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Tripodal tris-urea derivatives as gelators for organic solvents

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Published in:
European Journal of Organic Chemistry

DOI:
[10.1002/1099-0690\(200011\)2000:22<3675::AID-EJOC3675>3.0.CO;2-K](https://doi.org/10.1002/1099-0690(200011)2000:22<3675::AID-EJOC3675>3.0.CO;2-K)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2000

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

DE Loos, M., Ligtenbarg, A. G. J., van Esch, J. H., Kooijman, H., Spek, A. L., Hage, R., Kellogg, R. M., & Feringa, B. L. (2000). Tripodal tris-urea derivatives as gelators for organic solvents. *European Journal of Organic Chemistry*, 2000(22), 3675 - 3678. [https://doi.org/10.1002/1099-0690\(200011\)2000:22<3675::AID-EJOC3675>3.0.CO;2-K](https://doi.org/10.1002/1099-0690(200011)2000:22<3675::AID-EJOC3675>3.0.CO;2-K)

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SUPPORTING INFORMATION

Title: Tripodal Tris-Urea Derivatives as Gelators for Organic Solvents

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Ref. No.: O00275

^1H 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 , $\delta = 7.26$; DMSO-d_6 , $\delta = 2.49$). ^{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 , $\delta = 76.91$; DMSO-d_6 , $\delta = 39.5$) 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, filtered off and eventually recrystallised from CHCl_3 . Conversion was complete.

1: ^1H NMR (DMSO-d_6): $\delta = 8.50$ (s, 3H), 7.36 (d, 6H, $J=7.69$ Hz), 7.18 (t, 6H, $J=8.87$ 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-d_6): $\delta = 155.28$, 140.42, 128.56, 120.97, 117.70, 53.92, 37.50; CI: 504 ($\text{M} + \text{H}^+$).

2: ^1H NMR (DMSO-d_6): $\delta = 9.39$ (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-d_6): $\delta = 154.48$, 147.17, 140.32, 125.06, 116.77, 53.48, 37.56. $\text{C}_{18}\text{H}_{30}\text{N}_{10}\text{O}_9$

3: ^1H NMR (DMSO-d_6): $\delta = 7.32$ -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-d_6): $\delta = 158.16$, 140.82, 128.14, 126.92, 126.45, 54.31, 42.90, 37.78; IR (KBr): $\nu = 1627$, 1579 cm^{-1} ; CI: 546 ($\text{M} + \text{H}^+$). $\text{C}_{30}\text{H}_{39}\text{N}_7\text{O}_3$: calcd. C 66.03, H 7.20, N 17.97; found: C 65.9, H 7.23, N 18.01.

4: ^1H NMR (CDCl_3): $\delta = 6.18$ (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): $\delta = 159.68$, 55.06, 39.99, 38.37, 32.48, 20.09, 13.79; IR (KBr): $\nu = 1630$, 1585 cm^{-1} ; $\text{C}_{21}\text{H}_{45}\text{N}_7\text{O}_3$: calcd. C 56.86, H 10.22, N 22.10; found: C 56.78, H 10.17, N 22.10.

5: ^1H NMR (CDCl_3): $\delta = 6.06$ (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): $\delta = 159.63$, 54.97, 40.47, 38.40, 31.76, 30.52, 29.48, 29.32, 27.12, 22.55, 14.06.

6: ^1H 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; $\text{C}_{45}\text{H}_{93}\text{N}_7\text{O}_3$: calcd. C 69.27, H 12.01, N 12.57; found: C 69.23, H 12.02, N 12.41.

7: ^1H NMR ($\text{DMSO}-d_6$): 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 ($\text{DMSO}-d_6$): 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} ; $\text{C}_{30}\text{H}_{63}\text{N}_7\text{O}_3$.

Crystal structure determination of 1.

$\text{C}_{27}\text{H}_{33}\text{N}_7\text{O}_3$, M_r = 503.60, colourless, block-shaped crystal (0.2 x 0.3 x 0.3 mm), monoclinic, space group $\text{P2}_1/\text{c}$ (no. 14) with a = 12.4748(12), b = 17.761(3), c = 13.4073(10) Å, β = 117.304(7)°, V = 2639.6(6) Å³, Z = 4, D_x = 1.267 g cm⁻³, $F(000)$ = 1072, $\mu(\text{Mo K}\alpha)$ = 0.086 mm⁻¹. 14467 reflections measured, 5958 independent, R_{int} = 0.0558, ($1.6^\circ < \theta < 27.4^\circ$, 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 carried 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, $w = 1/[\sigma^2(F^2) + (0.0438P)^2 + 0.39P]$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, $R1$ = 0.0480 (for 4059 reflections with $I > 2\sigma(I)$), S = 1.032, $-0.19 < \Delta\rho < 0.19$ e Å⁻³. Scattering factors were taken from the International Tables for Crystallography [c].

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