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Dimerization of tris(o-ureidobenzyl)amines: a novel class of aggregates†

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Dimeric aggregates are formed by the assembly of two tripodal moieties which are held together, both in solution and in the solid state, by a belt of 6 hydrogen-bonded urea functions.

When two or more identical subunits are geometrically and functionally complementary, they may self-assemble to form a super molecule.1 Urea or thiourea functionalities are excellent candidates to construct molecules that self-assemble by hydrogen-bonding not only in the solid state but are able to persist in solution.2 Rebek3 and Böhmer4 have independently established that calix[4]arenes containing four urea functions at the upper rim form dimers by interdigitation of the all eight ureas in a head-to-tail directional array of 16 hydrogen bonds. Mendoza and coworkers have described dimeric capsules derived from previously reported tris(ureido)calix[6]arenes.5 Herein we report a novel type of self-assembled dimeric aggregate derived from tris(o-ureidobenzyl)amines which resemble the structure of ureidocalixaranes. 6

The tris(ureas) 1–3 shown in Scheme 1, easily available7 from previously reported tris(o-azidobenzyl)amines,8 showed dramatic differences in their 1H NMR spectra when recorded in CDCl3 or DMSO-δ6. While the spectra of 1–3 in DMSO-δ6 displayed the expected patterns consistent with averaged C3v symmetries (Fig. 1a), by changing the solvent to CDCl3, a new set of signals corresponding to a dimer (see below) emerged in each case. The ratio in which both species, monomer and dimer, were present in CDCl3 depended on the substituent R2 to a great extent. Thus, while for the tris(urea) 1 (R2 = p-tol) only the signals attributed to the dimer were apparent, for the tris(ureas) 2 and 3 (R2 = Bn) their spectra were interpreted as corresponding to equilibrium mixtures of both compounds (Fig. 1b).

The dimeric species featured two well separated doublets assigned to the diastereotopic methylene protons of the (ArCH2)3N fragment (Jgem = 14.5–15.7 Hz), instead of the singlet observed for the same nuclei in DMSO-δ6. In the dimers emerging from 2 and 3 the ABX systems formed by the three protons of the –CH2NH– fragments were clearly evident. The signals assigned to the NH protons of the dimers (near 5.2 and 6.3 ppm). The involvement of the urea carbonyl groups as hydrogen bonding acceptors is supported by the values of their carbon atoms in the 13C NMR spectra, which were shifted to downfield in CDCl3 (Δδ = 2.8–3.2 ppm). FT-IR of CHCl3 solutions of 1 (13.7 mM) and 2 (16.4 mM) revealed typical hydrogen-bonded NH-stretching bands9 at 3317–3327 cm−1.

All those data revealed that the dimers 1·1, 2·2 and 3·3 should possess a highly ordered, hydrogen-bonded structure. Further indication of the existence of 1·1 and 3·3 in solution came from ESI-MS experiments. This technique was used in virtue of its gentle ionization and has been reported to reflect, at least qualitatively, solution phenomena.10 The spectra in CHCl3 showed the molecular ions of the protonated dimers 1·1 (1463) and 3·3 (1547).

Thus, monomers and their dimeric aggregates coexist in equilibrium in CDCl3. Preliminary calculations of the dimerization constant of 1 by 1H NMR experiments at three concentrations (in the range 1–10 mM in CDCl3) following known equations11 showed values (82518, 83832 and 84755 M−1) which are comparable within the experimental error margin.

† Electronic supplementary information (ESI) available: 1H NMR spectra. See http://www.rsc.org/suppdata/cc/b0/b007955n/

Scheme 1

Fig. 1 (a) 1H NMR spectrum (300 MHz) of the tris(urea) 2 in DMSO-δ6 (the singlet at 3.39 ppm is H2O from the solvent), (b) 1H NMR spectrum measured in CDCl3 showing a mixture of 2 and 2·2.

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Since DMSO-$d_6$ is able to disrupt the intermolecular hydrogen bonds, only the monomeric species could be observed in this solvent. The thermodynamic stability of the dimeric aggregate 1:1 proved to be higher than 2:2 and 3:3. The dimer 1:1 is virtually the only species observed (≥98%) in a 30 mM CDCl$_3$ solution of 1. In contrast, the $^1$H NMR spectra of 2:2 and 3:3 in CDCl$_3$ solutions of the same concentration displayed considerable amounts of their respective monomers (15–20%). These dimerization equilibria were concentration dependent, and could be shifted toward the monomer by decreasing the concentration. These equilibria could be also totally shifted to the monomeric tris(urea) by adding DMSO-$d_6$ (40%) to the CDCl$_3$ solution. Finally, the composition of a mixture of CDCl$_3$ solutions of the same concentration displayed considerable amounts of signals attributable to the heterodimer $2\cdot d$ ($7.63$ ppm) and $3\cdot d$ ($7.80$ ppm) appeared (Fig. 3c), two of them due to the homodimers $2\cdot d$ and $3\cdot d$ (Fig. 3a-b), the doublet at 7.53 ppm was assigned to the monomer $3\cdot d$; (c) mixture of equimolecular quantities of 2:2 and 3:3 for a Marie Curie fellowship (contract HPMF-CT-1999-00126).

Notes and references

6. All the tris(urea)1–3 were characterized on the basis of their IR, $^1$H and $^{13}$C NMR spectra and CHN-analyses.
7. Sequential treatment of the corresponding tris(azide) with LiAlH$_4$ (64–68% yield) and p-tolyl or benzyl isocyanate, led to the tris(ureas)1–3 in good yields (61–99%).