Benzocaine (BZC), a local anaesthetic and one of the best known representatives of biologically active esters of 4-aminobenzoic acid, is an Active Pharmaceutical Ingredient (API) of many commercially available drugs. Unfortunately, its water solubility of 0.131 mg/ml makes it unsuitable for enteral administration. Solubility of an API is an important aspect affecting properties and application of a final drug product. It strongly depends on intermolecular interactions present in the solid form of a given compound, making analysis of H-bonding pattern crucial for investigation of crystal properties. It was shown that BZC exhibits specific tendency for molecular aggregation and H-bonding pattern formation, common to all three polymorphs of BZC reported so far (Sinha & Pattabhi, 1987; Lynch & McClenaghan, 2002; Chan et al., 2009). In order to induce changes in BZC aggregation and synthons hierarchy a series of high-pressure experiments was performed. Pressure has proven to induce a phase transition in crystals of BZC, introducing its new polymorph. Herein, we present a thorough analysis and comparison of intermolecular interactions and molecular packing for all four polymorphs of BZC.