Intermolecular interactions in 1,1'-Binaphthyl, polymorphs and symmetry breaking

C. Ignacio Sainz-Díaz[a], Africa P. Martín-Islán[b], Julyan H. E. Cartwright[a], Alfonso Hernández-Laguna[b], *[a]Instituto Andaluz de Ciencias de la Tierra, CSIC - Universidad de Granada, Av. Fuentenueva s/n, 18002-Granada (Spain). sainz@lec.ugr.es. [b]Estación Experimental del Zaidín, CSIC, C/ Profesor Albareda,1, 18008-Granada (Spain).* E-mail: sainz@lec.ugr.es

A theoretical-experimental work is presented related with the chiral symmetry breaking of melting crystallization of 1,1'-binaphthyl derivatives and polymorphism. We confirm that the chiral symmetry breaking can be observed in crystallization from a melt of 1,1'-binaphthyl by a constant stirring during the crystallization. Crystallographic studies by Powder X-ray diffraction (PXRD) reveal two crystallographic forms of 1,1'-binaphthyl: one chiral form ($P42_12_1$) with either R or S enantiomers of the trans-1,1'-binaphthyl conformer and another racemic crystal (C2/c) with both enantiomers of the cis-1,1'-binaphthyl conformer. Quantum mechanical calculations of the crystal lattice for 1,1'-binaphthyl and 2,2'-dihydroxy-1,1'-binaphthyl polymorphs were performed by Density Functional Theory approximation. Our calculations reproduce the crystal lattice parameters and PXRD pattern finding the $P42_12_1$ form with lower energy than the C2/c form for 1,1'-binaphthyl. The main intermolecular interactions in 1,1'-binaphthyl crystals are weak aromatic CH/π hydrogen bonds, which are responsible for enantiomeric discrimination in the molecular recognition during crystallization. The C2/c form achieves a more efficient packing than the chiral one, but intermolecular interactions in $P42_12_1$ form are stronger than in C2/c form. In 2,2'-dihydroxy-1,1'-binaphthyl the intermolecular interactions are stronger with hydrogen bonds between the hydroxyl groups and polymorphs can be predicted by Monte Carlo simulated annealing.

Keywords: 1,1'-binaphthyl, intermolecular interactions, chiral recognition