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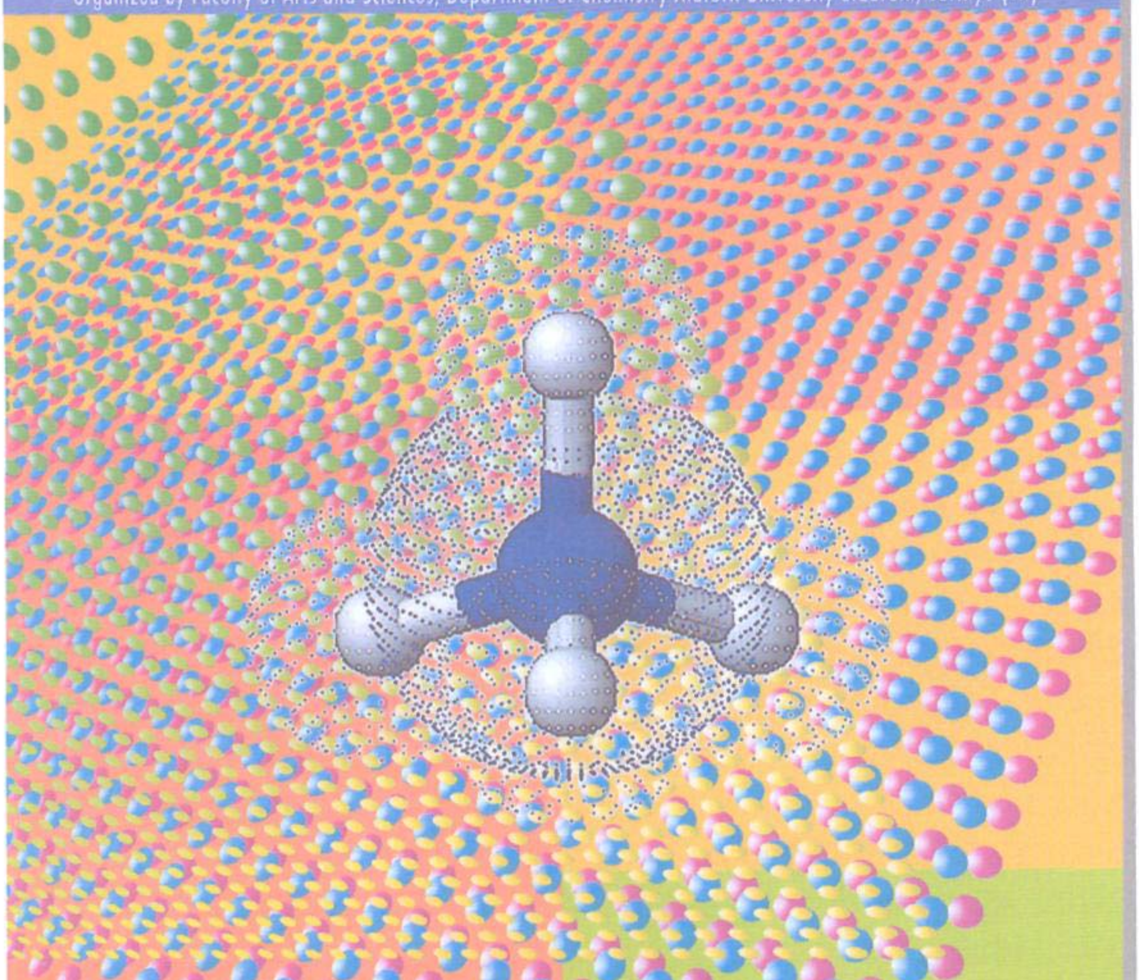
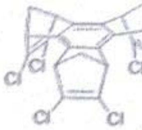


Benzocyclotrimers: C_3-symmetric, enantiopure, cup-shaped structures

Giuseppe Borsato,[a] Fabrizio Fabris[b] and Ottorino De Lucchi[b]
[a]Dipartimento di Scienze Ambientali, [b]Dipartimento di Chimica, Università Ca' Foscari di Venezia,
Dorsoduro 2137, I-30123 Venezia, Italy
delucchi@unive.it

After several years of research, we are now able to produce benzocyclotrimers (BCTs) with the desired *syn*-stereochemistry in multigram quantities. These molecules present an unique architecture, related and complementary to that of other substances with well known and useful applications in supramolecular chemistry, such as cyclodextrins, cycloveratrilenes, calixarenes and triphenylenes. Three features distinguish BCTs from other related molecules: (*i*) BCTs are rigid, concave cup-shaped structures exclusively formed by carbon-carbon bonds; (*ii*) the rim of the cavity can be variously functionalised with three to six functional groups; (*iii*) it is possible to produce C_3-symmetric BCTs in enantiopure form.



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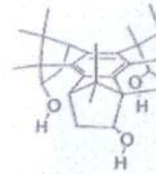

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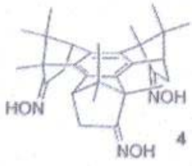

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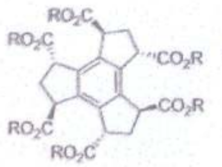

2 (R = H, Me, Menth)

$3xH_2O$

CH_4@4

The *syn* and *anti* hexachloro-BCTs **1** are readily available and react with oxidants to afford triindanehexacarboxylic acid **2**. The several isomers convert into a single D_3 symmetric structure on treatment with bases and to a single diastereoisomer when subjected to transesterification with menthol.[1] Once deprotected, the hexaacid is an enantiopure fully fuctionalized structure with features that can be implemented in the fields of liquid crystals, metal complexes and supramolecular polymers. The chiral enantiopure BCTs **3** and **4** display unique features. For example, benzotriborneol **3** contains three hydroxyl functionalities unidirectioned on one side of the molecule and behaves as a chiral receptor for ammonium ions.[2] It links also a water molecule in a way that the central oxygen atom is stereogenic ($3xH_2O$). Though "chiral" water is likely present in biology no other simple organic molecules possess such a feature. Benzotriborneol can be oxidised to benzotricamphor that gives the trioxime **4** upon reaction with hydroxylamine. The trioxime forms a very peculiar honeycomb crystal structure and dimerises in solution in the presence of small molecules through hydrogen bonds between the oxime functionalities giving rise to novel molecular capsules (*e.g.* CH_4@**4**).

References:

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