Design, synthesis and structure of new dendritic melamines. First use of a tandem C-2-substituted serinol—O,O-masked 4-piperidone as a peripheral unit in iterative synthesis

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The iterative chemoselective amination of cyanuric chloride to dimers of new G-2 dendritic N-substituted-2,4,6-triamino-s-triazines (melamines) having C-2-substituted 2-aminopropane-1,3-diols (‘serinols’) in tandem with the ethylene ketal of 4-piperidone as peripheral units is reported. The structure as a function of increasing molecular size was studied by NMR spectroscopy, DFT calculation and AFM imaging. A concise nomenclature defining the restricted rotational phenomena about the newly created C(s-triazine)2N(exocyclic) partial double bonds, seen as axes of (pro)diastereomerism, is used. We propose a new form of frontier rotamerism for the dendrimer surface, which operates over a long range.

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1. Introduction

Resulting from pharmaceutical chemistry, Serinol is the trivial nomenclature of 2-aminopropane-1,3-diol, seen as the reduced form of Serine and the parent term for a series of compounds comprising its commercial C-2-substituted analogues A–C (Chart 1).1

It was in 1985 when Newkome et al.2 used TRIS (C) in the synthesis of the first so-called ‘arborol’ that the chemistry of dendrimers came about. Subsequent developments of these ‘cascade syntheses’3 suggested that TRIS could be a very attractive serinolic building-block for dendritic structures. It could, for example, play several roles within such structures: peripheral unit, tetravalent branch cell and core.2b Both Serinol itself, as well as its cyclic acetals, proved of interest in the fields of biomedicine and nanomaterials for dendritic constructions of macromolecules. No attention, however, has been hitherto paid to Methylserinol A and Ethylserinol B. The last decade has seen much development in the field of melamine-based dendrimers. This has flowed from the first results of Simanek et al.4a in 2000. There have been various approaches to this new class of macromolecule taken. First, in the domain of iterative convergent versus divergent syntheses,4a–f one such approach consisted in the adding the ‘classic’ (but still useful) chemoselective amination of cyanuric chloride. Not long after

Chart 1. The C-2-substituted serinols’ family.