STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 74 (2018)

Supporting information for article:

Crystal structure analysis of a star-shaped triazine compound: a combination of single-crystal 3D electron diffraction and powder X-ray diffraction

Tatiana Gorelik, Jacco van de Streek, Herbert Meier, Lars Andernach and Till Opatz

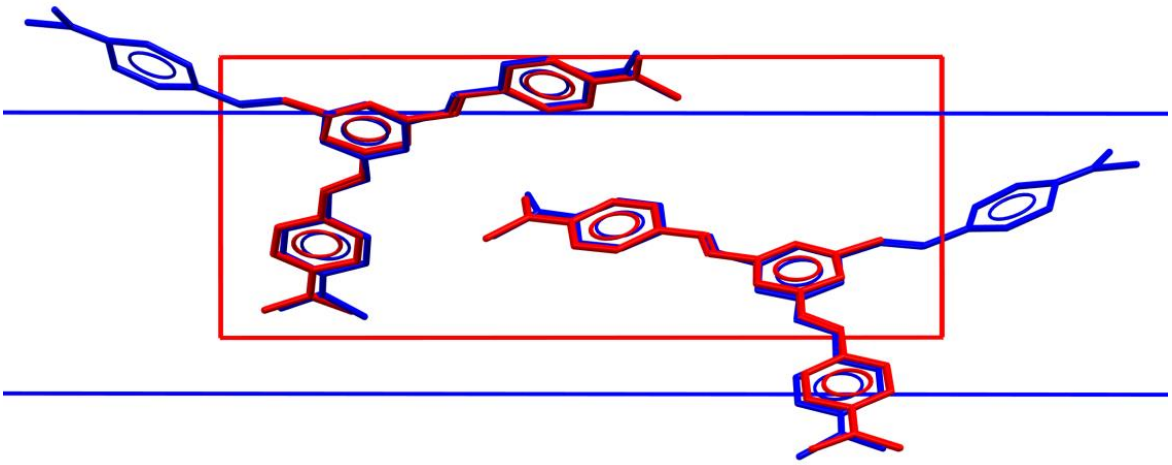

Figure S1. Overlay of the crystal structures of **1** (blue) and **3** (red) (crystallizing in *P2₁* space group), showing the similarity between the two crystal structures.

On the accuracy of the lattice parameters from ED data – angles between the lattice basis vectors

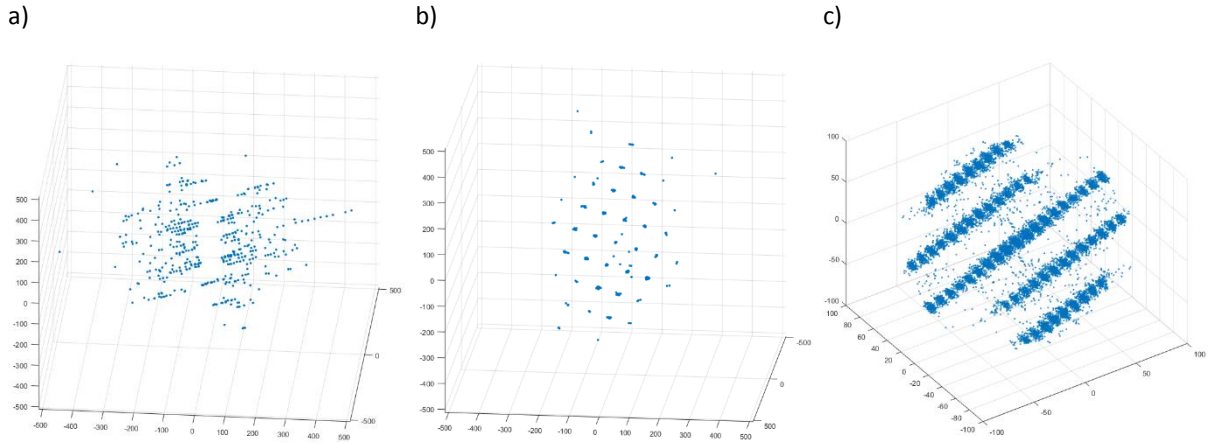

Figure S2 3D positions of electron diffraction Bragg reflections used for the unit-cell parameters determination along an arbitrary orientation (a), along the longest crystallographic axis (b), difference vectors calculated from these peak positions (c).

The unit cell parameters are determined from the 3D positions of reflections extracted from 3D electron diffraction data (Figure S2a, S2b). As a first step difference vectors (Figure S2c) are calculated from the peak positions, these vectors are then analysed to obtain the basis vectors of the lattice.

Angles between the unit cell vectors, determined from electron diffraction data are usually well-defined. It was not the case for **(1)**: α=90.6°, β=91.3°, γ=88.1°, although the angles have to be 90° due to the orthorhombic symmetry of the material. Figure S2 shows 3D peaks positions extracted from ED data used for the unit cell determination, arbitrary oriented (a) and along the longest crystallographic axis. There is a geometric uncertainty in the peaks positions due to different geometrical factors – excitation error, numerical diffraction centring error, crystal bending, etc. These effects are known for electron diffraction and are resolved by clustering procedures[1] implemented in most 3D ED data processing software (ADT, ETD, RED)[2]. When no diffuse scattering is present in the data and crystal bending can be neglected, the geometric error stays more or less constant and is related to

[1] S. Schlitt, T.E. Gorelik, A.A. Stewart, E. Schömer, Th. Raasch, U. Kolb, (2012), Application of clustering techniques to electron diffraction data: determination of unit-cell parameters, Acta Cryst. A68, 536–546.

[2] Relevant references are in the main text.

the number of pixels in a 2D diffraction pattern. In this study a 1k CCD was used, so the following discussion is relevant for 1024x1024 diffraction patterns.

a) b)

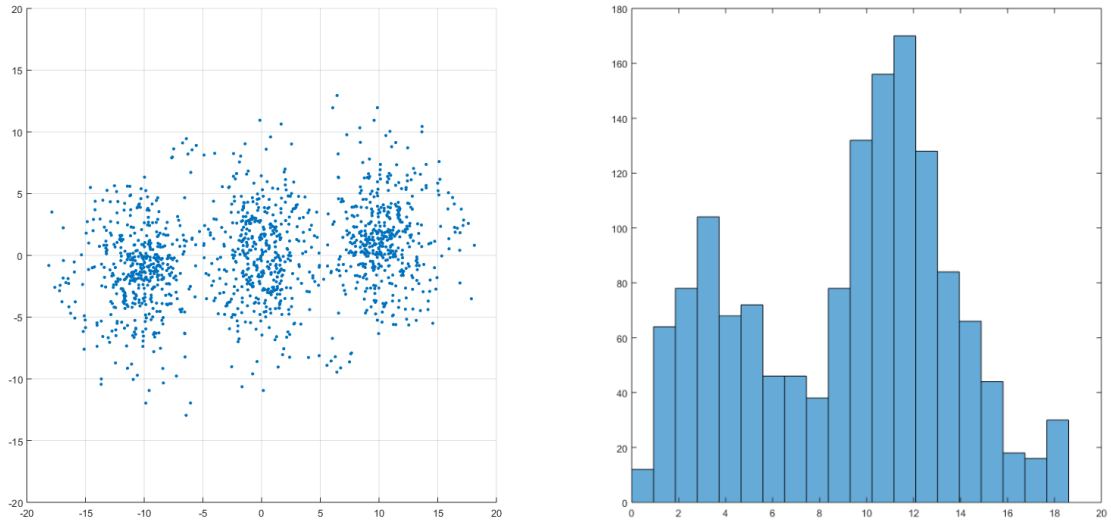

Figure S3 Difference vectors for the first 3 clusters (a); histogram of the difference vectors for the first tree clusters (b), horizontal axis in pixels.

The size of a cluster can be estimated from the width of the peaks in the histogram shown in Figure S3b. Here, the zero-cluster has a "dip" in the middle as the zero distances were not allowed during the difference vectors calculation. From the second cluster at 12 pixels' distance from the centre, one can see that the cluster diameter (FWHM) is about 8 pixels. For short lattice parameters (long reciprocal space vectors) the error due to the cluster blurring will be low as the ratio of the vector length to the cluster size is relatively large. For short reciprocal vectors (long crystallographic axes in the direct space) the length to cluster diameter ratio is small. In the present study the length of the vector is about 12 pixels, the length to diameter ratio is 12/8=1.5. In this situation the positions of the clusters are not properly defined, which makes especially the angles determination of the unit cell unstable. The lengths of the unit vectors are also affected by the cluster blurring, is however geometrically better defined.

The situation could have been improved if a larger camera length was used for the data collection. The distance between the clusters in pixels would increase, while effects associated with the cluster blurring would almost stay the same.

Keywords for HF:

```
#p hf/cc-pvtz geom=connectivity int=grid=ultra
```

Keywords for DFT geometry optimisation:

```
#p opt=tight freq=noraman b3lyp/6-31G(d,p) int=grid=ultra
```

Table 1. Energy differences and dipole moment values for calculated structures (HF/cc-pvtz)

Structure	symmetry	ΔE in kcal/mol	total dipole moment in Debye	x-component	y-component	z-component
I	C3	0.00	0.64	0.00	0.00	0.64

II	C1	0.00	0.22	0.00	0.00	0.22
III	C1	0.36	1.78	1.09	1.25	0.64
1	C1	65.81	3.22	-3.16	0.60	0.18
opt **1**	C1	0.35	1.67	1.09	1.25	0.21

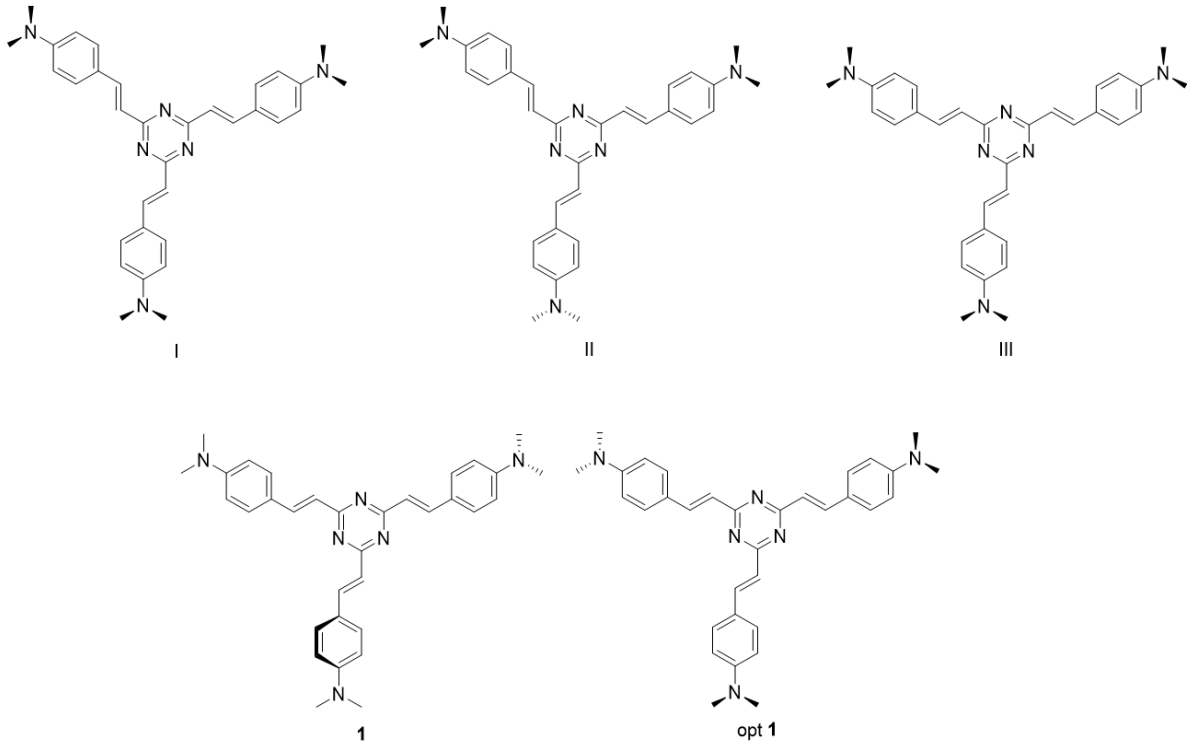

Figure S4. Different molecular conformations used for the dipole moment calculations.

Atomic coordinates

from crystal structure of **1**:

```
C       -0.016229000      0.910930000      0.000538000
C       -0.516824000      2.236740000      0.042084000
N       -0.898193000     -0.106573000      0.029471000
N        1.309398000      0.859754000     -0.076832000
C       -1.833227000      2.481288000      0.118150000
C       -0.313859000     -1.278229000     -0.030105000
C        1.775358000     -0.371710000     -0.137815000
C       -2.467546000      3.779791000      0.192297000
N        0.992439000     -1.466736000     -0.118770000
C       -1.073795000     -2.410190000     -0.179701000
C        3.184631000     -0.663106000     -0.238304000
C       -1.762385000      4.993457000      0.361451000
C       -3.860512000      3.870320000     -0.085562000
C       -2.361760000     -2.283050000     -0.125483000
C        4.183668000      0.214817000     -0.065445000
C       -2.377252000      6.212201000      0.217268000
C       -4.509785000      5.076286000     -0.204877000
C       -3.241767000     -3.378363000      0.086354000
C        5.578451000     -0.074459000     -0.104184000
C       -3.779561000      6.259827000     -0.022867000
```

C	-4.625948000	-3.174790000	0.183958000
C	-2.825815000	-4.725970000	0.006836000
C	6.125125000	-1.361915000	-0.132185000
C	6.464527000	0.991693000	-0.032921000
N	-4.373060000	7.399676000	-0.052661000
C	-5.508530000	-4.201197000	0.186323000
C	-3.684912000	-5.759562000	0.007809000
C	7.463976000	-1.569251000	-0.092245000
C	7.821587000	0.818293000	0.016750000
C	-3.774106000	8.696452000	0.242706000
C	-5.797572000	7.650501000	-0.414488000
C	-5.044522000	-5.517763000	0.083934000
C	8.366273000	-0.482661000	-0.001734000
N	-5.847106000	-6.523841000	0.039055000
N	9.720559000	-0.715191000	-0.064008000
C	-5.482496000	-7.945861000	0.001283000
C	-7.317697000	-6.611927000	0.032678000
C	10.131730000	-2.098100000	0.068177000
C	10.760591000	0.291326000	0.246433000
H	0.180835000	3.072360000	0.011658000
H	-2.492022000	1.614180000	0.124790000
H	-0.610190000	-3.382687000	-0.338628000
H	3.462453000	-1.688877000	-0.476073000
H	-0.703274000	4.960510000	0.612805000
H	-4.432353000	2.951655000	-0.207998000
H	-2.790468000	-1.289512000	-0.248086000
H	3.901448000	1.249612000	0.122893000
H	-1.798794000	7.132316000	0.285807000
H	-5.573188000	5.111960000	-0.436822000
H	-5.003603000	-2.156256000	0.260442000
H	-1.759492000	-4.937210000	-0.058279000
H	5.457236000	-2.220273000	-0.187520000
H	6.064936000	2.004573000	-0.015880000
H	-6.576263000	-4.003209000	0.267637000
H	-3.312689000	-6.781284000	-0.050986000
H	7.850930000	-2.586472000	-0.130351000
H	8.479995000	1.684027000	0.070456000
H	-4.343897000	9.125830000	1.065439000
H	-3.901394000	9.311481000	-0.646933000
H	-2.721769000	8.594064000	0.503542000
H	-6.258886000	8.137106000	0.443598000
H	-6.309997000	6.722450000	-0.663613000
H	-5.790988000	8.336191000	-1.260480000
H	-5.947034000	-8.412639000	0.868605000
H	-4.401377000	-8.075837000	0.015759000
H	-5.916580000	-8.357635000	-0.908609000
H	-7.771757000	-5.622977000	0.074630000
H	-7.600409000	-7.212140000	0.896244000
H	-7.597344000	-7.135361000	-0.880435000
H	10.799807000	-2.146738000	0.926784000
H	10.683897000	-2.349703000	-0.836110000
H	9.272266000	-2.753696000	0.200175000
H	11.363890000	-0.119049000	1.054875000
H	10.314952000	1.243178000	0.531570000
H	11.373940000	0.395528000	-0.647364000

for DFT-optimised structure of **1** (opt **1**):

C	-0.170490000	0.769301000	-0.012660000
C	0.124610000	2.201351000	-0.020120000

N	0.847120000	-0.111579000	-0.002650000
N	-1.472880000	0.432761000	-0.016370000
C	1.376310000	2.707121000	-0.018810000
C	0.489629000	-1.406599000	0.004010000
C	-1.727930000	-0.889979000	-0.009250000
C	1.769070000	4.109191000	-0.025560000
N	-0.784431000	-1.850539000	0.001250000
C	1.525869000	-2.437299000	0.015050000
C	-3.115430000	-1.346219000	-0.012940000
C	0.856540000	5.182861000	-0.020060000
C	3.135010000	4.445760000	-0.032220000
C	2.849049000	-2.168300000	0.018500000
C	-4.174010000	-0.507339000	-0.024550000
C	1.276831000	6.502321000	-0.025780000
C	3.576240000	5.761210000	-0.037860000
C	3.949799000	-3.121000000	0.028980000
C	-5.586430000	-0.858468000	-0.029170000
C	2.654981000	6.833930000	-0.044710000
C	5.274979000	-2.648590000	0.035120000
C	3.780379000	-4.519950000	0.027720000
C	-6.069001000	-2.182368000	-0.009670000
C	-6.553880000	0.162982000	-0.048380000
N	3.078291000	8.152090000	-0.075450000
C	6.368339000	-3.502690000	0.043490000
C	4.858459000	-5.388900000	0.036490000
C	-7.423701000	-2.468878000	-0.013530000
C	-7.915410000	-0.103438000	-0.052300000
C	2.112451000	9.224421000	0.093530000
C	4.491251000	8.456250000	0.070710000
C	6.191089000	-4.905610000	0.054130000
C	-8.392801000	-1.434568000	-0.044470000
N	7.270819000	-5.771850000	0.087090000
N	-9.747711000	-1.718078000	-0.072310000
C	7.056019000	-7.199780000	-0.074970000
C	8.617449000	-5.247330000	-0.060560000
C	-10.203161000	-3.086018000	0.108400000
C	-10.710650000	-0.638278000	0.058860000
H	-0.756250000	2.835731000	-0.027620000
H	2.191040000	1.985581000	-0.013130000
H	1.140919000	-3.452209000	0.020500000
H	-3.229421000	-2.425699000	-0.006270000
H	-0.210260000	4.981601000	-0.006040000
H	3.872200000	3.646630000	-0.028940000
H	3.130700000	-1.117010000	0.013550000
H	-3.947440000	0.557271000	-0.032290000
H	0.527951000	7.284441000	-0.013760000
H	4.641890000	5.953080000	-0.035550000
H	5.449339000	-1.575440000	0.028950000
H	2.779399000	-4.940180000	0.014960000
H	-5.366831000	-3.010118000	0.013820000
H	-6.222980000	1.198562000	-0.056460000
H	7.363189000	-3.075250000	0.040450000
H	4.664879000	-6.454310000	0.027870000
H	-7.733871000	-3.506148000	0.009360000
H	-8.608840000	0.728152000	-0.060090000
H	2.626271000	10.183520000	0.017370000
H	1.599841000	9.186501000	1.066690000
H	1.348111000	9.196651000	-0.691690000
H	5.080991000	7.986610000	-0.725130000
H	4.900791000	8.123370000	1.036620000
H	4.635271000	9.534690000	-0.006300000
H	8.013589000	-7.716280000	0.002240000
H	6.606169000	-7.455160000	-1.046350000
H	6.404029000	-7.594370000	0.712930000
H	8.851299000	-4.528920000	0.733770000
H	8.775069000	-4.745740000	-1.027520000
H	9.331929000	-6.067750000	0.017500000
H	-11.290961000	-3.113408000	0.033430000
H	-9.916281000	-3.504608000	1.084920000

H	-9.802131000	-3.743698000	-0.671510000
H	-11.719280000	-1.047258000	-0.012380000
H	-10.593990000	0.095702000	-0.747010000
H	-10.623540000	-0.104758000	1.017580000

for C_3 symmetric structure **I**:

C	1.006075000	-0.844916000	-0.025490000
N	1.295079000	0.466284000	-0.025427000
C	0.228681000	1.293744000	-0.025490000
N	-1.051353000	0.888429000	-0.025427000
C	-1.234756000	-0.448829000	-0.025490000
N	-0.243726000	-1.354713000	-0.025427000
C	-2.597855000	-0.975146000	-0.025625000
C	0.454426000	2.737381000	-0.025625000
C	2.143429000	-1.762235000	-0.025625000
C	1.683336000	3.297376000	-0.026065000
C	2.013943000	-3.106500000	-0.026065000
C	-3.697279000	-0.190876000	-0.026065000
C	3.075625000	-4.102422000	-0.026338000
C	-5.090614000	-0.612358000	-0.026338000
C	2.014989000	4.714780000	-0.026338000
C	3.365391000	5.109546000	-0.032564000
C	3.749702000	6.442652000	-0.031885000
C	2.783190000	7.474913000	-0.032601000
C	1.420465000	7.084537000	-0.014499000
C	1.057179000	5.748270000	-0.014971000
C	-5.506737000	-1.958591000	-0.014971000
C	-6.845622000	-2.312110000	-0.014499000
C	-7.865060000	-1.327143000	-0.032601000
C	-7.454351000	0.026011000	-0.031885000
C	-6.107692000	0.359741000	-0.032564000
C	2.742301000	-5.469287000	-0.032564000
C	3.704649000	-6.468663000	-0.031885000
C	5.081870000	-6.147770000	-0.032601000
C	5.425157000	-4.772427000	-0.014499000
C	4.449558000	-3.789679000	-0.014971000
N	-9.204548000	-1.677358000	-0.056766000
C	-9.590550000	-3.067406000	0.116387000
C	-10.218918000	-0.647879000	0.090551000
N	3.149639000	8.810051000	-0.056766000
C	4.548379000	9.173782000	0.090551000
C	2.138823000	9.839363000	0.116387000
N	6.054909000	-7.132693000	-0.056766000
C	7.451726000	-6.771957000	0.116387000
C	5.670539000	-8.525903000	0.090551000
H	-2.657682000	-2.059064000	-0.025942000
H	-0.454361000	3.331152000	-0.025942000
H	3.112043000	-1.272088000	-0.025942000
H	2.527563000	2.610382000	-0.027268000
H	0.996876000	-3.494125000	-0.027268000
H	-3.524439000	0.883743000	-0.027268000
H	4.135928000	4.342567000	-0.033966000
H	4.806142000	6.680045000	-0.029553000
H	0.638803000	7.833818000	0.001702000
H	0.000000000	5.501278000	-0.001505000
H	-4.764247000	-2.750639000	-0.001505000
H	-7.103687000	-3.363689000	0.001702000
H	-8.188160000	0.822219000	-0.029553000
H	-5.828737000	1.410535000	-0.033966000
H	1.692809000	-5.753102000	-0.033966000
H	3.382018000	-7.502264000	-0.029553000
H	6.464884000	-4.470129000	0.001702000
H	4.764247000	-2.750639000	-0.001505000
H	-9.280007000	-3.477695000	1.089258000
H	-10.675866000	-3.148613000	0.044287000

H	-9.159776000	-3.699062000	-0.669119000
H	-10.153050000	-0.120347000	1.054297000
H	-11.206493000	-1.105502000	0.020024000
H	-10.143117000	0.099014000	-0.708261000
H	4.972301000	8.852973000	1.054297000
H	5.157307000	8.734690000	-0.708261000
H	4.645854000	10.257859000	0.020024000
H	1.376406000	9.782130000	-0.669119000
H	1.628231000	9.775569000	1.089258000
H	2.611154000	10.819878000	0.044287000
H	8.064712000	-7.671265000	0.044287000
H	7.783370000	-6.083068000	-0.669119000
H	7.651776000	-6.297874000	1.089258000
H	5.180749000	-8.732626000	1.054297000
H	4.985810000	-8.833704000	-0.708261000
H	6.560639000	-9.152357000	0.020024000

for C_1 symmetric structure **II**:

C	-0.805064000	1.037972000	0.000740000
N	-1.364058000	-0.182787000	-0.004910000
C	-0.496150000	-1.216484000	-0.014830000
N	0.840559000	-1.090178000	-0.018890000
C	1.301825000	0.178330000	-0.012390000
N	0.524120000	1.272794000	-0.002640000
C	2.745244000	0.405441000	-0.016130000
C	-1.021293000	-2.580017000	-0.021670000
C	-1.723420000	2.174435000	0.011370000
C	-2.340675000	-2.868195000	-0.018810000
C	-1.313471000	3.461168000	0.017940000
C	3.654627000	-0.592915000	-0.026350000
C	-2.141384000	4.658457000	0.028450000
C	5.105480000	-0.474559000	-0.030750000
C	-2.963884000	-4.183720000	-0.024750000
C	-4.367185000	-4.284699000	-0.026600000
C	-5.024090000	-5.506720000	-0.030750000
C	-4.297107000	-6.719609000	-0.041090000
C	-2.882631000	-6.625597000	-0.027480000
C	-2.245622000	-5.396052000	-0.023030000
C	5.796068000	0.753609000	-0.012750000
C	7.179383000	0.816982000	-0.016470000
C	7.968230000	-0.360560000	-0.045820000
C	7.281516000	-1.596720000	-0.051870000
C	5.894766000	-1.639111000	-0.048140000
C	-1.527479000	5.924339000	0.039840000
C	-2.257625000	7.104039000	0.048780000
C	-3.671542000	7.080517000	0.054510000
C	-4.297011000	5.808524000	0.031380000
C	-3.550416000	4.642292000	0.022240000
N	9.351363000	-0.300326000	-0.074200000
C	10.022235000	0.975825000	0.106330000
C	10.126469000	-1.521518000	0.061390000
N	-4.937025000	-7.947272000	-0.070040000
C	-6.380519000	-8.008663000	0.081820000
C	-4.165468000	-9.167541000	0.093840000
N	-4.415076000	8.248177000	0.088070000
C	-3.746260000	9.530010000	-0.053480000
C	-5.857236000	8.190895000	-0.079550000
H	3.032226000	1.452371000	-0.010500000
H	-0.258223000	-3.352101000	-0.029750000
H	-2.773593000	1.899498000	0.013950000
H	-3.020981000	-2.018600000	-0.012100000
H	-0.237546000	3.625706000	0.015950000
H	3.259158000	-1.606949000	-0.033020000
H	-4.958578000	-3.372436000	-0.020490000
H	-6.106806000	-5.515954000	-0.024550000
H	-2.276598000	-7.522991000	-0.018620000
H	-1.160088000	-5.377691000	-0.013220000
H	5.237289000	1.684250000	0.009450000

H	7.653374000	1.790391000	0.005210000
H	7.831004000	-2.529704000	-0.058250000
H	5.400579000	-2.607476000	-0.054950000
H	-0.441750000	5.980620000	0.037520000
H	-1.724456000	8.046457000	0.049990000
H	-5.377145000	5.732209000	0.018800000
H	-4.077020000	3.692980000	0.005110000
H	9.808046000	1.435185000	1.083240000
H	11.100061000	0.826962000	0.029970000
H	9.731974000	1.689838000	-0.673100000
H	9.954254000	-2.030458000	1.022000000
H	11.188057000	-1.281780000	-0.011080000
H	9.892174000	-2.229715000	-0.741890000
H	-6.723951000	-7.611583000	1.049200000
H	-6.885806000	-7.446100000	-0.711840000
H	-6.704725000	-9.047337000	0.006000000
H	-3.410968000	-9.268249000	-0.694930000
H	-3.649413000	-9.218002000	1.064610000
H	-4.834248000	-10.025974000	0.019630000
H	-4.484191000	10.329486000	0.023880000
H	-3.009724000	9.681905000	0.744110000
H	-3.226717000	9.634617000	-1.018130000
H	-6.156617000	7.774994000	-1.053530000
H	-6.323511000	7.583061000	0.704500000
H	-6.266582000	9.198792000	-0.000320000

for C_1 symmetric structure **III**:

C	0.489493000	-1.406591000	-0.026060000
N	0.847080000	-0.111574000	-0.025395000
C	-0.170473000	0.769422000	-0.024878000
N	-1.472907000	0.433006000	-0.024620000
C	-1.728052000	-0.889733000	-0.025389000
N	-0.784604000	-1.850412000	-0.026104000
C	-3.115592000	-1.345842000	-0.025486000
C	0.124728000	2.201469000	-0.024477000
C	1.525668000	-2.437412000	-0.026610000
C	1.376468000	2.707134000	-0.026873000
C	2.848884000	-2.168545000	-0.025749000
C	-4.174146000	-0.506843000	-0.025978000
C	3.949557000	-3.121379000	-0.026011000
C	-5.586603000	-0.857856000	-0.026070000
C	1.769322000	4.109196000	-0.026853000
C	3.135234000	4.445723000	-0.040200000
C	3.576551000	5.761146000	-0.040187000
C	2.655361000	6.833944000	-0.034062000
C	1.277329000	6.502304000	-0.008221000
C	0.856961000	5.182858000	-0.008349000
C	-6.069173000	-2.181833000	-0.013477000
C	-7.423899000	-2.468240000	-0.012649000
C	-8.393058000	-1.433698000	-0.031550000
C	-7.915601000	-0.102563000	-0.032382000
C	-6.554042000	0.163748000	-0.033317000
C	5.274809000	-2.649122000	-0.028833000
C	6.368097000	-3.503354000	-0.027679000
C	6.190743000	-4.906297000	-0.031475000
C	4.857995000	-5.389366000	-0.017078000
C	3.779980000	-4.520287000	-0.017844000
N	-9.748117000	-1.716937000	-0.054711000
C	-10.202785000	-3.086108000	0.118503000
C	-10.710318000	-0.638056000	0.088870000
N	3.078581000	8.152241000	-0.059018000
C	4.492550000	8.455400000	0.079238000
C	2.113963000	9.223535000	0.122920000
N	7.270503000	-5.772786000	-0.054996000
C	8.616570000	-5.247593000	0.095278000
C	7.054850000	-7.199847000	0.113382000
H	-3.229655000	-2.425334000	-0.025852000
H	-0.756087000	2.835947000	-0.023171000

H	1.140643000	-3.452309000	-0.027992000
H	2.191145000	1.985521000	-0.030508000
H	3.130614000	-1.117266000	-0.025535000
H	-3.947514000	0.557784000	-0.027371000
H	3.872345000	3.646541000	-0.046979000
H	4.642210000	5.952949000	-0.043639000
H	0.528633000	7.284381000	0.013801000
H	-0.209743000	4.981564000	0.011392000
H	-5.366972000	-3.009761000	0.000719000
H	-7.734047000	-3.505629000	0.004480000
H	-8.608996000	0.729090000	-0.030950000
H	-6.223101000	1.199349000	-0.035785000
H	5.449251000	-1.575973000	-0.027800000
H	7.362976000	-3.075996000	-0.022605000
H	4.664266000	-6.454705000	-0.003564000
H	2.778908000	-4.940354000	-0.007306000
H	-9.911254000	-3.511603000	1.090663000
H	-11.290927000	-3.112927000	0.048552000
H	-9.805535000	-3.738267000	-0.667951000
H	-10.618426000	-0.111347000	1.050903000
H	-11.719316000	-1.046485000	0.019726000
H	-10.597601000	0.101612000	-0.712345000
H	4.908778000	8.116214000	1.040080000
H	5.076697000	7.990935000	-0.723727000
H	4.636107000	9.534318000	0.008275000
H	1.344728000	9.200966000	-0.657684000
H	1.607424000	9.179314000	1.098983000
H	2.627434000	10.183067000	0.049831000
H	9.331264000	-6.068518000	0.024737000
H	8.853798000	-4.533622000	-0.702049000
H	8.770268000	-4.740669000	1.060081000
H	6.600613000	-7.450215000	1.084027000
H	6.406372000	-7.598433000	-0.675406000
H	8.012719000	-7.716793000	0.043147000