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This manuscript deals with the synthesis, solid state structural and solution phase thermodynamic studies of a conceptually new cyclic trisaccharide, having expanded glycosidic bonds. Challenges to backbone modified cyclodextrin synthesis are several, due to which a cyclodextrin synthesis is still not a common place, in spite of the acknowledged fact that cyclodextrins continue to offer the most in scientific and technological advancements manifold. We undertook an approach to develop cyclic oligosaccharides by targeting a backbone modification. The approach involves incorporation of a methylene moiety at the inter-glycosidic bond, such that the sequence is C1-O-CH2-C4', as opposed to such sequence of C1-O-C4' present in natural cyclic oligosaccharides. In this manuscript, we present the synthesis of a glycosidic bond expanded linear trisaccharide, which is subjected to a cyclo-glycosylation, leading to the formation of a glycosidic bond expanded cyclic trisaccharide. Upon synthesis, we were fortunate to secure the single crystal X-ray structural determination of the cyclic trisaccharide, which revealed a pleasant surprise, with a rarely known trigonal symmetry of the molecule in the P3 space group. Structural analysis reveals several facets of the structure and the same is compared to naturally-occurring cyclodextrins. We further undertook to evaluate the host properties of this new cyclic trisaccharide and identify its specificity of binding to organic amines, with enhanced binding affinity to 1-aminoadamantane.