Tripodal tris-urea derivatives as gelators for organic solvents

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SUPPORTING INFORMATION

Title: Tripodal Tris-Urea Derivatives as Gelators for Organic Solvents
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^{1}H NMR spectra were recorded on a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer. Chemical shifts are denoted in δ-units (ppm) relative to residual solvent peaks ($CDCl_3$, δ = 7.26; DMSO-d6, δ = 2.49). ^{13}C NMR spectra were recorded on a Varian Gemini-200 (50.32 MHz) or a Varian VXR-300 (75.48 MHz) spectrometer. Chemical shifts are denoted in δ-units (ppm) relative to the solvent ($CDCl_3$, δ = 76.91; DMSO-d6, δ = 39.5) and converted to the TMS scale.

General procedure for the synthesis of 1-7.
To a solution of tris(2-aminoethyl) amine (1 eqv.) in $CHCl_3$ was added the corresponding isocyanate (3 eqv.) in $CHCl_3$. After stirring for 2 hours the solvent was evaporated *in vacuo* and the remaining white solid was stirred in diethyl ether, filterd off and eventually recrystallised from $CHCl_3$. Conversion was complete.

1: ^{1}H NMR (DMSO-d6): δ = 8.50 (s, 3H), 7.36 (d, 6H, J=7.69 Hz), 7.18 (t, 6H, J=&.87 Hz), 6.86 (t, 3H, J=7.33 Hz), 6.16 (m, 3H), 3.17 (m, 6H), 2.58 (t, 6H, J=6.41 Hz); ^{13}C NMR (DMSO-d6): δ = 155.28 , 140.42, 128.56, 120.97, 117.70, 53.92, 37.50; CI: 504 ($M + H^+$).

2: ^{1}H NMR (DMSO-d6): δ = 9.39 (s, 3H), 8.108 (d, 6H, J=9.52 Hz), 7.58 (d, 6H, J=9.52 Hz), 6.47 (s, 3H), 3.21 (m, 6H), 2.62 (m, 6H); ^{13}C NMR (DMSO-d6): δ = 154.48, 147.17, 140.32, 125.06, 116.77, 53.48, 37.56. $C_{18}H_{30}N_{10}O_9$

3: ^{1}H NMR (DMSO-d6): δ = 7.32-7.18 (m, 15H), 6.44 (t, 3H, J=5.86 Hz), 6.02 (m, 3H), 4.19 (d, 6H, J=5.49 Hz), 3.08 (d, 6H, J=5.50 Hz), 2.49 (d, 6H, J=6.23 Hz); ^{13}C NMR (DMSO-d6): δ = 158.16, 140.82, 128.14, 126.92, 126.45, 54.31, 42.90, 37.78; IR (KBr): ν = 1627, 1579 cm^{-1}; CI: 546 ($M + H^+$). $C_{30}H_{39}N_7O_3$: calcd. C 66.03, H 7.20, N 17.97; found: C 65.9, H 7.23, N 18.01.

4: ^{1}H NMR ($CDCl_3$): δ = 6.18 (s, 3H), 5.62 (s, 3H), 3.13-3.07 (m, 12H), 2.48 (m, 6H), 1.48-1.28 (m, 12H), 0.89 (t, 9H, J=7.14 Hz); ^{13}C NMR ($CDCl_3$): δ = 159.68, 55.06, 39.99, 38.37, 32.48, 20.09, 13.79; IR (KBr): ν = 1630, 1585 cm^{-1}; $C_{21}H_{45}N_7O_3$: calcd. C 56.86, H 10.22, N 22.10; found: C 56.78, H 10.17, N 22.10.

5: ^{1}H NMR ($CDCl_3$): δ = 6.06 (s, 3H), 5.54 (s, 3H), 3.09 (m, 12H), 2.46 (s, 6H), 1.44 (m, 6H), 1.25 (s, 30H), 0.85 (t, 9H, J=6.95 Hz); ^{13}C NMR ($CDCl_3$): δ = 159.63, 54.97, 40.47, 38.40, 31.76, 30.52, 29.48, 29.32, 27.12, 22.55, 14.06.

6: ^{1}H NMR ($CDCl_3$): δ = 5.96 (s, 3H), 5.45 (s, 3H), 3.10 (m, 12H), 2.47 (s, 6H), 1.44 (m, 6H), 1.23 (s, 54H), 0.85 (t, 6H, J=6.22 Hz);^{13}C NMR ($CDCl_3$): δ = 159.48, 54.87, 40.41, 38.30, 31.83, 30.42, 29.63, 29.47, 29.29, 27.04, 22.59, 13.99; $C_{45}H_{93}N_7O_3$: calcd. C 69.27, H 12.01, N 12.57; found: C 69.23, H 12.02, N 12.41.

7: ^{1}H NMR (DMSO-d6): δ = 5.78 (t, 3H, J=5.49 Hz), 5.64 (d, 3H, J=8.69 Hz), 3.41 (m, 3H), 3.00 (m, 6H), 2.41 (t, 6H, 6.22 Hz), 1.41-1.22 (m, 24H), 0.81 (m, 18H); ^{13}C NMR (DMSO-d6): δ = 158.12, 54.61, 49.89, 37.72, 34.29, 27.90, 27.67, 22.17, 13.93, 10.08; IR (KBr): ν = 1628, 1574 cm^{-1}; $C_{30}H_{63}N_7O_3$.

Crystal structure determination of 1.

$C_{27}H_{33}N_7O_3$, M_r = 503.60, colourless, block-shaped crystal (0.2 x 0.3 x 0.3 mm), monoclinic, space group $P2_1/c$ (no. 14) with a = 12.4748(12), b = 17.761(3), c = 13.4073(10) Å, b = 117.304(7)°, V = 2639.6(6) Å^3, Z = 4, D_x = 1.267 g cm^{-3}, F(000) = 1072, m(Mo Kα) = 0.086 mm^{-1}. 14467 reflections measured, 5958 independent, R_{int} = 0.0558, (1.6° < q < 27.4°, T = 150 K, Mo $K\alpha$ radiation, graphite monochromator, λ = 0.71073 Å) on a Nonius KappaCCD diffractometer on rotating anode. The structure was solved by automated direct methods (SHELXS97 [a]). Refinement on F^2 was caried out by full-matrix least-squares techniques (SHELXL-97 [b]). Hydrogen atoms were located on a difference Fourier map; their coordinates were included as parameters in the refinement. Refinement of 433 parameters converged at a final wR2 value of 0.1145, w = 1/[σ^2 (F^2) + (0.0438P)^2 + 0.39P], where P = (Max(F^2_o, 0) + 2F^2_c)/3, R1 = 0.0480 (for 4059 reflections with I > 2σ (I)), S = 1.032, -0.19 < Δr < 0.19 e Å^{-3}. Scattering factors were taken from the International Tables for Crystallography [c].

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[a] Sheldrick, G. M. SHELXS97 Program for crystal structure determination. University of Göttingen, Germany, **1997.**

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