Polymorphs of 4,4-Diphenyl-2,5-cyclohexadienone

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4,4-Diphenyl-2,5-cyclohexadienone **1** exists as a cluster of four conformational polymorphs A, B, C and D [1]. X-ray crystal structures show 19 crystallographic distinct molecular conformations due to rotation of gem-diphenyl rings: form A ($P2_1$, Z'=1), form B (*P*-1, Z'=4), form C (*P*-1, Z'=12) and form D (*Pbca*, Z'=2). These crystal structures are analyzed in terms of having different C-H…O hydrogen bonds and phenyl ring conformations. Crystal lattice and molecular conformation energies (Cerius^2, DFT) suggest that forms A and D are more stable than triclinic forms B, C. The stable form A has molecule **1** in a lower energy conformation whereas molecular conformations in forms D, B and C having increasing Z' numbers are progressively higher in energy. Variable-temperature PXRD shows transformation of various forms present in the solid to the stable form A upon heating to ca. 70 °C. Further heating of A to 110-120 °C and cooling gives form B, implying that the melt phase is the kinetic form (ca. 2 kcal/mol less stable than form A, Dreiding). The monoclinic form A is SHG active (ca. 2 x urea); this morph can be prepared in pure form by heating the mixture of polymorphs to ca. 70 °C. X-ray crystal structures, VT-PXRD measurements, energy computations and phenyl ring conformations of tetramorphic cluster **1** will be discussed.

[1] Kumar V.S.S., Addlagatta A., Nangia A., et al., *Angew. Chem. Int. Ed.*, 2002, **41**, 3848-3851.

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