1H NMR Spectroscopy of the Hydrogen-Bonded Imide Groups of Hub(M)3:3CA Provides a Useful Method for the Characterization of These Aggregates. Simanek, Eric E.; Wazeer, Mohammed I. M.; Mathias, John P.; Whitesides, George M. Department of Chemistry, Harvard University, Cambridge, MA, USA. Journal of Organic Chemistry (1994), 59(17), 4904-9.

Abstract

Variable-temp. 1H NMR spectroscopy of the region between 13 and 16 ppm can be used in the conformational anal. of hydrogen-bonded aggregates comprising 1 equiv of a trismelamine [hub(M)3] and 3 equiv of an isocyanuric acid (CA). Two types of isomers are obsd.: a sym. C3 isomer (identified by two lines in this spectral region at low temp.) and an asym. C1 isomer (identified by six lines at low temp.), each existing as a pair of enantiomers. The isomers have similar structures: the N-H connectivity established by nuclear Overhauser effects is consistent with a rosette motif. The relative concns. of isomers depend slightly on solvent (CD2Cl2, CDCl3, C2D2Cl4) and on the structure of the CA (barbital, dibromobarbituric acid, triphenylpropylisocyanuric acid, and neohexylisocyanuric acid); the C3 isomer is favored over the C1 isomer by ca. 0.7 kcal/mol in all cases. This N-H region of the NMR spectrum also carries information about the dynamic behavior of these aggregates. The exchange of hydrogen-bonded imide protons between different environments leads to the coalescence of pairs of imide lines. This exchange-mediated coalescence occurs at different temps. and allows (with addnl. NOE data) individual CA groups to be identified. The activation energy for the exchange process or processes leading to coalescence of pairs of imide lines is .apprx.14 kcal/mol. This process is faster than the interconversion between C3 and C1 isomers.