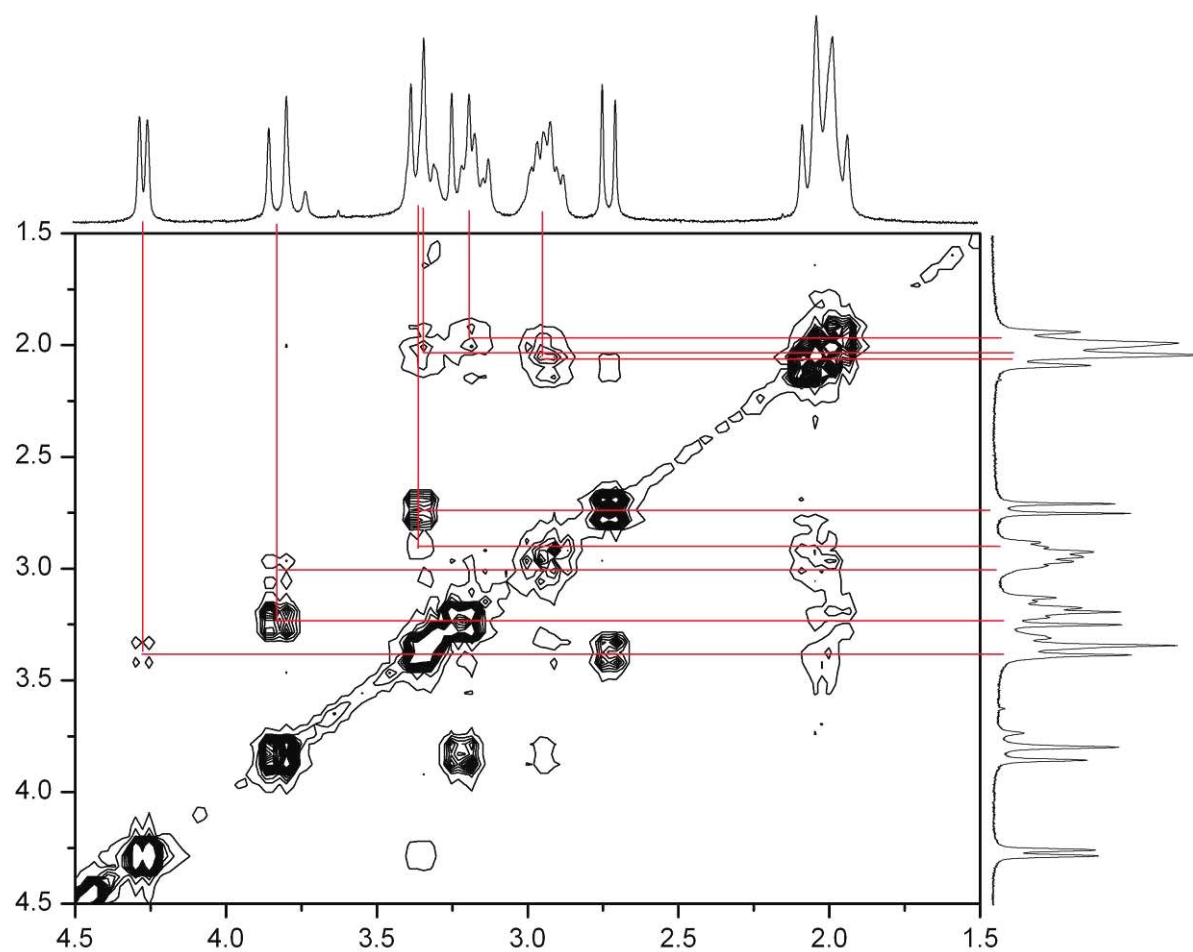
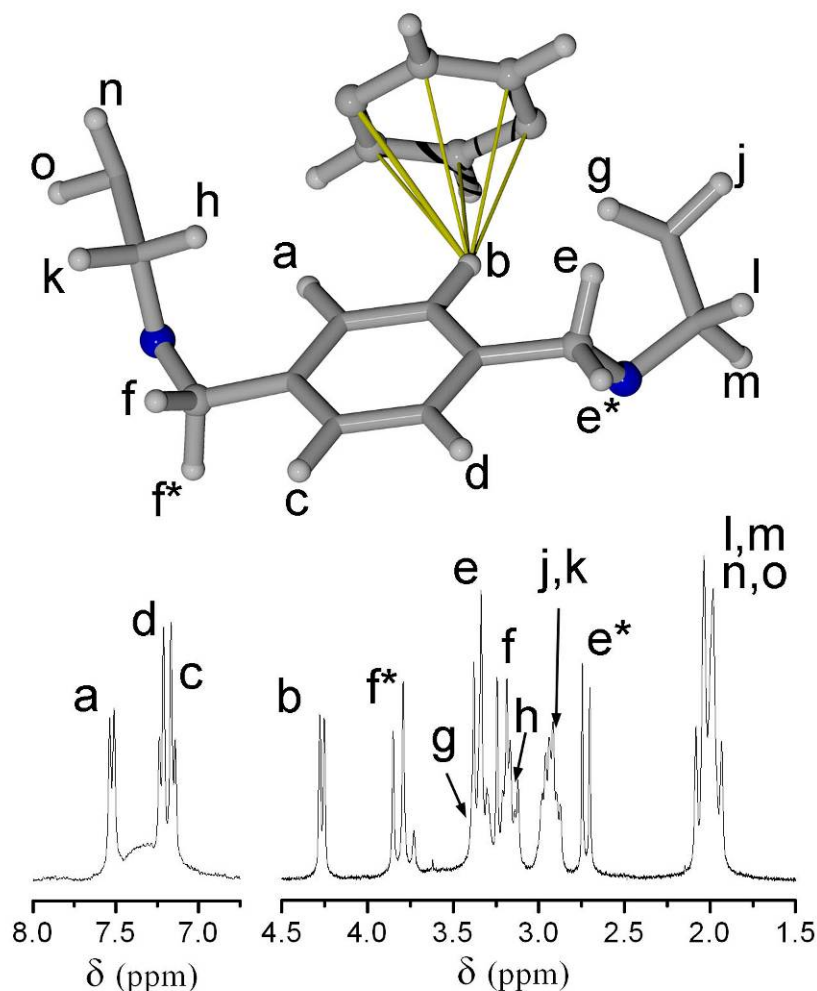


Figure S8. Assignment of 1-D spectra of **1**.



According to the 1-D spectra, aromatic protons **b** are subject to a strong shielding effect (indicated by the upfield shift of their resonance) due to their proximity to a neighbouring aromatic electronic ring. Conversely, adjacent protons **a** are shifted downfield because of deshielding. Protons **c,d** are relatively unaffected. Resonances due to α -methylene protons **f** and **g** are split indicating individual environments for each proton. Weak through bond couplings were used to discriminate **f** and **g** (see Fig. S4). Beyond the 1,4-xylyl groups there are two exclusive sets of mutually coupled protons which can be identified with two non-identical ethylene groups. This makes up a repeating unit for **1-1** as shown. Assignments were made on the basis of the chemical shift and nOe correlations of the protons with reference to the computed structure. Because of several overlapping signals it is difficult to unequivocally completely assign the proton NMR spectra although ^{13}C spectra confirms six non-equivalent aromatic carbons and six methylene type carbons (i.e. two distinct xylyl α -groups and four non-equivalent carbons for the cyclen groups) expected only for conformer **1-1**.

Samples of **1-1** were initially always contaminated with **1-2** (up to 30 mol%) . This was due to heating for dissolution.

Figure S9. Integrated difference spectrum of **1-1** from Figure 3(b) (see manuscript) with areas of resonances due to compound **1-1** integrated in order to show that the high temperature conformer is the major contaminant.

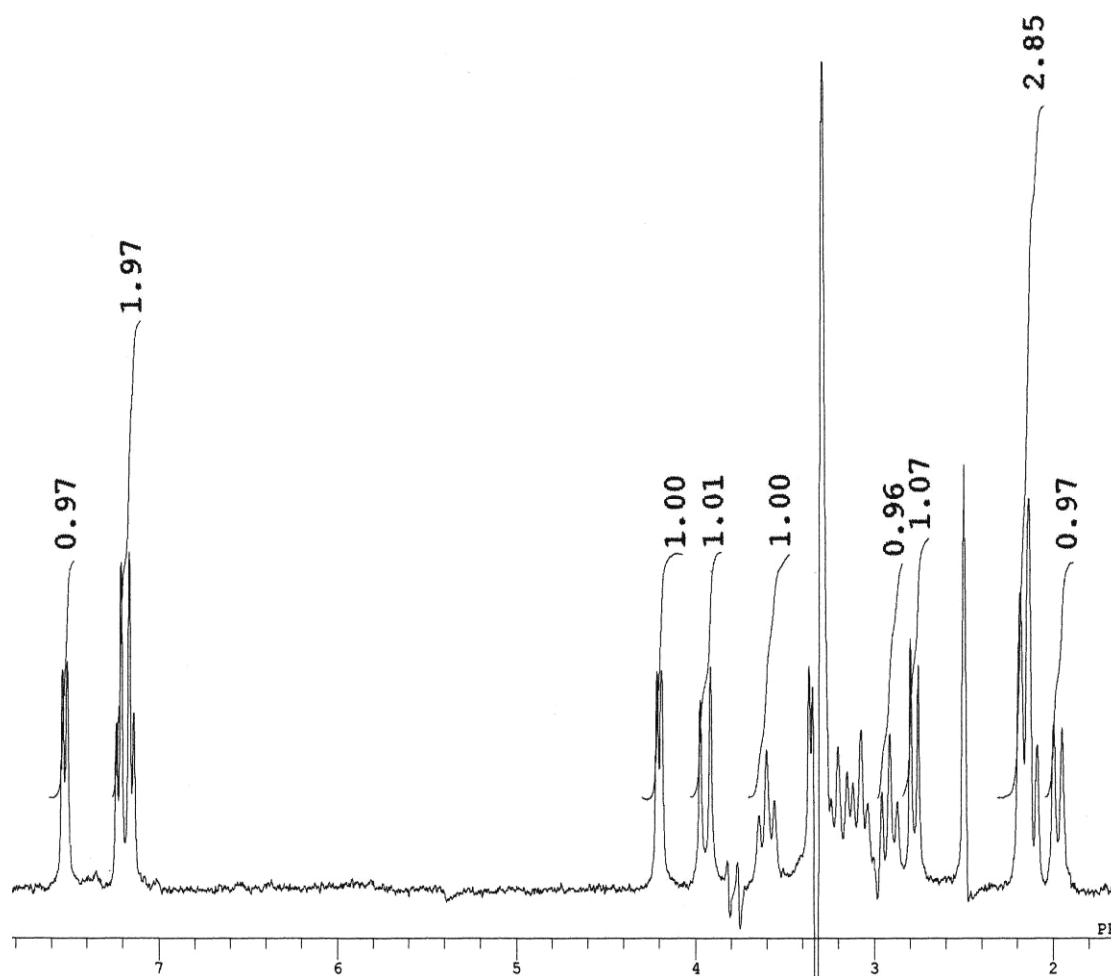
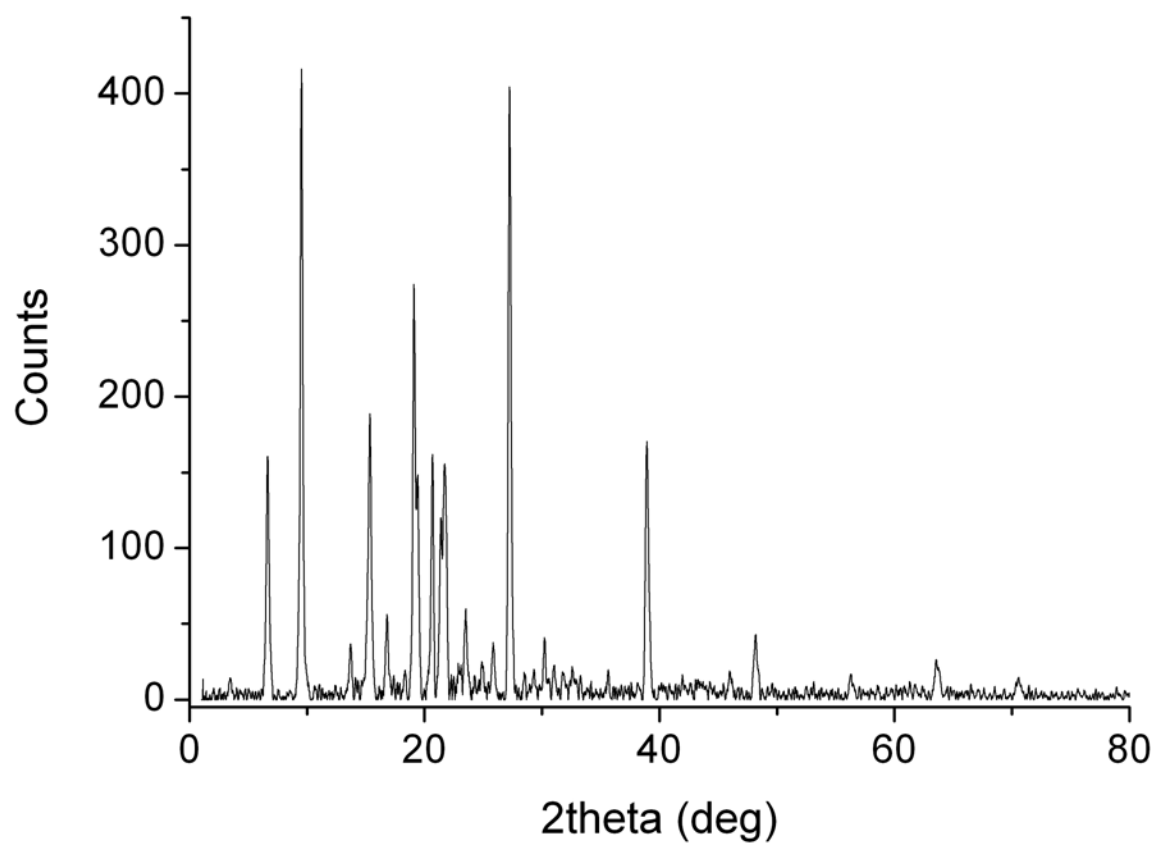


Figure 10. Powder X-ray diffraction pattern of **1**.

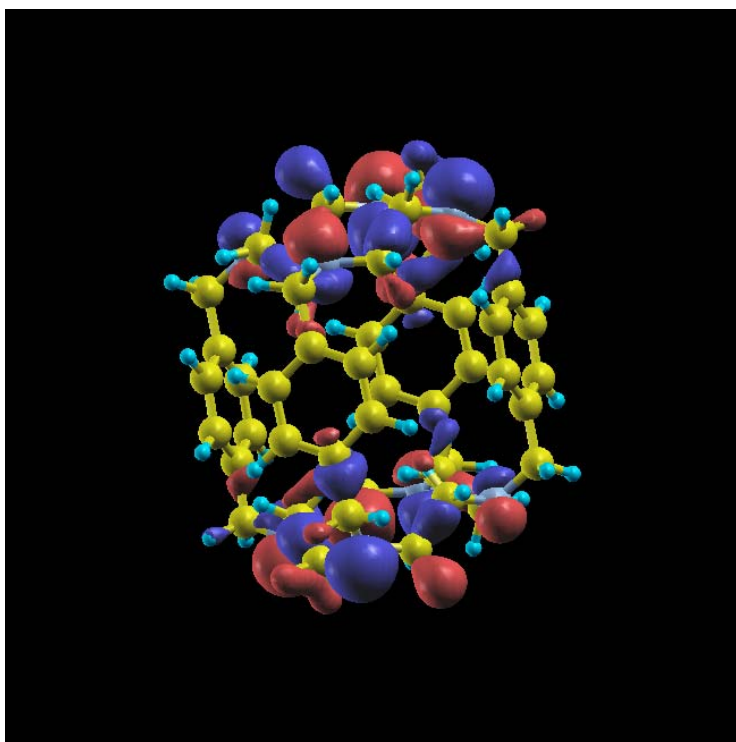


Indexed using McMaille Version 4. (A. Le Bail).

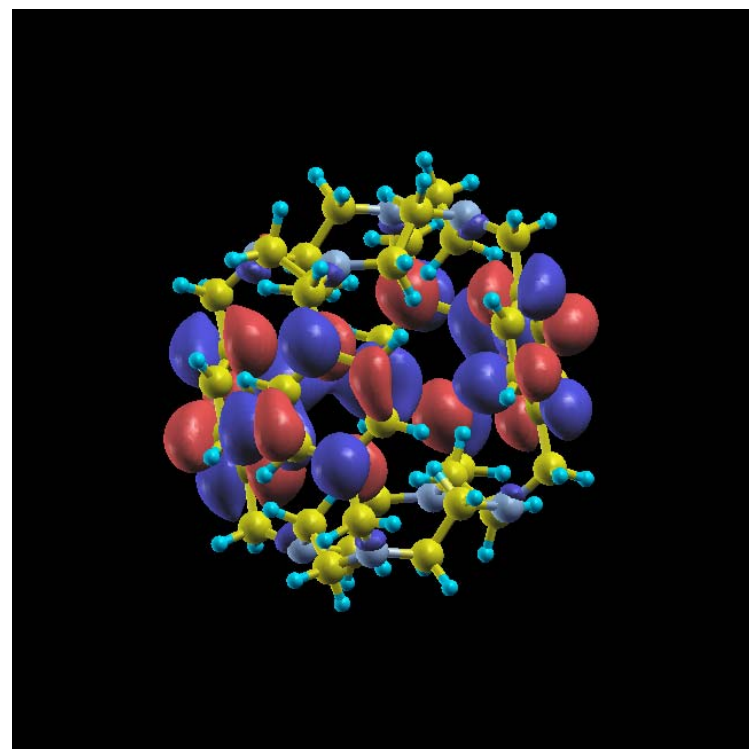
$a = 5.303$, $b = 13.292$, $c = 14.079$, $\beta = 113.847$, $V = 907.6 \text{ \AA}^3$.

Figure S11. Structure of the (A) HOMO and (B) LUMO for the box-like conformer **1–2**.

(A)



(B)



Coordinates of the calculated structures.

Compound 1-1

120

Generated by VMD

C	5.687000	9.986000	7.625000
C	4.487000	10.022000	6.664000
C	5.276000	10.647000	4.401000
C	6.334000	11.647000	4.888000
C	8.425000	12.145000	6.035000
C	9.266000	11.592000	7.198000
C	7.571000	11.850000	8.990000
C	6.499000	11.067000	9.749000
C	3.837000	8.719000	4.685000
C	8.433000	10.558000	4.155000
C	4.563000	9.618000	9.794000
C	9.420000	10.254000	9.233000
C	5.173000	8.241000	10.015000
C	3.846000	7.288000	5.209000
C	8.303000	9.049000	3.986000
C	9.702000	8.830000	8.790000
C	6.048000	7.961000	11.168000
C	6.626000	6.765000	11.290000
C	6.407000	5.727000	10.273000
C	5.582000	5.973000	9.261000
C	4.929000	7.267000	9.138000
C	4.966000	6.587000	5.166000
C	5.044000	5.259000	5.697000
C	3.979000	4.696000	6.242000
C	2.715000	5.456000	6.317000
C	2.649000	6.695000	5.819000
C	8.615000	8.213000	4.965000
C	8.427000	6.776000	4.798000
C	7.931000	6.275000	3.675000
C	7.610000	7.193000	2.568000

C	7.794000	8.511000	2.713000
C	10.958000	8.575000	8.079000
C	11.174000	7.373000	7.543000
C	10.164000	6.313000	7.689000
C	9.046000	6.558000	8.363000
C	8.806000	7.861000	8.926000
C	7.171000	4.424000	10.454000
C	4.072000	3.253000	6.718000
C	7.564000	4.807000	3.445000
C	10.453000	4.963000	7.047000
C	5.881000	2.690000	9.351000
C	8.321000	2.675000	9.206000
C	9.547000	3.399000	8.633000
C	5.589000	1.906000	8.064000
C	9.337000	2.922000	6.255000
C	8.932000	3.355000	4.834000
C	6.520000	2.866000	4.450000
C	6.008000	2.049000	5.664000
N	4.863000	9.575000	5.312000
N	5.378000	10.529000	8.955000
N	7.663000	11.147000	5.267000
N	8.528000	10.978000	8.302000
N	7.109000	3.487000	9.332000
N	9.410000	3.963000	7.282000
N	7.579000	3.890000	4.608000
N	5.444000	2.717000	6.848000
H	5.264000	1.348000	5.211000
H	6.830000	1.408000	6.018000
H	4.681000	1.291000	8.260000
H	6.393000	1.173000	7.897000
H	8.632000	2.243000	10.188000
H	8.091000	1.808000	8.572000
H	5.886000	1.947000	10.189000
H	5.042000	3.373000	9.562000
H	7.718000	12.897000	6.420000
H	9.121000	12.717000	5.381000

H	5.926000	12.185000	5.760000
H	6.413000	12.407000	4.071000
H	8.168000	11.059000	3.197000
H	9.497000	10.787000	4.336000
H	7.549000	9.215000	1.912000
H	8.961000	8.576000	5.935000
H	7.204000	6.773000	1.641000
H	8.599000	6.132000	5.660000
H	5.653000	3.372000	4.001000
H	6.840000	2.089000	3.713000
H	8.197000	4.405000	2.620000
H	6.539000	4.811000	3.043000
H	9.641000	4.122000	4.483000
H	9.110000	2.467000	4.180000
H	10.320000	2.397000	6.142000
H	8.634000	2.158000	6.612000
H	9.826000	4.228000	9.302000
H	10.398000	2.676000	8.677000
H	10.563000	5.116000	5.961000
H	11.452000	4.602000	7.395000
H	8.270000	5.794000	8.430000
H	12.094000	7.142000	6.995000
H	7.855000	8.044000	9.424000
H	11.687000	9.387000	7.996000
H	10.377000	10.807000	9.366000
H	8.936000	10.234000	10.221000
H	9.955000	10.825000	6.803000
H	9.914000	12.434000	7.556000
H	3.579000	3.167000	7.702000
H	3.476000	2.608000	6.030000
H	1.845000	4.982000	6.786000
H	6.018000	4.774000	5.721000
H	1.732000	7.291000	5.871000
H	5.871000	7.049000	4.771000
H	2.818000	9.158000	4.786000
H	4.056000	8.693000	3.604000

H	4.405000	11.291000	4.116000
H	5.621000	10.167000	3.470000
H	8.078000	12.533000	9.714000
H	7.077000	12.504000	8.254000
H	4.041000	11.042000	6.653000
H	3.694000	9.348000	7.028000
H	6.835000	3.937000	11.403000
H	8.229000	4.685000	10.624000
H	5.430000	5.239000	8.469000
H	7.282000	6.533000	12.136000
H	4.251000	7.415000	8.293000
H	6.196000	8.746000	11.915000
H	3.579000	9.496000	9.311000
H	4.386000	10.128000	10.757000
H	6.055000	11.743000	10.504000
H	7.010000	10.268000	10.324000
H	6.511000	10.555000	7.189000
H	6.067000	8.945000	7.653000

Compound 1-2

120

C	5.317650	9.405706	7.602648
C	4.182479	10.232950	7.022164
C	5.050426	10.072408	4.718368
C	5.900343	11.365013	4.764577
C	8.345116	11.650771	5.142174
C	8.843238	10.578791	6.165285
C	7.832491	11.246424	8.298771
C	7.247713	9.960985	8.985028
C	2.827436	9.150784	5.232959
C	7.592056	10.525999	3.045165
C	5.143398	9.234944	10.012160
C	10.273274	10.657473	8.200492
C	5.467508	7.740089	10.243243
C	3.075062	7.651024	5.346345
C	7.933551	9.061777	3.215890
C	10.494904	9.156098	8.360494
C	6.689855	7.345560	10.828341
C	6.976092	6.014673	11.042035
C	6.041935	5.008735	10.721805
C	4.813328	5.415148	10.213877
C	4.520329	6.736886	9.944940
C	2.083192	6.723715	4.991512
C	2.301568	5.325373	5.118185
C	3.499078	4.844664	5.655863
C	4.468421	5.786110	6.025664
C	4.245254	7.138807	5.849536
C	9.229500	8.649012	3.644995
C	9.503643	7.299103	3.914837
C	8.574013	6.283134	3.700185
C	7.315688	6.699912	3.195682
C	7.002860	8.030492	2.966548
C	11.710455	8.633594	8.882435

C	11.940823	7.267356	9.037486
C	10.934063	6.322056	8.721958
C	9.716003	6.832547	8.252057
C	9.545637	8.187602	8.032811
C	6.378268	3.521752	10.922713
C	3.776137	3.336193	5.759722
C	8.882967	4.797686	3.972873
C	11.161078	4.829983	8.827793
C	5.624313	2.340725	8.846729
C	8.055489	2.656683	9.245507
C	8.917853	3.927190	9.306535
C	5.133059	3.380745	7.812582
C	9.853388	3.724679	7.012093
C	8.705654	4.604838	6.413846
C	6.772557	3.991265	5.011227
C	6.197043	2.716032	5.695553
N	3.889797	10.077700	5.593029
N	5.791719	9.875821	8.886499
N	7.264250	11.293614	4.259056
N	9.055329	11.130267	7.513278
N	6.689854	2.769574	9.720520
N	10.106568	3.873184	8.453470
N	8.245022	4.119781	5.105772
N	4.941436	2.852443	6.469132
H	6.961776	2.270196	6.349213
H	5.988530	1.957584	4.949982
H	5.811112	4.263911	7.861182
H	4.171179	3.799405	8.165258
H	8.611268	1.838060	9.813590
H	7.996535	2.318656	8.211218
H	5.904291	1.390443	8.325310
H	4.723259	2.002348	9.417691
H	9.221198	12.029363	4.528934
H	8.056265	12.576968	5.726923
H	5.950215	11.698847	5.805597
H	5.355100	12.197045	4.233908

H	6.692407	10.592758	2.351202
H	8.440052	11.023621	2.545446
H	6.014557	8.280011	2.563028
H	9.966439	9.392921	3.820610
H	6.597622	5.905838	2.933517
H	10.492339	7.029481	4.293177
H	6.430822	3.968360	3.981650
H	6.340345	4.932756	5.424920
H	8.635772	4.211805	3.076455
H	9.989120	4.744661	4.101350
H	8.975636	5.671302	6.366722
H	7.890151	4.579037	7.108623
H	9.617808	2.634650	6.789345
H	10.828630	3.904542	6.572901
H	9.252916	4.070963	10.344483
H	8.264878	4.786569	9.139154
H	11.401167	4.545268	9.915734
H	12.075005	4.555507	8.271154
H	8.924270	6.192614	7.959134
H	12.934168	6.963237	9.405254
H	8.612137	8.496849	7.508973
H	12.497109	9.337384	9.085236
H	10.331622	11.110040	9.167651
H	11.138644	11.073771	7.696230
H	9.800873	10.161845	5.854585
H	8.139176	9.709318	6.185496
H	3.806718	2.874323	4.756953
H	2.858475	2.926477	6.246154
H	5.403328	5.454305	6.485654
H	1.514205	4.674322	4.719749
H	5.097399	7.828640	6.067818
H	1.135413	7.063428	4.534320
H	1.926658	9.360087	5.851902
H	2.542290	9.409408	4.157788
H	4.678865	9.913143	3.684647
H	5.763038	9.235886	4.916676

H	7.040572	11.691686	7.652110
H	8.015881	12.008933	9.055411
H	4.395908	11.278006	7.249507
H	3.235487	10.041842	7.607065
H	7.207884	3.439896	11.622332
H	5.498965	3.017141	11.385507
H	4.022690	4.593540	10.002708
H	7.948646	5.787271	11.487188
H	3.553423	7.021583	9.580646
H	7.415869	8.093295	11.140931
H	5.383569	9.760340	10.936165
H	4.033720	9.316460	9.880743
H	7.450339	9.997518	10.040034
H	7.682855	9.070662	8.539545
H	5.010471	8.320914	7.693478
H	6.166117	9.402911	6.870092

Compound 1-3

120

C	5.317650	9.405706	7.602648
C	4.182479	10.232950	7.022164
C	5.050426	10.072408	4.718368
C	5.900343	11.365013	4.764577
C	8.345116	11.650771	5.142174
C	8.843238	10.578791	6.165285
C	7.832491	11.246424	8.298771
C	7.247713	9.960985	8.985028
C	2.827436	9.150784	5.232959
C	7.592056	10.525999	3.045165
C	5.143398	9.234944	10.012160
C	10.273274	10.657473	8.200492
C	5.467508	7.740089	10.243243
C	3.075062	7.651024	5.346345
C	7.933551	9.061777	3.215890
C	10.494904	9.156098	8.360494
C	6.689855	7.345560	10.828341
C	6.976092	6.014673	11.042035
C	6.041935	5.008735	10.721805
C	4.813328	5.415148	10.213877
C	4.520329	6.736886	9.944940
C	2.083192	6.723715	4.991512
C	2.301568	5.325373	5.118185
C	3.499078	4.844664	5.655863
C	4.468421	5.786110	6.025664
C	4.245254	7.138807	5.849536
C	9.229500	8.649012	3.644995
C	9.503643	7.299103	3.914837
C	8.574013	6.283134	3.700185
C	7.315688	6.699912	3.195682
C	7.002860	8.030492	2.966548
C	11.710455	8.633594	8.882435
C	11.940823	7.267356	9.037486

C	10.934063	6.322056	8.721958
C	9.716003	6.832547	8.252057
C	9.545637	8.187602	8.032811
C	6.378268	3.521752	10.922713
C	3.776137	3.336193	5.759722
C	8.882967	4.797686	3.972873
C	11.161078	4.829983	8.827793
C	5.624313	2.340725	8.846729
C	8.055489	2.656683	9.245507
C	8.917853	3.927190	9.306535
C	5.133059	3.380745	7.812582
C	9.853388	3.724679	7.012093
C	8.705654	4.604838	6.413846
C	6.772557	3.991265	5.011227
C	6.197043	2.716032	5.695553
N	3.889797	10.077700	5.593029
N	5.791719	9.875821	8.886499
N	7.264250	11.293614	4.259056
N	9.055329	11.130267	7.513278
N	6.689854	2.769574	9.720520
N	10.106568	3.873184	8.453470
N	8.245022	4.119781	5.105772
N	4.941436	2.852443	6.469132
H	6.961776	2.270196	6.349213
H	5.988530	1.957584	4.949982
H	5.811112	4.263911	7.861182
H	4.171179	3.799405	8.165258
H	8.611268	1.838060	9.813590
H	7.996535	2.318656	8.211218
H	5.904291	1.390443	8.325310
H	4.723259	2.002348	9.417691
H	9.221198	12.029363	4.528934
H	8.056265	12.576968	5.726923
H	5.950215	11.698847	5.805597
H	5.355100	12.197045	4.233908
H	6.692407	10.592758	2.351202

H	8.440052	11.023621	2.545446
H	6.014557	8.280011	2.563028
H	9.966439	9.392921	3.820610
H	6.597622	5.905838	2.933517
H	10.492339	7.029481	4.293177
H	6.430822	3.968360	3.981650
H	6.340345	4.932756	5.424920
H	8.635772	4.211805	3.076455
H	9.989120	4.744661	4.101350
H	8.975636	5.671302	6.366722
H	7.890151	4.579037	7.108623
H	9.617808	2.634650	6.789345
H	10.828630	3.904542	6.572901
H	9.252916	4.070963	10.344483
H	8.264878	4.786569	9.139154
H	11.401167	4.545268	9.915734
H	12.075005	4.555507	8.271154
H	8.924270	6.192614	7.959134
H	12.934168	6.963237	9.405254
H	8.612137	8.496849	7.508973
H	12.497109	9.337384	9.085236
H	10.331622	11.110040	9.167651
H	11.138644	11.073771	7.696230
H	9.800873	10.161845	5.854585
H	8.139176	9.709318	6.185496
H	3.806718	2.874323	4.756953
H	2.858475	2.926477	6.246154
H	5.403328	5.454305	6.485654
H	1.514205	4.674322	4.719749
H	5.097399	7.828640	6.067818
H	1.135413	7.063428	4.534320
H	1.926658	9.360087	5.851902
H	2.542290	9.409408	4.157788
H	4.678865	9.913143	3.684647
H	5.763038	9.235886	4.916676
H	7.040572	11.691686	7.652110

H	8.015881	12.008933	9.055411
H	4.395908	11.278006	7.249507
H	3.235487	10.041842	7.607065
H	7.207884	3.439896	11.622332
H	5.498965	3.017141	11.385507
H	4.022690	4.593540	10.002708
H	7.948646	5.787271	11.487188
H	3.553423	7.021583	9.580646
H	7.415869	8.093295	11.140931
H	5.383569	9.760340	10.936165
H	4.033720	9.316460	9.880743
H	7.450339	9.997518	10.040034
H	7.682855	9.070662	8.539545
H	5.010471	8.320914	7.693478
H	6.166117	9.402911	6.870092

Compound 1-4

120

C	5.649131071548	5.885918971598	6.305194084326
C	5.975880396502	6.955910249122	5.209606016422
C	7.562746428587	8.598631470824	6.294226021249
C	6.528645158391	9.712349190189	6.502722065282
C	6.302149010382	9.119480889472	8.902337760084
C	7.599116985854	8.583815555243	9.527864381568
C	7.036718541688	6.153975933296	9.096732243598
C	5.529084316120	5.886549490186	8.806189904625
C	3.027858072837	7.793994390770	7.624550518282
C	3.012395414168	8.403638900709	8.888373872298
C	3.461705585731	9.716876030658	9.022974117168
C	3.952794357668	10.412631471065	7.901504904657
C	3.518945174637	9.949179504036	6.641728240912
C	3.057479061451	8.640148620124	6.506067700267
C	3.492575052322	6.360099125224	7.480975890442
C	5.260432674841	11.178842891524	8.017180986940
C	8.503674856809	6.837313530205	10.961353546984
C	8.373389361072	6.675913859738	5.058951573378
C	9.739021384996	7.170300453499	4.619381817839
C	9.899852799630	6.904432463309	10.352039482834
C	10.796244196026	7.915044807450	10.724064993075
C	12.036010343876	8.054243558161	10.096019167467
C	12.416224999264	7.207636639456	9.046924038397
C	11.529589711328	6.180389583519	8.689726987454
C	10.309741530709	6.016225373506	9.344750747023
C	10.629718064367	7.780885109676	5.516897951819
C	11.931634285302	8.095226536014	5.136993397589
C	12.422892925088	7.747449196524	3.872815125827
C	11.532841852410	7.159716872779	2.966006984732
C	10.208807114810	6.893354917543	3.328458177901
C	13.867606085101	8.022573262255	3.520496000071
C	13.694389303038	7.461911650312	8.270421463386
C	16.148405220856	7.238645028016	8.343735480659

C	14.667426816112	5.189242913435	8.304601800475
C	16.192409106090	7.883981287194	4.013505856497
C	14.703254023269	5.813582339454	3.920966890951
C	17.482894950022	7.469816793933	4.744837388400
C	15.485556267389	4.639959554951	4.552591615017
C	14.312916348781	4.695017974175	6.840600024505
C	16.457427079200	7.119965115016	6.851599806813
C	18.976497952931	7.400721882296	6.693731303259
C	19.114920367757	5.892426783656	6.777660988117
C	18.686851923645	5.233426359643	7.944732919773
C	17.940484409533	4.064524253902	7.852843116836
C	17.616541390299	3.543448730979	6.588831997866
C	18.442817718490	3.926761659433	5.519423484853
C	19.192542247852	5.103958235411	5.613751708997
C	16.190447361389	3.088172271037	6.314636020782
N	7.278215749552	7.660201845851	5.187530343975
N	4.988375634905	6.371824433526	7.525359797303
N	6.414237541894	10.208255990268	7.900234755132
N	7.383977087985	7.221938572874	10.068191976353
N	14.876767659572	7.238820793942	4.288601615327
N	14.837421374594	6.616322651815	8.636623219121
N	17.606409439682	7.782254466212	6.185865228959
N	15.420596628490	4.305976839466	5.977139129058
H	13.626297975502	5.612902954439	4.043168658257
H	14.904531064591	5.688205127662	2.827565195278
H	16.036736545100	8.960574310279	4.198577875879
H	16.431584761077	7.783386896690	2.927305939872
H	14.012134844356	7.866956622194	2.424773931541
H	14.077942673126	9.087093842621	3.715728943519
H	11.883361831913	6.890990646141	1.964334252425
H	12.594781655895	8.596001288894	5.845475307615
H	9.537803467246	6.420677500837	2.604463008760
H	10.317673861306	7.984973438712	6.543608152853
H	8.037330177151	5.920970481700	4.328797751298
H	8.531672353306	6.132615001800	6.021507289877
H	7.692145856969	8.030781771448	7.227017995238

H	8.538021932361	9.058233725228	6.077344584036
H	5.173498050077	7.706481845112	5.209439512185
H	5.911854775728	6.438453146580	4.235280405123
H	5.365966460670	4.786380753686	8.897096794352
H	4.949411392123	6.355529304045	9.617661747773
H	6.573921505952	5.357321454069	6.586784033764
H	5.012662490112	5.117274364462	5.814356275392
H	3.097413281068	5.712558688634	8.286359346748
H	3.165860059530	5.928216832268	6.519252576208
H	2.898326915735	8.223970529596	5.505503973143
H	2.820758225652	7.803729543436	9.784052791328
H	3.690041650712	10.558800678756	5.748660354169
H	3.609464115575	10.132098371896	10.025541657741
H	5.351999248599	11.683046764995	8.992599763585
H	5.383718554008	11.932650534912	7.222738087707
H	6.771109856200	10.578548133358	5.863285201599
H	5.551303615699	9.333402541176	6.157920866636
H	5.741496947108	8.275450945726	8.467927196676
H	5.690335237355	9.489796436314	9.733581068244
H	7.416596739715	5.220767627432	9.538901840734
H	7.588226790794	6.266005701578	8.143195131860
H	7.891153025777	9.221908428756	10.380491214850
H	8.452399570600	8.629325811947	8.823933216425
H	8.296752722337	5.820169426133	11.334108068429
H	8.472460845581	7.511668071803	11.835197832401
H	9.656991364149	5.193185281779	9.043507863841
H	10.509780157884	8.620212421819	11.511436295317
H	11.780884175086	5.508874438945	7.864325923819
H	12.710134947134	8.859336554413	10.405024847848
H	15.570279092038	4.665079896298	8.647790190640
H	13.843776557253	4.823891470935	8.942766038525
H	13.454677661729	7.388607094397	7.189389808614
H	13.999811776307	8.505673956110	8.448889511163
H	16.903685465559	6.742057464441	8.972175152816
H	16.097072450397	8.290618623613	8.673332021646
H	13.748230074605	5.485016154599	6.321650313200

H	13.602265372710	3.846461516545	6.972406883011
H	16.554046530738	4.747821811165	4.294267830067
H	15.135731077083	3.766907600133	3.948639023233
H	15.574028608152	7.509840527477	6.330147037251
H	16.473026290068	6.039964334989	6.625533651105
H	18.292783285378	8.010957258531	4.222347164872
H	17.663083865216	6.393840320451	4.554901451581
H	15.740718606385	2.617432129837	7.204477167575
H	16.134875637132	2.357254921248	5.481415820293
H	18.372370595203	3.404848410261	4.559453072161
H	17.459869910174	3.659014685926	8.749310282690
H	19.712714161223	5.484065345816	4.729125522796
H	19.706503541198	7.865078407737	6.010053296026
H	19.101351175238	7.859370484682	7.688034448355
H	18.792366247655	5.731981860632	8.913601481050