4.7. X-ray analysis on single crystals

4.7.1. Macrocycle 103c

After several attempts single crystals of **103c** could be grown by slow diffusion of methanol into a solution of macrocycle in chloroform and the structure solved by X-ray diffraction. The molecular structure of **103c** is depicted in Figure 98 and 99 as ORTEP representation. It possesses crystallographic Ci symmetry. Whereas all ring atoms and the acetylenic carbon atoms exhibit normal thermal displacement parameters those of the side chains differ drastically and reflect the differences in packing. The side chain attached to O1 shows small displacement parameters and all anti conformation as normal for alkyl chains (Figure 98). The one at O3 exhibits large Uij only at the terminal carbon atoms whereas the one at O2 has very large thermal parameters all over the chain including O2. These findings reflect the differences in positional freedom and the non-perfect packing for the latter two side chains which mainly fill the hole left side in the center of the macrocycle. The maximum diameter within the ring (C1 and C1') is roughly 18 Å, and the distance between N1 and N1' are about 10 Å apart from each other. Almost all atoms of the macrocycle are in one plane, whereas the bpy units are turned out of the plane with torsional angles of ≈ 39° (Figure 99). The data does not allow an unambiguous assignment of the bpy nitrogen atoms which may be disordered and they were selected arbitrary. Similar to Moore's, Henze's, and Grave's macrocycles, **103c** formes layered structures with channels. The layers have an ABCABC sequence in which, if viewed along the a axis, every third layer lies directly on top of the other (Figures 100 and 101). The AA distance is 108.14 pm. The molecules within the layers are in close contact to the bipyridine units, the distance between the two layers A and B at this part is approximately 3.69 Å. Another close contact was observed between the macrocycles from one layer (A) at O1 with one of the acetylene bound of the macrocycles from next layer (B) (3.84 Å).

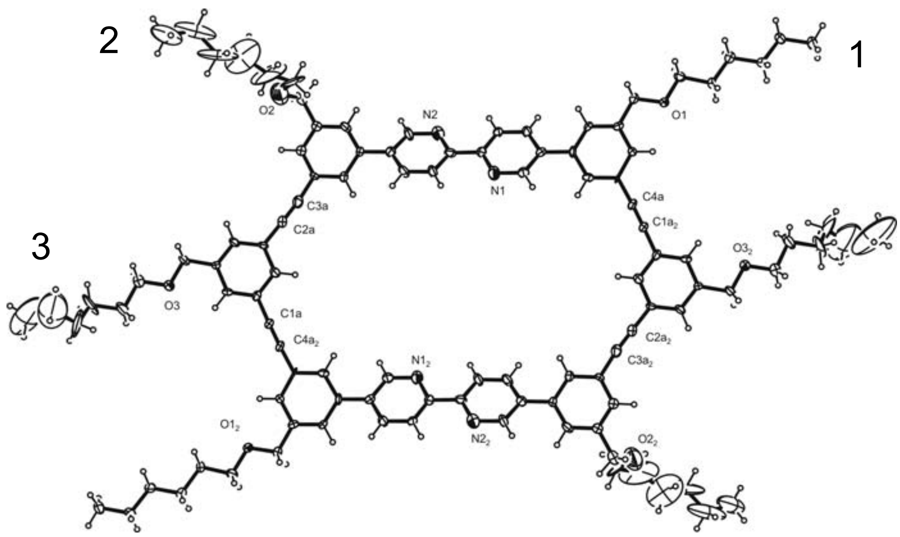

Figure 98. ORTEP plot [101] of macrocycle **103c**, view perpendicular to the macrocycle, 50% probability ellipsoids.

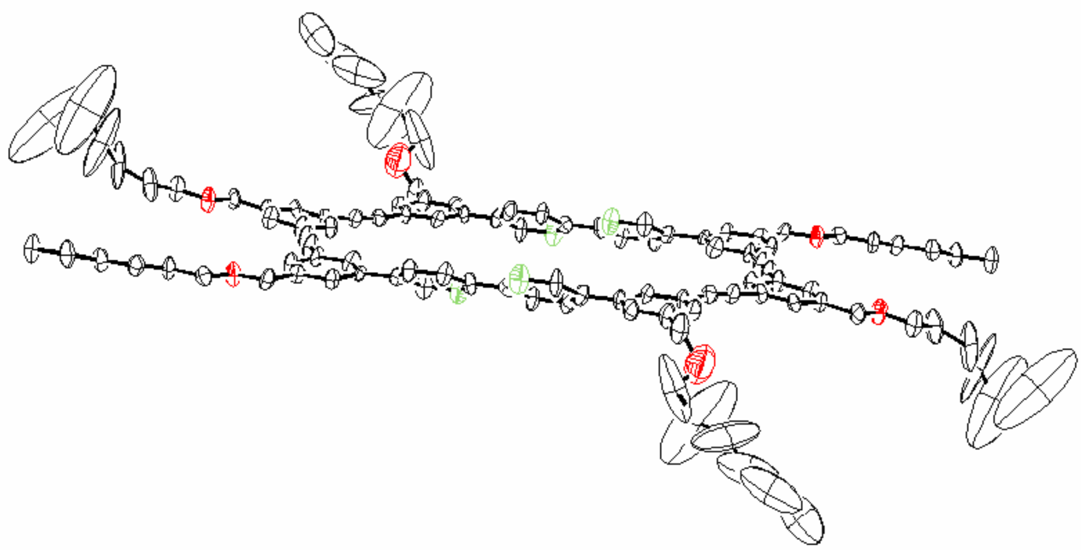

Figure 99. ORTEP plot of macrocycle **103c**, view parallel to the macrocycle, 50% probability ellipsoids.

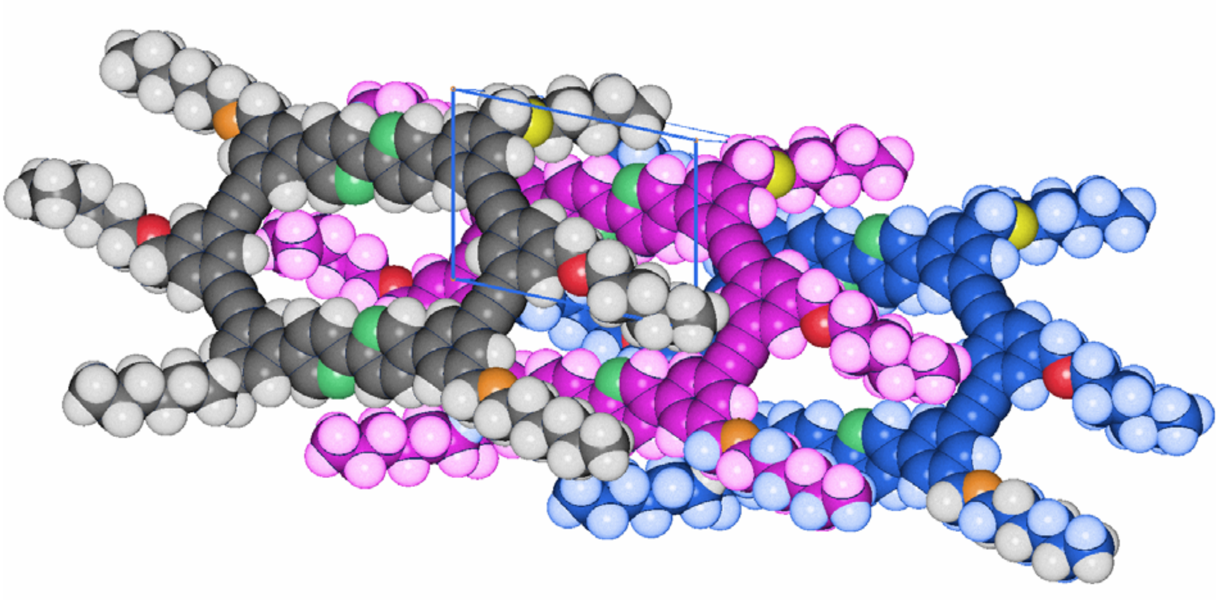

Figure 100. Space filling model (Schakal99)[102] of three molecules translated along the b axis by 1+y and -1+y. Two molecules are colored magenta and blue for easier distinguish. The oxygen atoms of the side chains are represented in different colors, O1 orange, O2 yellow and O3 red for clarity. One can clearly recognize that side chain 3 is directed towards the hole of the macrocycle like a clamp.

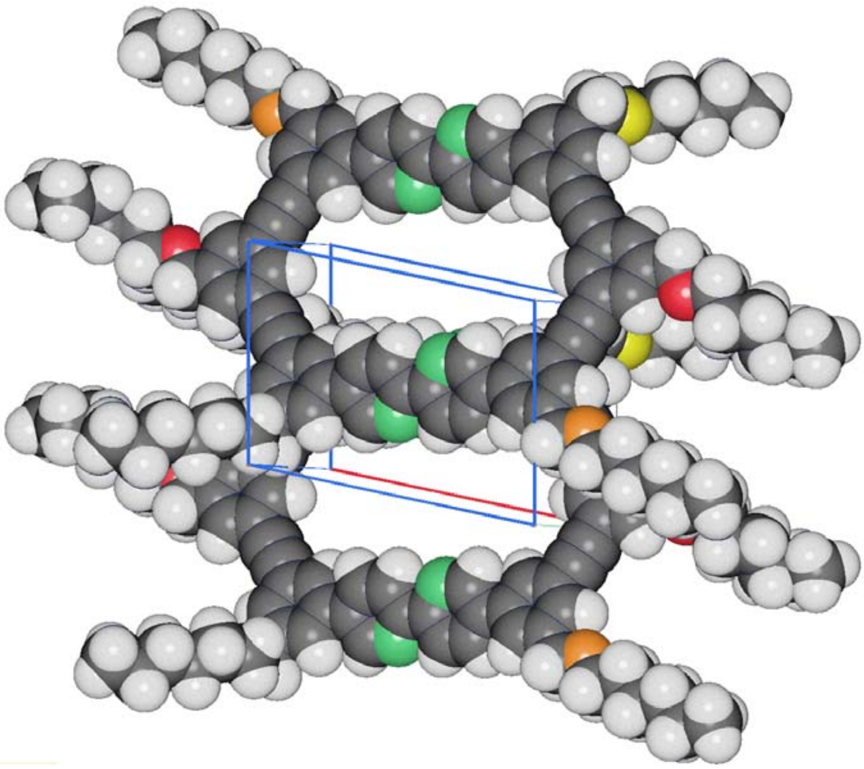

Figure 101. Space filling model of two molecules of **103c** translated by 1+x showing the stacking of the aromatic rings.

4.6.2. Macrocycle 106

Crystals of macrocycle **106** were grown by slow diffusion of methanol into a solution of macrocycle in chloroform. The molecular structure of **106** is depicted in figure 102 as ORTEP representation. All ring atoms and the acetylenic carbon atoms exhibit normal thermal displacement parameters, those of the side chains differ drastically and reflect the differences in packing. The side chain attached to O1 fills the hole left in the center of another macrocycle, exhibiting a large Uij at all carbon atoms. The one at O2 shows normal thermal displacement parameters. The distance between opposite triple bonds within the cavity amounts to approximately 15.6 Å and N1 and N1' are about 8.0 Å apart from each other. The cycle has almost planar sheets, with the bipyridine units turned out of the plane with torsional angles of ≈ 35° (Figure 103). The cycles form a layer structure which give rise to columns with channels (Figure 104, 105, and 106). The distance between two cycles in the column is approximately 8.4 Å. O2 of a macrocycle from one column has a short contact with one acetylene bond of one macrocycle from next column (3.61 Å).

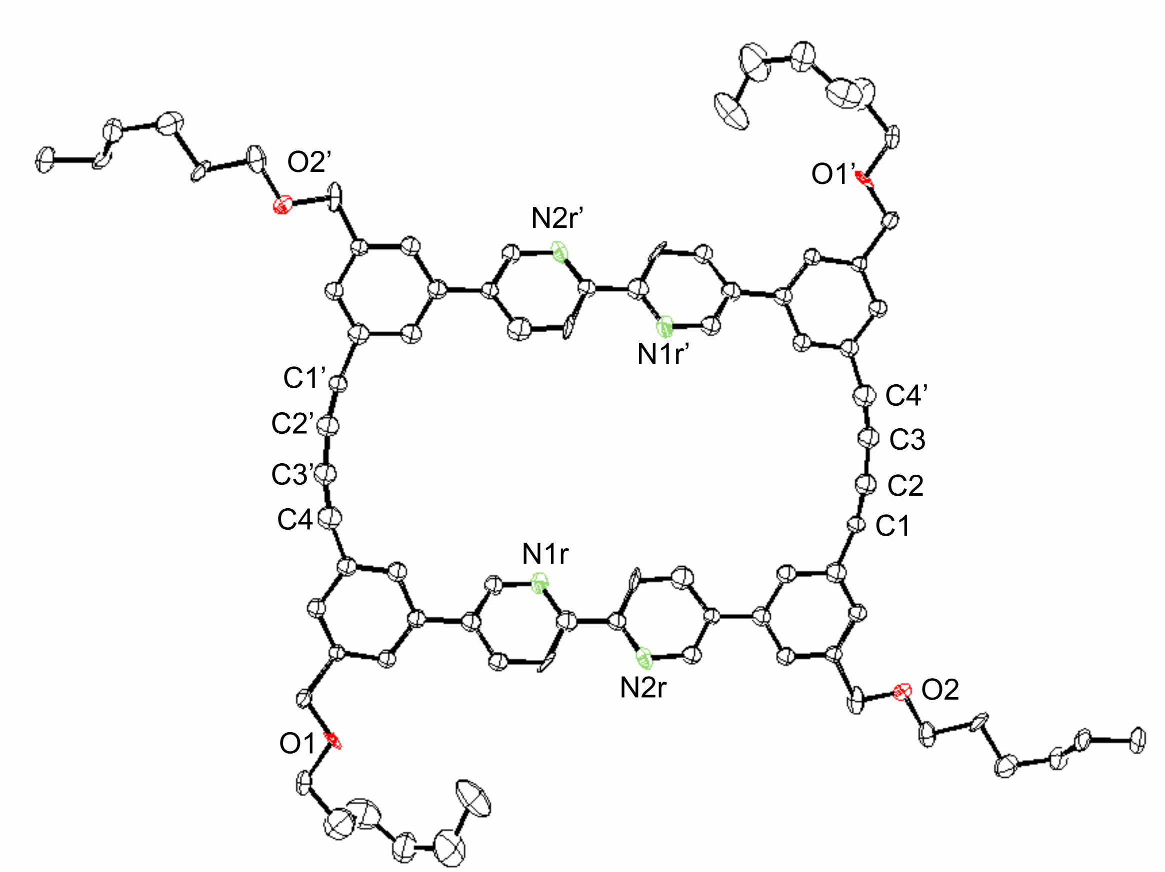

Figure 102. ORTEP plot of macrocycle **106**, view perpendicular to the macrocycle, 50% probability ellipsoids.

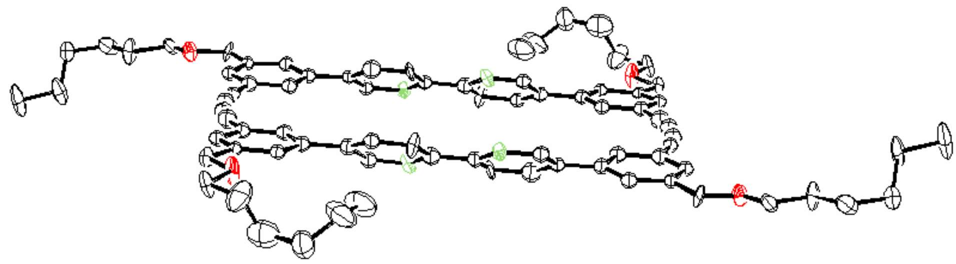

Figure 103. ORTEP plot of macrocycle **106**, view parallel to the macrocycle, 50% probability ellipsoids.

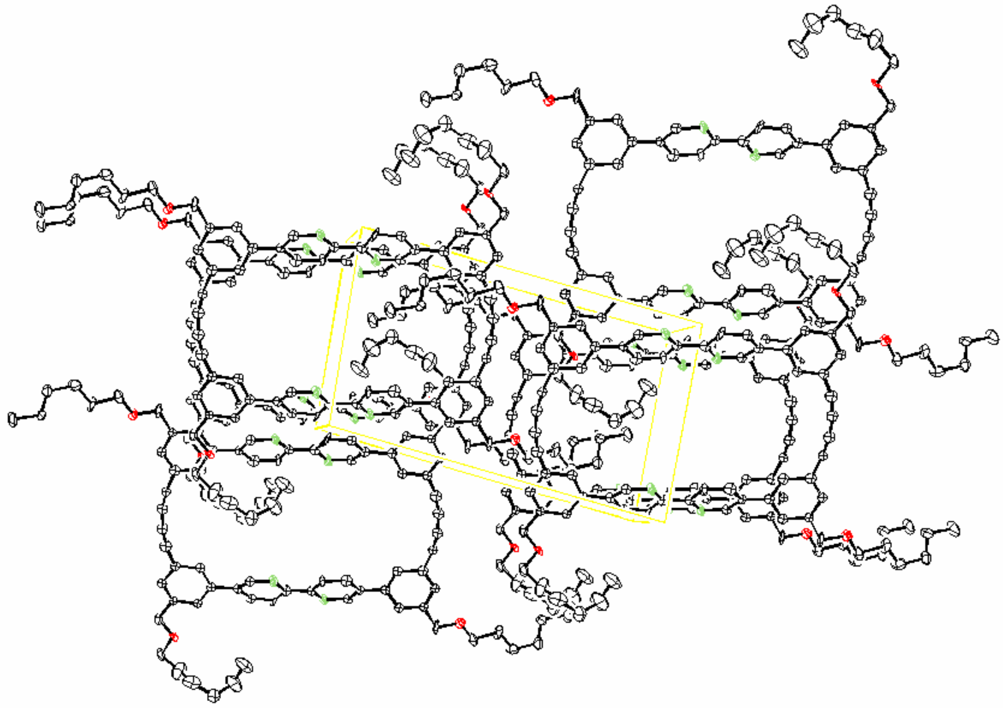

Figure 104. ORTEP plot of six molecules of **106** showing the stacking of the aromatic rings.

Figure 105. The interaction of four molecules of **106** and the complicated filling of the holes by the side chains 2 and 3 respectively.

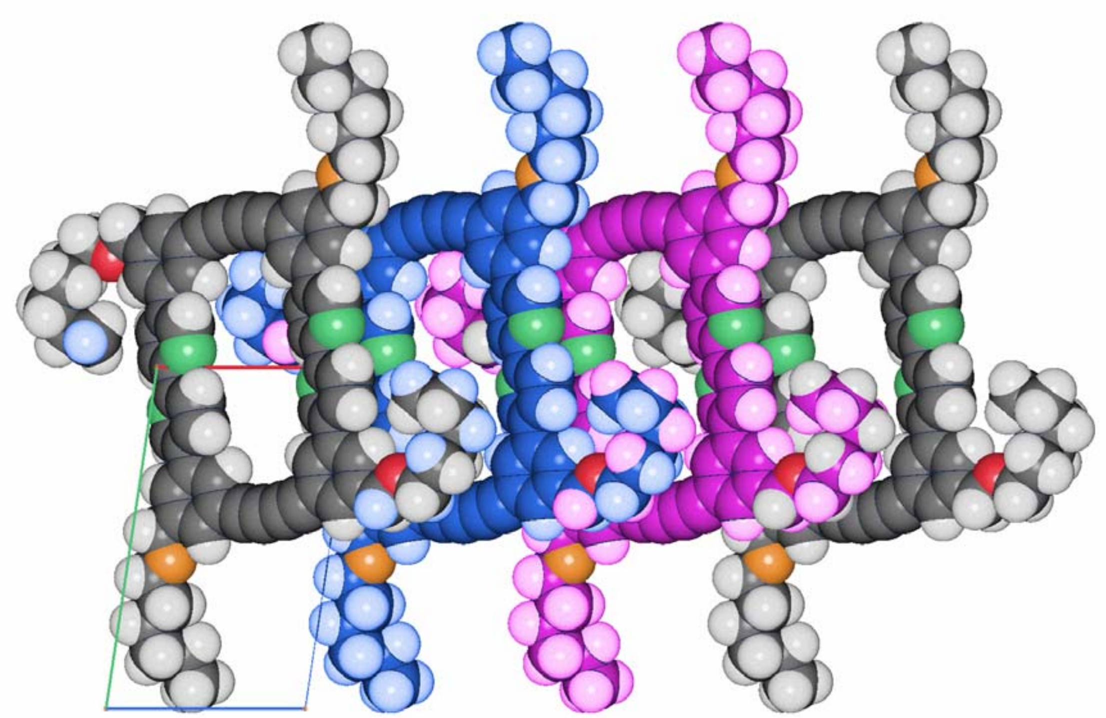

Figure 106. Space filling model (Schakal99)[102] of four molecules translated along the b axes by 1+y and -1+y. Two molecules are colored black and the other magenta and blue for easier distinguish. The oxygen atoms of the side chains are represented in different colors: orange and O3 red for clarity.