Molecular and Crystal Structure of Crown Ethers Containing Biphenyl Fragment

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X-ray diffraction study of dibenzo-14-crown-4, dibenzo-17-crown-5, dibenzo-20-crown-6 and tetrabenzo-24-crown-8 reveals unexpected independence of conformation of biphenyl fragment from size and conformation of macrocycle. Comparison of geometry of this fragment in isolated biphenyl, its ortho-dimetoxy derivative and crown ethers demonstrates that angle between two aromatic rings is determined by intramolecular repulsion between the oxygen atoms in ortho position of benzene ring and steric interactions of the C-H fragment of aromatic ring and nearest methylene group. Analysis of electron density distribution reveals the presence of numerous intramolecular C-H…O hydrogen bonds which may influence conformation of macrocycle. Crystal packing of crown ethers is determined by competition between trends to parallel arrangements of aromatic rings and aliphatic macrocycles. In the case of dibenzo-14-crown-4 benzene rings form stacks along (1 0 0) direction. Increase of macrocycle size results in parallel arrangement of aliphatic fragments. This leads to formation of cavities and channels in the crystal phase.

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