A New Class of Folding Oligomers: Crescent Oligoamides

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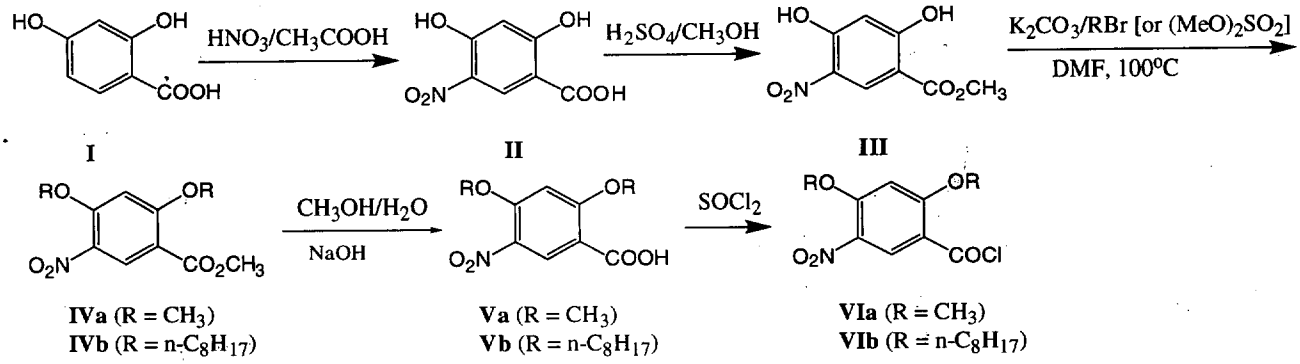
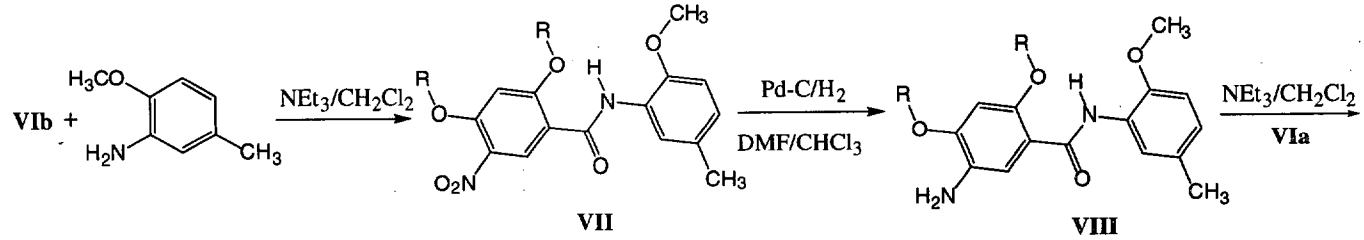
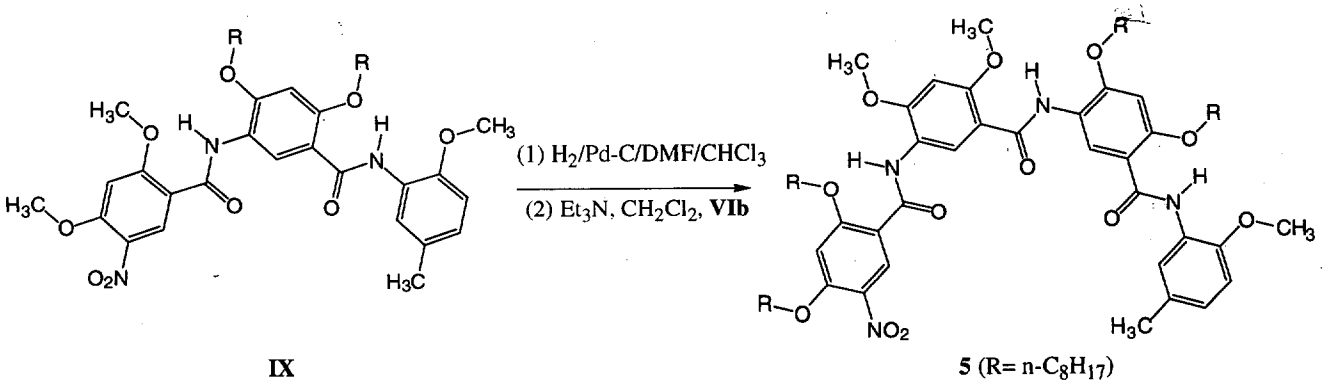
Supporting Information

I. Synthetic Procedures







2,4-Dihydroxy-5-nitrobenzoic acid (II). Acetic acid (300 mL) and nitric acid (280 mL) were mixed and cooled to 0 °C in an ice bath, to which 2,4-dihydroxybenzoic **I** (77 g, 50 mmol) was added portionwise. The reaction was warmed to room temperature and stirred for 12 hrs. The precipitated product **II** was collected by filtration and washed with minimum amount of water (70 g, yield 72%).

Methyl 2,4-dihydroxy-5-nitrobenzoate (III). Compound **II** (70g, 35 mmol) was dissolved into methanol (300 mL), to which conc. sulfuric acid (30 mL) was added. The reaction mixture was refluxed overnight. The precipitated product was collected by filtration and purified by washing from boiling methanol (48g, yield 64.4%). ^{1}H NMR (400 MHz, DMSO) δ 11.74(s, 1H), 11.20(s, 1H), 8.39(s, 1H), 6.58(s, 1H), 3.84(s, 3H).

Methyl 2,4-dimethoxy-5-nitrobenzoate (IVa). Dimethyl sulfate (58 mL, 600 mmol) was added dropwise to a mixture of compound **III** (32g, 0.15 mol), anhydrous potassium carbonate (60g, 0.45 mol) and DMF (300 mL) at 0 °C over a period of 2 hrs. The reaction mixture was then stirred at 100 °C for 72 hrs, after which the reaction mixture was filtered while still hot. DMF was removed under vacuum. The remaining residue was distilled under high vacuum (5 mm Hg). The product was obtained as an oil which quickly solidified at room temperature (18 g, 50%). ^{1}H NMR (400 MHz, DMSO) δ 3.77(s, 3H), 3.99(s, 1H), 4.04(s, 1H), 6.88(s, 1H), 8.37(s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 52.72, 57.75, 58.02, 99.20, 111.93, 130.46, 131.81, 158.45, 164.42, 164.56.

Methyl 2,4-dioctyloxy-5-nitrobenzoate (IVb). Compound **III** (25g, 0.12 mol), 1-bromooctane (75g, 0.38 mol) and anhydrous potassium carbonate (96 g, 0.69mol) were mixed in fresh DMF (300 mL) and stirred at 100 °C for 72 hrs, after which the reaction mixture was filtered while still hot. DMF was removed under vacuum. The remaining residue was dissolved in chloroform. The solution was washed by water (2 x 50 mL) and dried over anhydrous sodium sulfate. Removal of chloroform gave the product which was recrystallized from methanol (43 g, 85%). ^{1}H NMR (400 MHz, DMSO) δ 0.84 - 0.85 (br s, 3H), 1.24(m, 16H), 1.42(m, 4H), 1.73(m, 4H), 3.76(s, 3H), 4.18 - 4.24 (m, 4H), 6.83(s, 1H), 8.34(s, 1H). ^{13}C NMR (100 MHz, DMSO) δ 14.58, 22.73, 25.92, 25.95, 28.86, 28.94, 29.17, 29.21, 29.26, 29.31, 31.84, 31.86, 52.59, 70.11, 70.54, 100.17, 111.78, 130.48, 131.75, 157.82, 163.99, 164.52.

2,4-Dialkoxy-5-nitrobenzoic acid (Va and Vb). A mixture of compound **IV** (15 mmol), sodium hydroxide (1.2 g, 30.8 mmol) and MeOH/H_2O (50 mL/50 mL) was heated under reflux for overnight. Methanol was removed and to the solution was acidified by adding dilute hydrochloric acid (10%) to pH = 3. The precipitated white solid was collected by filtration. The purified product (yield 96%) was obtained by recrystallization from methanol.

2,4-Dimethoxy-5-nitrobenzoic acid (Va). ^{1}H NMR (400 MHz, DMSO) δ 12.85 (s, 1H), 8.35 (s, 1H), 6.85 (s, 1H), 4.03 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 165.50, 164.72, 158.27, 131.49, 130.75, 112.81, 98.95, 57.93, 57.59.

2,4-Dioctyloxy-5-nitrobenzoic acid (Vb). ^{1}H NMR (400 MHz, DMSO) δ 0.85-0.82(m, 6H), 1.24(m, 16H), 1.42(m, 4H), 1.75-1.70(m, 4H), 4.16 (t, J = 6 Hz, 2H), 4.23 (t, J = 6 Hz, 2H), 6.81(s, 1H), 8.32(s, 1H), 12.72(s, 1H). ^{13}C NMR (100 MHz, DMSO) 165.62, 164.06,157.60, 131.47, 130.71, 112.88, 99.90, 70.38, 69.93, 31.90, 29.37, 29.32, 29.28, 29.23, 28.98, 28.88, 25.96, 22.78, 14.61.

2,4-Dialkoxy-5-nitrobenzoyl chloride (VIa and VIb). A mixture of compound **Va** (or **Vb**, 10 to 12.5 mmol) and thionyl chloride (2 ml, 27 mmol), protected from the atmosphere by a drying tube, was heated under reflux for 4 hours. Excess thionyl chloride was removed under reduced pressure and giving the product as a white solid. The acid chloride was directly used for the next step without further purification.

3-(2,4-dioctyloxy-5-nitrobenzoylamino)-4-methoxytoluene (VII): Acid chloride **VIb** was prepared from the corresponding acid **Vb** (4.2g, 10 mmol) based on procedures described above. To a solution of 2-methoxy-5-methylaniline (2.0 g, 14 mmol) in methylene chloride (25 mL) was added triethylamine (5 mL) at 0 °C, followed by a solution of acid chloride **VIb** in methylene chloride (25 mL). The solution was stirred overnight at room temperature, washed by dilute hydrochloric acid (10%) and sodium bicarbonate solution and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was purified by washing with methanol to give the product **VII** as a white solid (5.0 g, 88.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93(s, 1H), 8.92(s, 1H), 8.42(s, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.50(s, 1H), 4.21 (t, J = 6.4 Hz, 2H), 4.10-4.07(t, 2H), 3.85(s, 3H), 2.31(s, 3H), 2.02-1.95(m, 2H), 1.87-1.80(m, 2H), 1.48-1.43(m, 4H), 1.37-1.24(m, 16H), 0.89-0.82(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.11, 161.05, 156.98, 146.48, 133.13, 131.56, 130.49, 127.78, 124.27, 121.49, 114.38, 109.84, 97.65, 70.79, 70.27, 55.60, 32.03, 31.97, 29.59, 29.50, 29.47, 29.41, 29.12, 29.00, 26.00, 25.94, 22.90, 22.86, 21.26, 14.35, 14.31. Anal. Calcd for $C_{31}H_{46}N_2O_6$: C, 68.59; H, 8.56; N, 5.16. Found: C, 68.66; H, 8.54; N, 5.09.

3-(5-(2,4-dimethoxy-5-nitrobenzoylamino)-2,4-dioctyloxybenzoylamino)-4-methoxytoluene (IX): Acid chloride **VIa** was prepared from the corresponding acid **Va** (0.72 g, 2 mmol) based on procedures described above. A mixture of compound **VII** (1.1 g, 2 mmol), 10% Pd-C (15% weight of **VII**), and DMF/chloroform (15 mL /15 mL) was degassed and stirred under an atmosphere of H_2 at 60°C for 4-6 hours. The mixture was then filtered and the solvent removed under vacuum. The residue was dissolved in chloroform, washed with dilute sodium bicarbonate solution and dried over anhydrous Na_2SO_4. Triethylamine (3 mL) was added to a solution of amine **VIII** in methylene chloride (15 mL)

at room temperature, followed by a solution of acid chloride **VIa** in methylene chloride (15 ml). The solution was stirred overnight at room temperature, washed by dilute hydrochloric acid (10%) and sodium bicarbonate solution and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The residue was purified by washing with ethyl acetate to give pure **IX** as a white solid (1.1g, 72.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 9.68 (s, 1H), 9.25 (s, 1H), 8.84 (s, 1H), 8.51(s, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 8.4, 1H), 6.29 (s, 2H), 4.13 (s, 3H), 4.08 (t, J = 6.8 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.33 (s, 3H), 1.95-1.90 (m, 4H), 1.48-1.42(m, 4H), 1.35-1.24 (m, 16H), 0.87-0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.30, 161.66, 159.83, 156.90, 153.58, 151.33, 146.53, 132.32, 131.07, 130.69, 128.50, 123.67, 123.26, 122.05, 121.68, 114.30, 113.61, 109.81,96.10, 95.60,69.89, 69.29, 57.42, 56.61, 55.63, 32.06, 32.04, 31.15, 29.78, 29.69, 29.57, 29.54, 26.13, 26.06, 22.91, 22.89, 21.31, 14.35, 14.31. Anal. Calcd for $C_{40}H_{55}N_3O_9$: C, 66.54; H, 7.69; N, 5.82. Found: C, 66.28; H, 7.73; N, 5.54.

3-(5-(5-(2,4-dioctyloxy-5-nitrobenzoylamino)-2,4-dimethoxybenzoylamino)-2,4-dioctyloxybenzoylamino)-4-methoxytoluene (5): Acid chloride **VIb** was prepared from the corresponding acid **Vb** (0.32 g, 0.76 mmol) based on procedures described above. A mixture of compound **IX** (0.5 g, 0.69 mmol), 10%Pd-C (15% weight of **IX**), and DMF/chloroform (15 mL/15 mL) was degassed and stirred under an atmosphere of H_2 at 60°C for 4-6 hours. The mixture was then filtered and the solvent removed under vacuum. The residue was dissolved in chloroform, washed with dilute sodium bicarbonate solution and dried over anhydrous Na_2SO_4. To a solution of the corresponding amine of **IX** and methylene chloride (15 mL) was added triethylamine (3 mL) at room temperature, followed by a solution of acid chloride **VIb** and methylene chloride (15 mL). The solution was stirred overnight at room temperature, washed with dilute hydrochloric acid (10%) and sodium bicarbonate solution and dried by anhydrous sodium sulfate. The solvent was removed under vacuum. The residue was purified by washing with ethyl acetate to give the purified product **5** as a white solid (0.5 g, 65.8% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 9.83 (s, 1H), 9.60 (s, 1H), 9.36 (s, 1H), 9.09 (s, 1H), 8.83 (s, 1H), 8.58 (s, 1H), 6.81(d, J = 6 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 6.44 (s, 1H), 6.33 (s, 2H), 4.22 (t, J = 7.2 Hz, 2H), 4.10 (t, J = 7.6 Hz, 2H), 4.04 (t, J = 6.8 Hz, 2H), 3.93-3.91(m, 8H), 3.84 (s, 3H), 2.34 (s, 3H), 2.02 (t, J = 6.8 Hz, 2H), 1.94-1.86 (m, 4H), 1.71(t, J = 6.8 Hz, 2H), 1.47-1.23 (m, 40H), 0.85-0.81(m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.28, 162.14, 161.32, 160.02, 156.61, 154.11, 153.37, 152.06, 151.57, 146.41, 132.33, 131.13, 130.60, 128.92, 123.84, 123.25, 122.95, 121.88, 121.57, 114.26, 114.10, 113.47, 109.66, 97.66, 96.26, 94.28, 71.12, 70.14, 69.30, 56.20, 55.90, 55.56, 32.06, 29.86, 29.80, 29.74, 29.70, 29.57, 29.53, 29.42, 29.13, 26.09, 25.91, 22.92, 22.87, 21.31, 14.28. Anal. Calcd for $C_{63}H_{92}N_4O_{12}$: C, 68.94; H, 8.46; N, 5.10. Found: C, 68.43; H, 8.81; N, 5.10.

Compounds **2**, **3**, **4**, and **6** were synthesized based on similar procedures for synthesizing **5**. The corresponding data from spectral and elemental analysis are listed below:

1-Methoxy-2-(2-Methoxybenzoylamino)benzene (2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.85 (s, 3H), 6.78 (m, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.97 (m, 2H), 7.02 (td, J = 7.8, 1 Hz, 1H), 8.28 (dd, J = 7.8, 1.8 Hz, 1H), 8.68 (m, 1H), 10.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.06, 56.12, 110.12, 111.74, 120.14, 121.20, 121.41, 122.03, 123.62, 128.83, 132.29, 133.33, 148.48, 157.52, 163.10, Anal. Calcd for $C_{15}H_{9215}NO_3$: C, 70.01; H, 5.89; N, 5.44. Found: C, 69.73; H, 5.77; N, 5.34.

1-(2,4-Dimethoxy-5-nitrobenzoylamino)-2-methoxybenzene (3). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.95 (s, 3H), 4.07 (s, 3H), 4.23 (s, 3H), 6.96 (br m, 1H), 7.02 (s, 1H), 7.10 (br s, 2H), 8.40 (d, J = 8 Hz, 1H), 8.64 (s, 1H), 10.40 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 57.08, 58.21, 58.45, 99.70, 111.95, 115.04, 120.51, 121.48, 124.64, 128.63, 130.01, 133.66, 149.24, 157.79, 160.92, 162.40. Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.82; H, 4.86; N, 8.43. Found: C, 57.28; H, 4.79; N, 8.32.

1-(5-(2,4-Dioctyloxy-5-nitrobenzoylamino)-2,4-dimethoxybenzoylamino)-2-methoxybenzene (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (m, 6H), 1.20-1.50 (m, 28H), 1.70 (m, 2H), 2.00 (m, 2H), 3.85 - 3.91 (m, 8H), 3.95 (s, 3H), 4.15 (t, J = 7.2 Hz, 2H), 6.25 (s, 1H), 6.31 (s, 1H), 6.87 (dd, J = 6.8, 2.4 Hz, 1H), 7.00 (m, 2H), 8.68 (dd, J = 7.2, 2.4 Hz, 1H), 8.80 (s, 1H), 9.16 (s, 1H), 9.59 (s, 1H), 10.38 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.08, 22.76, 25.93, 29.10, 29.16, 29.43, 29.51, 29.61, 29.64, 29.67, 29.78, 32.03, 56.01, 56.16, 56.42, 70.27, 70.92, 95.14, 98.07, 110.32, 114.74, 120.39, 121.60, 122.34, 123.02, 124.60, 129.50, 131.06, 133.32, 148.47, 152.50, 154.39, 156.47, 160.35, 162.03, 162.68. Anal. Calcd for $C_{43}H_{61}N_3O_9$: C, 67.59; H, 8.06; N, 5.50. Found: C, 67.43; H, 8.03; N, 5.47.

Methyl 5-(5-(5-(5-(5-(2,4-dioctyloxy-5-nitrobenzoylamino)-2,4-dioctyloxybenzoylamino) -2,4-diisobutoxybenzoylamino)-2,4-dimethoxybenzoylamio)-2,4-diisobutoxybenzoylamino)-2,4-dimethoxybenzoate (6) ^{1}H NMR (400 MHz, $CDCl_3$) 9.85(s, 1H), 9.81(s, 1H), 9.66(s, 1H), 9.52(s, 1H), 9.50(s, 1H), 9.21(s, 1H), 9.16(s, 1H), 9.07(s, 1H), 8.96(s, 1H), 8.90(s, 1H), 8.87(s, 1H), 6.49-6.44(m, 5H), 6.32(s, 1H), 4.31(t, J = 6.8, 2H), 4.12-3.73(m, 29H), 2.25-2.13(m, 4H), 1.95-1.93(m, 2H), 1.43-0.98(m, 70H), 0.86-0.80(m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.21, 163.25, 163.14, 162.79, 162.61, 161.18, 160.97, 157.02, 156.75, 154.74, 154.64, 154.47, 153.75,153.44, 153.10, 152.97, 152.62, 152.16,121.82, 121.45, 114.71, 114.59, 113.60, 113.50, 110.98, 95.56, 94.94, 77.62, 77.51, 77.31, 76.98, 76.45, 75.40, 75.30, 70.79, 70.40, 70.24, 69.38, 56.54, 56.14, 55.95, 51.80, 32.02, 31.97, 29.68, 29.66, 29.63, 29.54, 29.46, 29.42, 29.38, 29.31, 29.09, 29.06, 28.53,28.47, 28.31, 26.11, 26.07, 25.99, 25.97, 22.86, 22.85, 19.71, 19.63, 19.52, 19.46, 14.311, 14.29. Anal. Calcd for $C_{95}H_{136}N_6O_{21}$: C, 67.18; H, 8.09; N, 4.95. Found: C, 66.63; H, 8.12; N, 4.97.

II. Computational Details

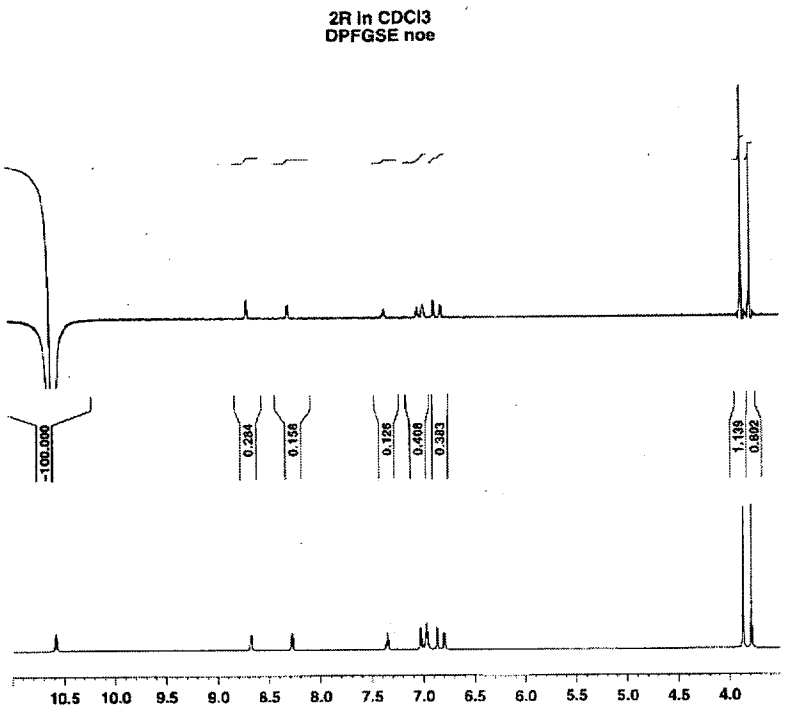
The Gaussian 94 program[1] was used for geometry optimizations and the Jaguar program[2] was used to obtain relative energies of the optimized structures. Geometry optimizations were done at the B3LYP/6-31G(d) level. The LMP2/6-311G(d) method was used for single point energy calculations. A total of four different models were considered for geometry optimizations. Model **2** has two methoxy groups in the same side of the N-H bond whereas models **2a** and **2b** have just one. In model **2c** all oxygen atoms are in the same side and opposite to the N-H side. All models are constrained to be planar. As expected, model **2** is the most stable. Models **2a**, **2b** and **2c** are 11.1, 14.5, and 27.4 kcal/mol respectively less stable than **2**.

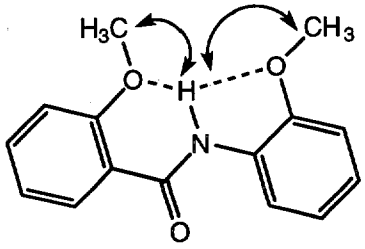
1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Ciolowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, Gaussian 94 (Rev. E.2) (Gaussian, Inc., Pittsburgh PA, 1995).

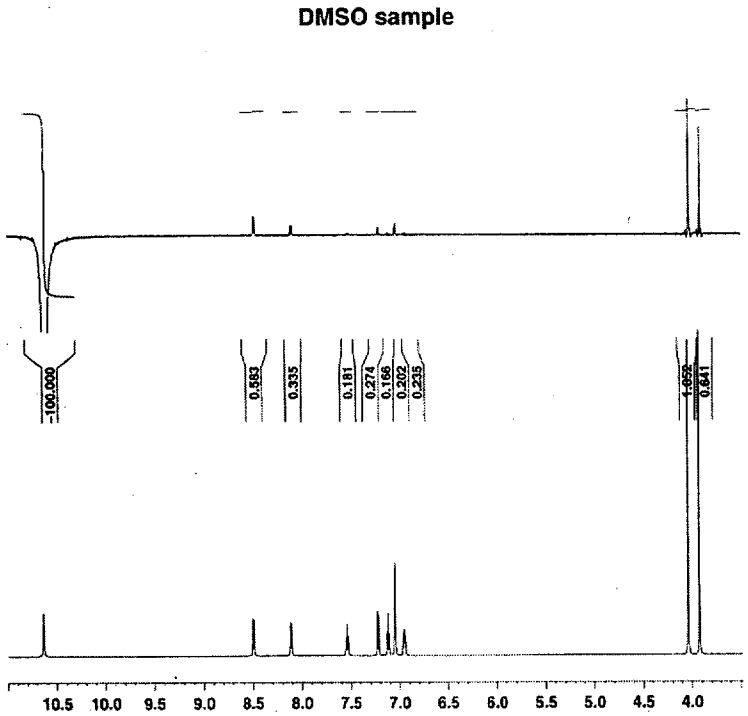
2. Jaguar v3.0, Schrodinger, Inc.; Portland, OR, 1997

III. NOE Difference and NOESY Spectra

NOE Difference Spectra (600 MHz) of Amide 2

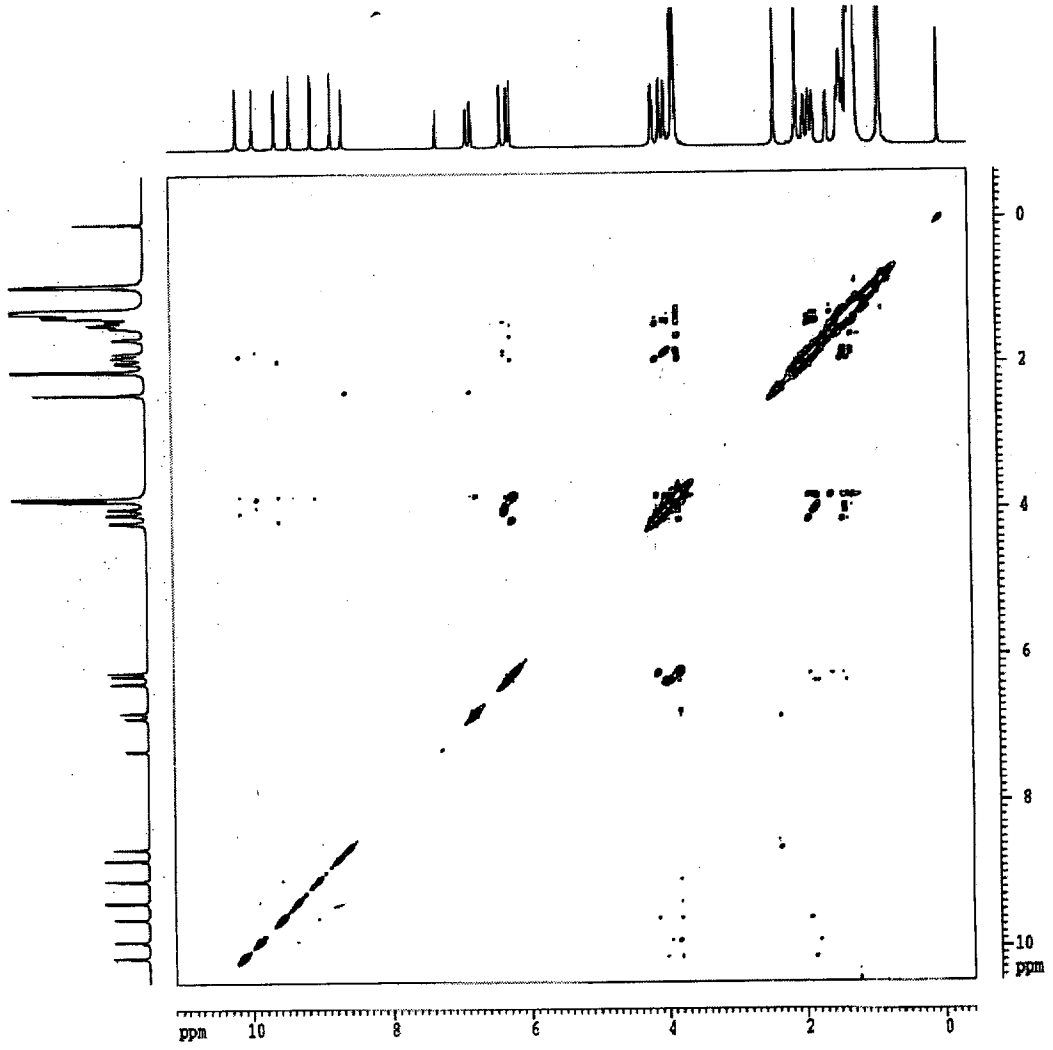


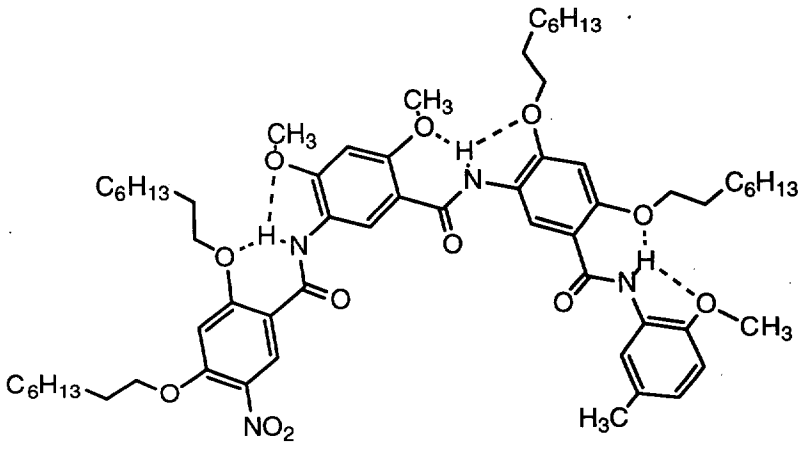




NOESY Spectrum of 5

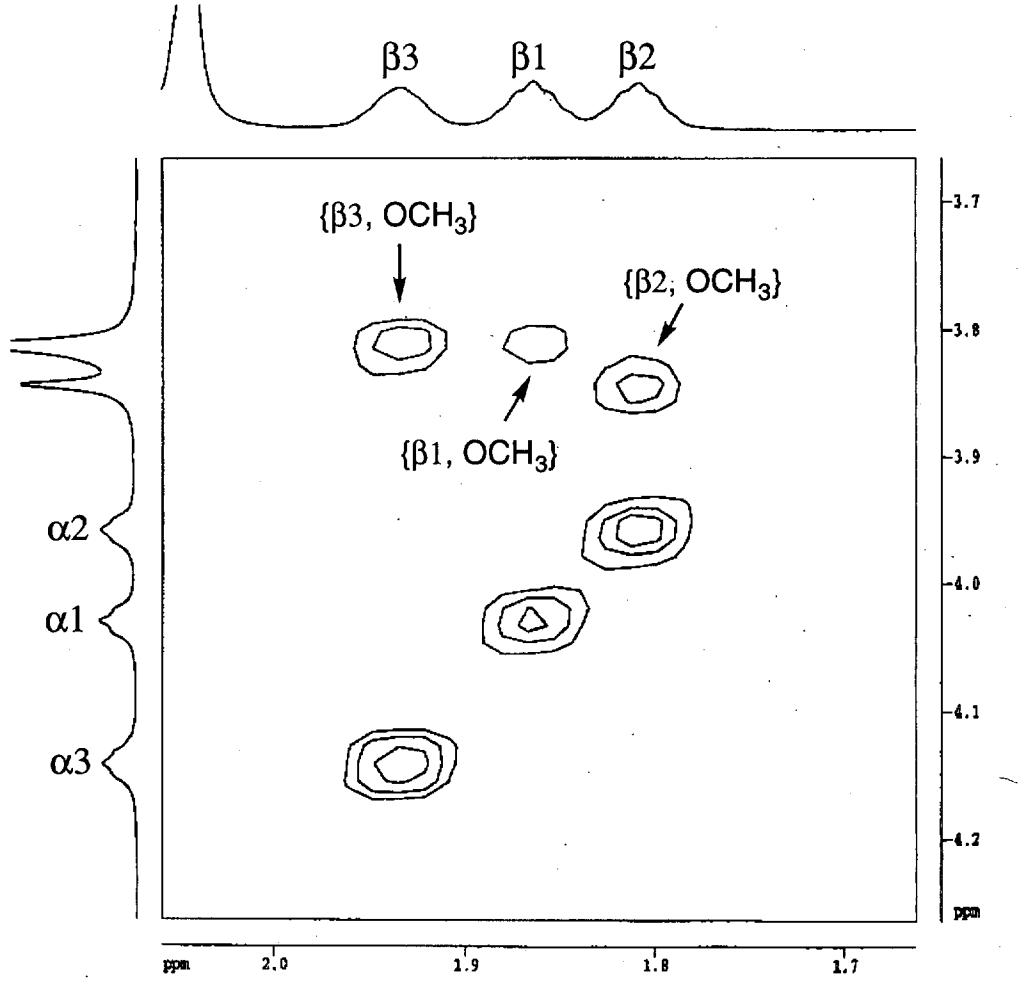
(800 MHz, $CDCl_3$, 300K, mixing time = 0.3 s)

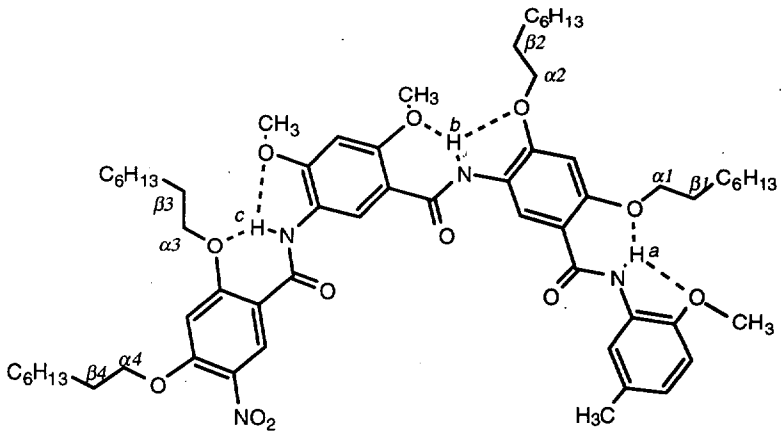




NOESY Spectrum of 5: Contacts between the Octyloxy β-Methylene Protons and the Methoxy Protons

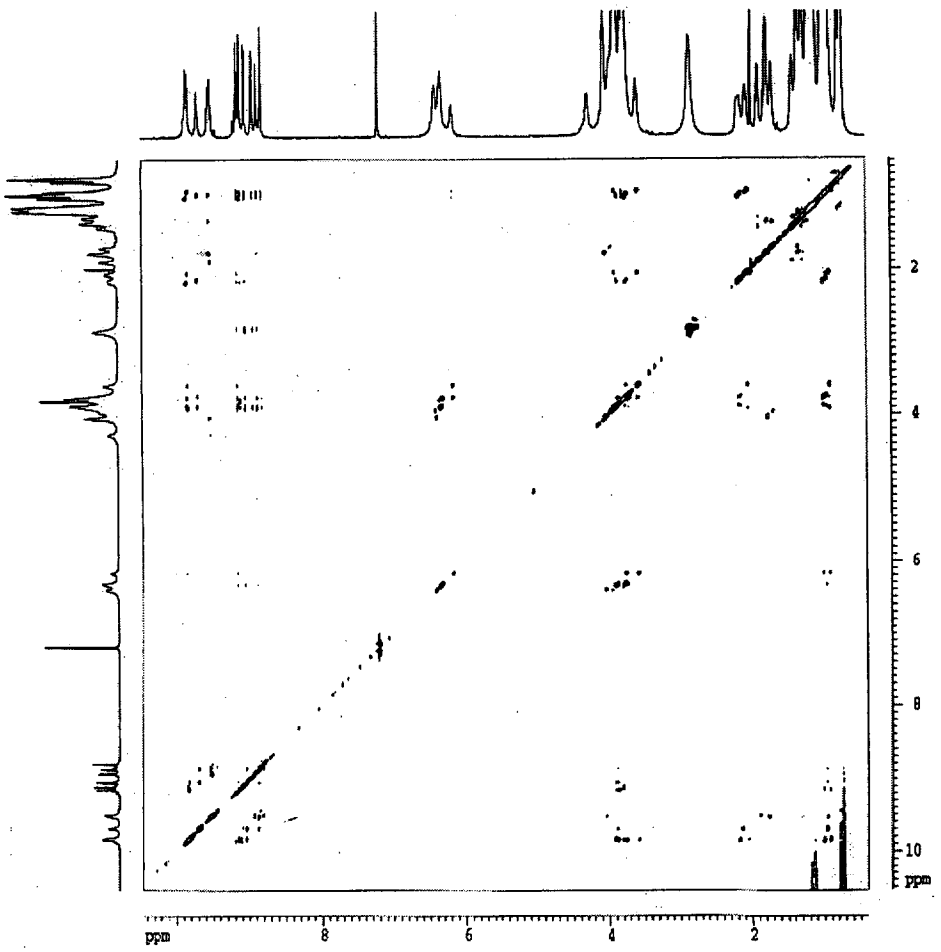
(800 MHz, $CDCl_3$, 300K, mixing time = 0.3 s)

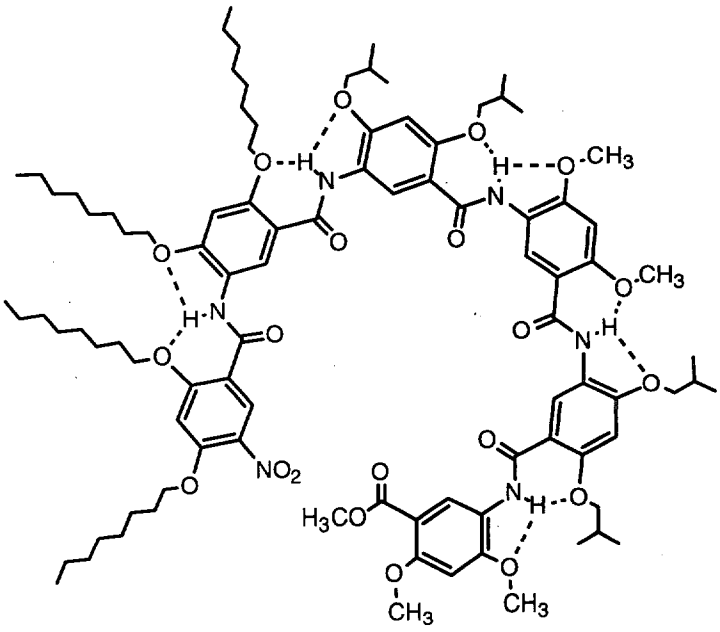




NOESY Spectrum of 6

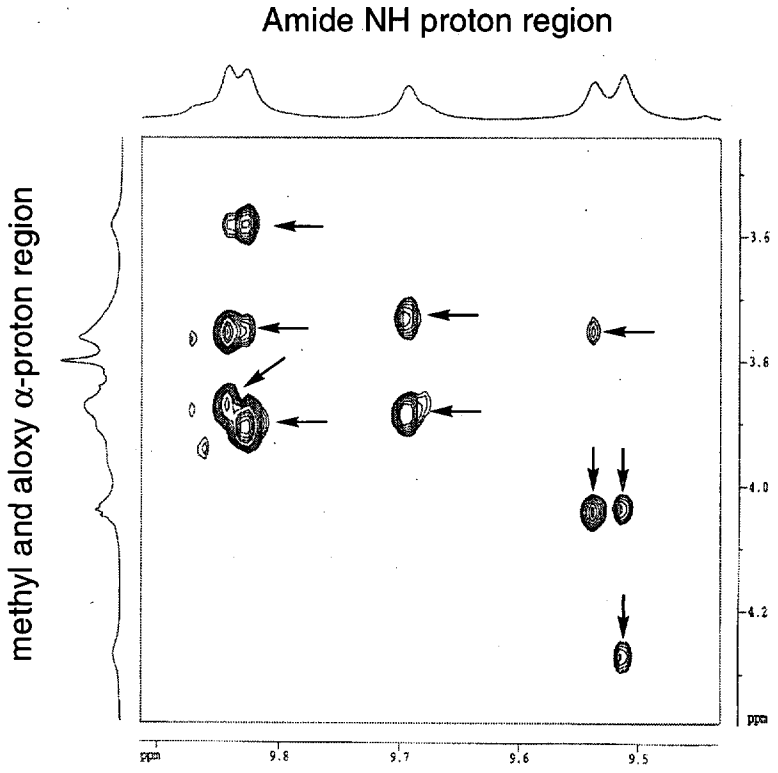
(800 MHz, $CDCl_3$, 280K, mixing time = 0.5 s)

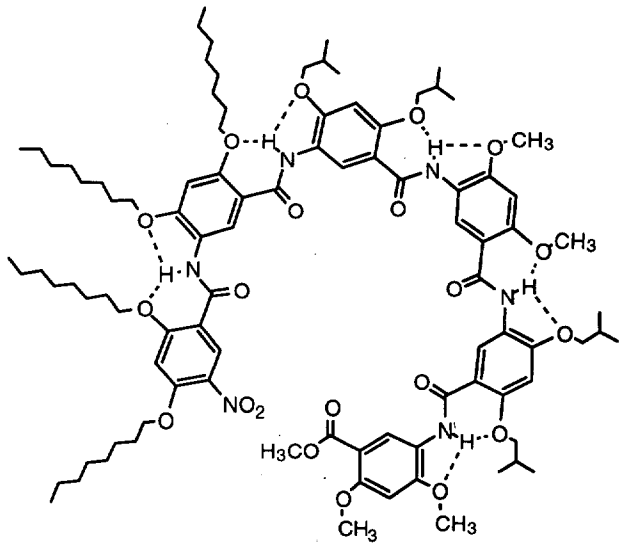




NOESY Spectrum of 6: Contacts between the Amide Protons and the Protons of the Methoxy and Octyloxy α-Methylene Groups

(800 MHz, $CDCl_3$, 280K, mixing time = 0.5 s)





IV. X-ray Data

Table 1. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	$C_{16}H_{16}N_2O_6$	
Formula weight	332.31	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	triclinicc, P 1 bar	
Unit cell dimensions	a = 7.1657(1) Å	α = 73.43(1) deg.
	b = 8.3342(2) Å	β = 84.69(1) deg.
	c = 13.2149(2) Å	γ = 88.50(1) deg.
Volume	753.18(2) A^3	
Z, Calculated density	2, 1.465 Mg/m^3	
Absorption coefficient	0.114 mm^-1	
F(000)	348	
Crystal size	0.36 x 0.36 x 0.22 mm	
Theta range for data collection	2.55 to 29.86 deg.	
Limiting indices	-9<=h<=9, -11<=k<=11, -17<=l<=17	
Reflections collected / unique	8494 / 3856 [R(int) = 0.0137]	
Completeness to theta = 29.86	88.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3856 / 0 / 236	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0386, wR2 = 0.1058	
R indices (all data)	R1 = 0.0436, wR2 = 0.1116	
Largest diff. peak and hole	0.324 and -0.264 e.A^-3	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2594(1)	4810(1)	3804(1)	17(1)
C(2)	2059(1)	6410(1)	3903(1)	17(1)
C(3)	1615(1)	7701(1)	3022(1)	18(1)
C(4)	1697(1)	7470(1)	2012(1)	18(1)
C(5)	2232(1)	5872(1)	1913(1)	18(1)
C(6)	2657(1)	4592(1)	2799(1)	17(1)
C(7)	3130(1)	3296(1)	4668(1)	18(1)
N(8)	3021(1)	3463(1)	5663(1)	19(1)
C(9)	3423(1)	2265(1)	6612(1)	17(1)
C(10)	3209(1)	2845(1)	7527(1)	18(1)
C(11)	3586(2)	1790(1)	8510(1)	22(1)
C(12)	4156(2)	148(1)	8596(1)	25(1)
C(13)	4361(2)	-429(1)	7704(1)	23(1)
C(14)	3999(1)	622(1)	6706(1)	20(1)
O(15)	3609(1)	1993(1)	4453(1)	29(1)
O(16)	2000(1)	6628(1)	4885(1)	24(1)
C(17)	1503(2)	8232(1)	5034(1)	26(1)
O(18)	1295(1)	8696(1)	1149(1)	23(1)
C(19)	761(2)	10313(1)	1280(1)	25(1)
N(20)	2395(1)	5475(1)	900(1)	22(1)
O(21A)	1774(16)	6450(16)	116(10)	36(2)
O(21B)	2150(40)	6590(20)	103(9)	51(3)
O(22A	3154(18)	4147(16)	883(8)	31(2)
O(22B	2750(40)	4028(14)	877(8)	39(2)
O(23)	2621(1)	4468(1)	7342(1)	23(1)
C(24)	2394(2)	5138(2)	8234(1)	26(1)

Table 3. Bond lengths [A] and angles [deg] for **3**.

C(1)-C(6)	1.3886(13)
C(1)-C(2)	1.4161(13)
C(1)-C(7)	1.5087(13)
C(2)-O(16)	1.3576(11)
C(2)-C(3)	1.3962(13)
C(3)-C(4)	1.3972(13)
C(4)-O(18)	1.3451(12)
C(4)-C(5)	1.4149(13)
C(5)-C(6)	1.3919(13)
C(5)-N(20)	1.4622(12)
C(7)-O(15)	1.2307(12)

C(7)-N(8)	1.3567(12)
N(8)-C(9)	1.4108(12)
C(9)-C(14)	1.3941(13)
C(9)-C(10)	1.4189(13)
C(10)-O(23)	1.3666(12)
C(10)-C(11)	1.3915(14)
C(11)-C(12)	1.3934(16)
C(12)-C(13)	1.3893(16)
C(13)-C(14)	1.4015(14)
O(16)-C(17)	1.4368(12)
O(18)-C(19)	1.4440(12)
N(20)-O(21B)	1.214(11)
N(20)-O(22A)	1.226(10)
N(20)-O(21A)	1.231(11)
N(20)-O(22B)	1.234(10)
O(23)-C(24)	1.4359(12)
C(6)-C(1)-C(2)	117.04(9)
C(6)-C(1)-C(7)	115.31(8)
C(2)-C(1)-C(7)	127.64(9)
O(16)-C(2)-C(3)	121.85(9)
O(16)-C(2)-C(1)	117.17(8)
C(3)-C(2)-C(1)	120.99(9)
C(2)-C(3)-C(4)	121.45(9)
O(18)-C(4)-C(3)	122.66(9)
O(18)-C(4)-C(5)	119.73(9)
C(3)-C(4)-C(5)	117.61(9)
C(6)-C(5)-C(4)	120.37(9)
C(6)-C(5)-N(20)	116.66(9)
C(4)-C(5)-N(20)	122.96(9)
C(1)-C(6)-C(5)	122.53(9)
O(15)-C(7)-N(8)	123.52(9)
O(15)-C(7)-C(1)	120.12(9)
N(8)-C(7)-C(1)	116.35(8)
C(7)-N(8)-C(9)	128.54(8)
C(14)-C(9)-N(8)	125.69(9)
C(14)-C(9)-C(10)	119.47(9)

N(8)-C(9)-C(10)	114.84(8)
O(23)-C(10)-C(11)	125.17(9)
O(23)-C(10)-C(9)	114.40(8)
C(11)-C(10)-C(9)	120.42(9)
C(10)-C(11)-C(12)	119.60(10)
C(13)-C(12)-C(11)	120.26(9)
C(12)-C(13)-C(14)	120.82(10)
C(9)-C(14)-C(13)	119.42(9)
C(2)-O(16)-C(17)	119.89(8)
C(4)-O(18)-C(19)	118.18(8)
O(21B)-N(20)-O(22A)	123.1(7)
O(21B)-N(20)-O(21A)	13.7(15)
O(22A)-N(20)-O(21A)	123.1(7)
O(21B)-N(20)-O(22B)	122.1(8)
O(22A)-N(20)-O(22B)	14.4(11)
O(21A)-N(20)-O(22B)	118.1(8)
O(21B)-N(20)-C(5)	118.2(6)
O(22A)-N(20)-C(5)	116.8(5)
O(21A)-N(20)-C(5)	120.1(6)
O(22B)-N(20)-C(5)	119.7(5)
C(10)-O(23)-C(24)	117.25(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **3**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	20(1)	15(1)	15(1)	-4(1)	-1(1)	0(1)
C(2)	19(1)	17(1)	16(1)	-7(1)	-1(1)	0(1)
C(3)	20(1)	14(1)	19(1)	-5(1)	-2(1)	2(1)
C(4)	18(1)	17(1)	17(1)	-3(1)	-3(1)	1(1)
C(5)	20(1)	18(1)	15(1)	-6(1)	-2(1)	0(1)
C(6)	20(1)	15(1)	17(1)	-5(1)	-1(1)	1(1)

C(7)	22(1)	16(1)	17(1)	-5(1)	-2(1)	1(1)
N(8)	27(1)	14(1)	15(1)	-4(1)	-3(1)	4(1)
C(9)	18(1)	17(1)	15(1)	-3(1)	-2(1)	0(1)
C(10)	19(1)	19(1)	18(1)	-5(1)	-2(1)	-1(1)
C(11)	23(1)	28(1)	16(1)	-5(1)	-2(1)	-2(1)
C(12)	24(1)	25(1)	20(1)	2(1)	-4(1)	-2(1)
C(13)	23(1)	17(1)	26(1)	-1(1)	-4(1)	1(1)
C(14)	21(1)	17(1)	21(1)	-5(1)	-2(1)	1(1)
O(15)	52(1)	18(1)	20(1)	-8(1)	-6(1)	9(1)
O(16)	39(1)	17(1)	17(1)	-8(1)	-4(1)	6(1)
C(17)	37(1)	18(1)	25(1)	-12(1)	-1(1)	4(1)
O(18)	31(1)	18(1)	18(1)	-3(1)	-6(1)	6(1)
C(19)	30(1)	18(1)	26(1)	-3(1)	-7(1)	5(1)
N(20)	28(1)	21(1)	16(1)	-6(1)	-2(1)	1(1)
O(21A)	57(4)	31(4)	20(2)	-8(2)	-16(2)	20(2)
O(21B)	112(7)	26(2)	12(2)	-3(1)	-6(3)	8(4)
O(22A)	44(3)	34(3)	22(1)	-20(2)	-12(2)	17(2)
O(22B)	78(6)	19(2)	26(2)	-10(1)	-19(3)	9(3)
O(23)	33(1)	20(1)	18(1)	-9(1)	-3(1)	5(1)
C(24)	29(1)	29(1)	23(1)	-16(1)	-2(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3**.

	x	y	z	U(eq)
H(3A)	1258	8737	3109	21
H(6A)	2996	3550	2713	21
H(8A)	2659	4426	5723	22
H(11A)	3460	2178	9107	27
H(12A)	4399	-564	9253	30
H(13A)	4743	-1526	7769	28
H(14A)	4143	227	6113	24
H(17A)	1528	8176	5769	38
H(17B)	266	8531	4821	38
H(17C)	2382	9059	4613	38

H(19A)	516	11065	607	37
H(19B)	1760	10751	1560	37
H(19C)	-347	10197	1763	37
H(24A)	1981	6280	8005	38
H(24B)	3570	5093	8535	38
H(24C)	1479	4491	8757	38

Table 6. Torsion angles [deg] for **3**.

C(6)-C(1)-C(2)-O(16)	-179.88(8)
C(7)-C(1)-C(2)-O(16)	-0.52(15)
C(6)-C(1)-C(2)-C(3)	0.04(14)
C(7)-C(1)-C(2)-C(3)	179.41(9)
O(16)-C(2)-C(3)-C(4)	179.39(9)
C(1)-C(2)-C(3)-C(4)	-0.53(15)
C(2)-C(3)-C(4)-O(18)	-179.34(9)
C(2)-C(3)-C(4)-C(5)	0.51(14)
O(18)-C(4)-C(5)-C(6)	179.83(9)
C(3)-C(4)-C(5)-C(6)	-0.02(14)
O(18)-C(4)-C(5)-N(20)	0.68(15)
C(3)-C(4)-C(5)-N(20)	-179.17(9)
C(2)-C(1)-C(6)-C(5)	0.45(15)
C(7)-C(1)-C(6)-C(5)	-178.99(9)
C(4)-C(5)-C(6)-C(1)	-0.47(15)
N(20)-C(5)-C(6)-C(1)	178.73(9)
C(6)-C(1)-C(7)-O(15)	1.11(14)
C(2)-C(1)-C(7)-O(15)	-178.26(10)
C(6)-C(1)-C(7)-N(8)	-177.94(8)
C(2)-C(1)-C(7)-N(8)	2.69(15)
O(15)-C(7)-N(8)-C(9)	0.64(17)
C(1)-C(7)-N(8)-C(9)	179.66(9)
C(7)-N(8)-C(9)-C(14)	-1.09(17)
C(7)-N(8)-C(9)-C(10)	178.64(9)
C(14)-C(9)-C(10)-O(23)	-179.41(9)

N(8)-C(9)-C(10)-O(23)	0.84(12)
C(14)-C(9)-C(10)-C(11)	0.59(15)
N(8)-C(9)-C(10)-C(11)	-179.16(9)
O(23)-C(10)-C(11)-C(12)	179.20(9)
C(9)-C(10)-C(11)-C(12)	-0.80(15)
C(10)-C(11)-C(12)-C(13)	0.55(16)
C(11)-C(12)-C(13)-C(14)	-0.08(16)
N(8)-C(9)-C(14)-C(13)	179.60(9)
C(10)-C(9)-C(14)-C(13)	-0.11(15)
C(12)-C(13)-C(14)-C(9)	-0.14(15)
C(3)-C(2)-O(16)-C(17)	-1.14(15)
C(1)-C(2)-O(16)-C(17)	178.78(9)
C(3)-C(4)-O(18)-C(19)	0.06(14)
C(5)-C(4)-O(18)-C(19)	-179.78(9)
C(6)-C(5)-N(20)-O(21B)	-175.5(16)
C(4)-C(5)-N(20)-O(21B)	3.7(16)
C(6)-C(5)-N(20)-O(22A)	-10.6(8)
C(4)-C(5)-N(20)-O(22A)	168.6(8)
C(6)-C(5)-N(20)-O(21A)	168.9(8)
C(4)-C(5)-N(20)-O(21A)	-11.9(8)
C(6)-C(5)-N(20)-O(22B)	5.4(14)
C(4)-C(5)-N(20)-O(22B)	-175.4(14)
C(11)-C(10)-O(23)-C(24)	0.61(14)
C(9)-C(10)-O(23)-C(24)	-179.39(8)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3** [A and deg.].

Hydrogen bonds with H..A < r(A) + 2.200 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N8-H8A	0.860	1.926	141.48	2.654	O16
N8-H8A	0.860	2.147	110.40	2.576	O23

Table 8. Crystal data and structure refinement for **4**.

Identification code	**4**
Empirical formula	C43 H61 N3 O9
Formula weight	763.95
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.2931(3) A alpha = 84.11(1) deg.
	b = 12.4808(4) A beta = 84.97(1) deg.
	c = 18.4099(2) A gamma = 78.71(1) deg.
Volume	2077.9(1) A^3
Z, Calculated density	2, 1.221 Mg/m^3
Absorption coefficient	0.085 mm^-1
F(000)	824
Crystal size	0.48 x 0.08 x 0.08 mm
Theta range for data collection	2.43 to 26.37 deg.
Limiting indices	-11<=h<=11, -15<=k<=15, -22<=l<=23
Reflections collected / unique	20073 / 8425 [R(int) = 0.0566]
Completeness to theta = 26.37	99.0 %
Max. and min. transmission	1.0000 and 0.6404
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8425 / 0 / 497
Goodness-of-fit on F^2	0.995
Final R indices [I>2sigma(I)]	R1 = 0.0757, wR2 = 0.2177
R indices (all data)	R1 = 0.1351, wR2 = 0.2459
Extinction coefficient	0.0021(14)
Largest diff. peak and hole	1.642 and -0.679 e.A^-3

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **4**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2382(3)	-108(2)	4935(2)	18(1)
C(2)	2803(3)	68(2)	4188(2)	19(1)
C(3)	3748(3)	805(2)	3953(2)	20(1)
C(4)	4213(3)	1433(2)	4438(2)	19(1)
C(5)	3735(3)	1290(2)	5179(2)	19(1)
C(6)	2851(3)	522(2)	5410(2)	18(1)
C(7)	1428(3)	-887(2)	5300(2)	19(1)
O(8)	1119(2)	-910(2)	5962(1)	24(1)
N(9)	970(3)	-1561(2)	4864(1)	19(1)
C(10)	82(3)	-2346(2)	5088(2)	17(1)
C(11)	-283(3)	-2925(2)	4536(2)	18(1)
C(12)	-1137(3)	-3734(2)	4705(2)	19(1)
C(13)	-1658(3)	-3964(2)	5427(2)	19(1)
C(14)	-1344(3)	-3375(2)	5986(2)	18(1)
C(15)	-462(3)	-2577(2)	5802(2)	18(1)
C(16)	-1938(3)	-3440(2)	6777(2)	19(1)
O(17)	-1760(2)	-2762(2)	7183(1)	24(1)
N(18)	-2692(3)	-4260(2)	7000(1)	20(1)
C(19)	-3432(3)	-4464(3)	7691(2)	21(1)
C(20)	-4047(4)	-5416(3)	7775(2)	23(1)
C(21)	-4856(4)	-5678(3)	8420(2)	25(1)
C(22)	-5023(4)	-4997(3)	8985(2)	28(1)
C(23)	-4402(4)	-4064(3)	8911(2)	30(1)
C(24)	-3601(4)	-3799(3)	8264(2)	24(1)
O(25)	-3797(3)	-6020(2)	7180(1)	29(1)
C(26)	-4384(4)	-7010(3)	7234(2)	36(1)
O(27)	-2476(2)	-4768(2)	5618(1)	22(1)
C(28)	-2939(4)	-5295(3)	5046(2)	23(1)
O(29)	270(2)	-2650(2)	3844(1)	23(1)
C(30)	-85(4)	-3212(3)	3260(2)	30(1)
N(31)	4127(3)	1913(2)	5730(2)	22(1)

O(32)	3711(3)	1688(2)	6376(1)	41(1)
O(33)	4805(3)	2647(2)	5555(1)	40(1)
O(34)	5086(2)	2169(2)	4223(1)	24(1)
C(35)	5718(4)	2240(3)	3478(2)	22(1)
C(36)	6550(4)	3178(3)	3411(2)	24(1)
C(37)	7392(4)	3284(3)	2668(2)	25(1)
C(38)	8120(4)	4291(3)	2559(2)	25(1)
C(39)	8908(4)	4442(3)	1808(2)	26(1)
C(40)	9538(4)	5483(3)	1685(2)	25(1)
C(41)	10277(4)	5677(3)	922(2)	28(1)
C(42)	10966(4)	6709(3)	820(2)	31(1)
C(43)	11845(4)	6837(3)	92(2)	40(1)
C(44)	12488(5)	7884(4)	-15(3)	56(1)
O(45)	2278(2)	-485(2)	3708(1)	22(1)
C(46)	2403(4)	-102(3)	2931(2)	29(1)
C(47)	1334(5)	-567(3)	2542(2)	42(1)
C(48)	1424(7)	-253(5)	1759(3)	77(2)
C(49)	1026(7)	1006(5)	1511(3)	90(2)
C(50)	1454(7)	1310(6)	718(3)	106(3)
C(51)	3044(6)	1229(5)	480(3)	69(2)
C(52)	3378(6)	1519(4)	-330(3)	63(1)
C(53)	3020(5)	709(4)	-788(3)	55(1)
C(54)	3449(5)	892(4)	-1605(3)	64(2)
C(55)	3071(9)	20(5)	-2063(3)	110(3)

Table 10. Bond lengths [A] and angles [deg] for **4**.

C(1)-C(6)	1.383(4)
C(1)-C(2)	1.404(4)
C(1)-C(7)	1.510(4)
C(2)-O(45)	1.354(4)
C(2)-C(3)	1.404(4)
C(3)-C(4)	1.393(4)
C(3)-H(3A)	0.9300
C(4)-O(34)	1.349(3)
C(4)-C(5)	1.402(4)

C(5)-C(6)	1.392(4)
C(5)-N(31)	1.450(4)
C(6)-H(6A)	0.9300
C(7)-O(8)	1.226(4)
C(7)-N(9)	1.368(4)
N(9)-C(10)	1.409(4)
N(9)-H(9A)	0.8600
C(10)-C(15)	1.390(4)
C(10)-C(11)	1.405(4)
C(11)-O(29)	1.366(3)
C(11)-C(12)	1.398(4)
C(12)-C(13)	1.396(4)
C(12)-H(12A)	0.9300
C(13)-O(27)	1.374(3)
C(13)-C(14)	1.405(4)
C(14)-C(15)	1.407(4)
C(14)-C(16)	1.512(4)
C(15)-H(15A)	0.9300
C(16)-O(17)	1.228(4)
C(16)-N(18)	1.360(4)
N(18)-C(19)	1.415(4)
N(18)-H(18A)	0.8600
C(19)-C(24)	1.388(4)
C(19)-C(20)	1.405(4)
C(20)-O(25)	1.371(4)
C(20)-C(21)	1.394(4)
C(21)-C(22)	1.389(5)
C(21)-H(21A)	0.9300
C(22)-C(23)	1.387(5)
C(22)-H(22A)	0.9300
C(23)-C(24)	1.393(4)
C(23)-H(23A)	0.9300
C(24)-H(24A)	0.9300
O(25)-C(26)	1.436(4)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600

C(26)-H(26C)	0.9600
O(27)-C(28)	1.433(4)
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
O(29)-C(30)	1.437(4)
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600
N(31)-O(33)	1.213(3)
N(31)-O(32)	1.239(3)
O(34)-C(35)	1.444(4)
C(35)-C(36)	1.514(4)
C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700
C(36)-C(37)	1.522(4)
C(36)-H(36A)	0.9700
C(36)-H(36B)	0.9700
C(37)-C(38)	1.528(4)
C(37)-H(37A)	0.9700
C(37)-H(37B)	0.9700
C(38)-C(39)	1.518(4)
C(38)-H(38A)	0.9700
C(38)-H(38B)	0.9700
C(39)-C(40)	1.515(4)
C(39)-H(39A)	0.9700
C(39)-H(39B)	0.9700
C(40)-C(41)	1.526(4)
C(40)-H(40A)	0.9700
C(40)-H(40B)	0.9700
C(41)-C(42)	1.534(5)
C(41)-H(41A)	0.9700
C(41)-H(41B)	0.9700
C(42)-C(43)	1.518(5)
C(42)-H(42A)	0.9700
C(42)-H(42B)	0.9700

C(43)-C(44)	1.528(5)
C(43)-H(43A)	0.9700
C(43)-H(43B)	0.9700
C(44)-H(44A)	0.9600
C(44)-H(44B)	0.9600
C(44)-H(44C)	0.9600
O(45)-C(46)	1.462(4)
C(46)-C(47)	1.508(5)
C(46)-H(46A)	0.9700
C(46)-H(46B)	0.9700
C(47)-C(48)	1.454(6)
C(47)-H(47A)	0.9700
C(47)-H(47B)	0.9700
C(48)-C(49)	1.571(7)
C(48)-H(48A)	0.9700
C(48)-H(48B)	0.9700
C(49)-C(50)	1.508(7)
C(49)-H(49A)	0.9700
C(49)-H(49B)	0.9700
C(50)-C(51)	1.490(8)
C(50)-H(50A)	0.9700
C(50)-H(50B)	0.9700
C(51)-C(52)	1.517(6)
C(51)-H(51A)	0.9700
C(51)-H(51B)	0.9700
C(52)-C(53)	1.484(6)
C(52)-H(52A)	0.9700
C(52)-H(52B)	0.9700
C(53)-C(54)	1.527(6)
C(53)-H(53A)	0.9700
C(53)-H(53B)	0.9700
C(54)-C(55)	1.552(7)
C(54)-H(54A)	0.9700
C(54)-H(54B)	0.9700
C(55)-H(55A)	0.9600
C(55)-H(55B)	0.9600

C(55)-H(55C)	0.9600
C(6)-C(1)-C(2)	117.3(3)
C(6)-C(1)-C(7)	114.3(3)
C(2)-C(1)-C(7)	128.3(3)
O(45)-C(2)-C(1)	118.5(3)
O(45)-C(2)-C(3)	121.4(3)
C(1)-C(2)-C(3)	120.2(3)
C(4)-C(3)-C(2)	121.7(3)
C(4)-C(3)-H(3A)	119.2
C(2)-C(3)-H(3A)	119.2
O(34)-C(4)-C(3)	122.9(3)
O(34)-C(4)-C(5)	119.2(3)
C(3)-C(4)-C(5)	117.9(3)
C(6)-C(5)-C(4)	119.8(3)
C(6)-C(5)-N(31)	117.5(3)
C(4)-C(5)-N(31)	122.7(3)
C(1)-C(6)-C(5)	123.0(3)
C(1)-C(6)-H(6A)	118.5
C(5)-C(6)-H(6A)	118.5
O(8)-C(7)-N(9)	122.8(3)
O(8)-C(7)-C(1)	120.0(3)
N(9)-C(7)-C(1)	117.2(3)
C(7)-N(9)-C(10)	126.7(3)
C(7)-N(9)-H(9A)	116.7
C(10)-N(9)-H(9A)	116.7
C(15)-C(10)-C(11)	118.4(3)
C(15)-C(10)-N(9)	125.1(3)
C(11)-C(10)-N(9)	116.5(3)
O(29)-C(11)-C(12)	123.7(3)
O(29)-C(11)-C(10)	115.5(2)
C(12)-C(11)-C(10)	120.7(3)
C(13)-C(12)-C(11)	120.0(3)
C(13)-C(12)-H(12A)	120.0
C(11)-C(12)-H(12A)	120.0
O(27)-C(13)-C(12)	121.7(3)
O(27)-C(13)-C(14)	118.0(3)

C(12)-C(13)-C(14)	120.3(3)
C(13)-C(14)-C(15)	118.5(3)
C(13)-C(14)-C(16)	127.1(3)
C(15)-C(14)-C(16)	114.3(3)
C(10)-C(15)-C(14)	122.0(3)
C(10)-C(15)-H(15A)	119.0
C(14)-C(15)-H(15A)	119.0
O(17)-C(16)-N(18)	122.8(3)
O(17)-C(16)-C(14)	120.4(3)
N(18)-C(16)-C(14)	116.7(3)
C(16)-N(18)-C(19)	128.2(3)
C(16)-N(18)-H(18A)	115.9
C(19)-N(18)-H(18A)	115.9
C(24)-C(19)-C(20)	119.5(3)
C(24)-C(19)-N(18)	125.3(3)
C(20)-C(19)-N(18)	115.2(3)
O(25)-C(20)-C(21)	124.8(3)
O(25)-C(20)-C(19)	114.7(3)
C(21)-C(20)-C(19)	120.5(3)
C(22)-C(21)-C(20)	119.1(3)
C(22)-C(21)-H(21A)	120.5
C(20)-C(21)-H(21A)	120.5
C(23)-C(22)-C(21)	120.8(3)
C(23)-C(22)-H(22A)	119.6
C(21)-C(22)-H(22A)	119.6
C(22)-C(23)-C(24)	120.1(3)
C(22)-C(23)-H(23A)	120.0
C(24)-C(23)-H(23A)	120.0
C(19)-C(24)-C(23)	120.0(3)
C(19)-C(24)-H(24A)	120.0
C(23)-C(24)-H(24A)	120.0
C(20)-O(25)-C(26)	117.4(2)
O(25)-C(26)-H(26A)	109.5
O(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
O(25)-C(26)-H(26C)	109.5

H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(13)-O(27)-C(28)	118.6(2)
O(27)-C(28)-H(28A)	109.5
O(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
O(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(11)-O(29)-C(30)	117.6(2)
O(29)-C(30)-H(30A)	109.5
O(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
O(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
O(33)-N(31)-O(32)	121.6(3)
O(33)-N(31)-C(5)	120.5(3)
O(32)-N(31)-C(5)	117.8(2)
C(4)-O(34)-C(35)	119.8(2)
O(34)-C(35)-C(36)	106.2(3)
O(34)-C(35)-H(35A)	110.5
C(36)-C(35)-H(35A)	110.5
O(34)-C(35)-H(35B)	110.5
C(36)-C(35)-H(35B)	110.5
H(35A)-C(35)-H(35B)	108.7
C(35)-C(36)-C(37)	112.0(3)
C(35)-C(36)-H(36A)	109.2
C(37)-C(36)-H(36A)	109.2
C(35)-C(36)-H(36B)	109.2
C(37)-C(36)-H(36B)	109.2
H(36A)-C(36)-H(36B)	107.9
C(36)-C(37)-C(38)	112.9(3)
C(36)-C(37)-H(37A)	109.0
C(38)-C(37)-H(37A)	109.0
C(36)-C(37)-H(37B)	109.0

C(38)-C(37)-H(37B)	109.0
H(37A)-C(37)-H(37B)	107.8
C(39)-C(38)-C(37)	113.9(3)
C(39)-C(38)-H(38A)	108.8
C(37)-C(38)-H(38A)	108.8
C(39)-C(38)-H(38B)	108.8
C(37)-C(38)-H(38B)	108.8
H(38A)-C(38)-H(38B)	107.7
C(40)-C(39)-C(38)	113.6(3)
C(40)-C(39)-H(39A)	108.8
C(38)-C(39)-H(39A)	108.8
C(40)-C(39)-H(39B)	108.8
C(38)-C(39)-H(39B)	108.8
H(39A)-C(39)-H(39B)	107.7
C(39)-C(40)-C(41)	114.6(3)
C(39)-C(40)-H(40A)	108.6
C(41)-C(40)-H(40A)	108.6
C(39)-C(40)-H(40B)	108.6
C(41)-C(40)-H(40B)	108.6
H(40A)-C(40)-H(40B)	107.6
C(40)-C(41)-C(42)	113.6(3)
C(40)-C(41)-H(41A)	108.8
C(42)-C(41)-H(41A)	108.8
C(40)-C(41)-H(41B)	108.8
C(42)-C(41)-H(41B)	108.8
H(41A)-C(41)-H(41B)	107.7
C(43)-C(42)-C(41)	113.7(3)
C(43)-C(42)-H(42A)	108.8
C(41)-C(42)-H(42A)	108.8
C(43)-C(42)-H(42B)	108.8
C(41)-C(42)-H(42B)	108.8
H(42A)-C(42)-H(42B)	107.7
C(42)-C(43)-C(44)	113.4(3)
C(42)-C(43)-H(43A)	108.9
C(44)-C(43)-H(43A)	108.9
C(42)-C(43)-H(43B)	108.9

C(44)-C(43)-H(43B)	108.9
H(43A)-C(43)-H(43B)	107.7
C(43)-C(44)-H(44A)	109.5
C(43)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(43)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(2)-O(45)-C(46)	117.9(2)
O(45)-C(46)-C(47)	108.3(3)
O(45)-C(46)-H(46A)	110.0
C(47)-C(46)-H(46A)	110.0
O(45)-C(46)-H(46B)	110.0
C(47)-C(46)-H(46B)	110.0
H(46A)-C(46)-H(46B)	108.4
C(48)-C(47)-C(46)	111.8(3)
C(48)-C(47)-H(47A)	109.3
C(46)-C(47)-H(47A)	109.3
C(48)-C(47)-H(47B)	109.3
C(46)-C(47)-H(47B)	109.3
H(47A)-C(47)-H(47B)	107.9
C(47)-C(48)-C(49)	116.9(5)
C(47)-C(48)-H(48A)	108.1
C(49)-C(48)-H(48A)	108.1
C(47)-C(48)-H(48B)	108.1
C(49)-C(48)-H(48B)	108.1
H(48A)-C(48)-H(48B)	107.3
C(50)-C(49)-C(48)	114.7(5)
C(50)-C(49)-H(49A)	108.6
C(48)-C(49)-H(49A)	108.6
C(50)-C(49)-H(49B)	108.6
C(48)-C(49)-H(49B)	108.6
H(49A)-C(49)-H(49B)	107.6
C(51)-C(50)-C(49)	118.9(5)
C(51)-C(50)-H(50A)	107.6
C(49)-C(50)-H(50A)	107.6

C(51)-C(50)-H(50B)	107.6
C(49)-C(50)-H(50B)	107.6
H(50A)-C(50)-H(50B)	107.0
C(50)-C(51)-C(52)	115.4(5)
C(50)-C(51)-H(51A)	108.4
C(52)-C(51)-H(51A)	108.4
C(50)-C(51)-H(51B)	108.4
C(52)-C(51)-H(51B)	108.4
H(51A)-C(51)-H(51B)	107.5
C(53)-C(52)-C(51)	112.1(4)
C(53)-C(52)-H(52A)	109.2
C(51)-C(52)-H(52A)	109.2
C(53)-C(52)-H(52B)	109.2
C(51)-C(52)-H(52B)	109.2
H(52A)-C(52)-H(52B)	107.9
C(52)-C(53)-C(54)	115.1(4)
C(52)-C(53)-H(53A)	108.5
C(54)-C(53)-H(53A)	108.5
C(52)-C(53)-H(53B)	108.5
C(54)-C(53)-H(53B)	108.5
H(53A)-C(53)-H(53B)	107.5
C(53)-C(54)-C(55)	113.4(4)
C(53)-C(54)-H(54A)	108.9
C(55)-C(54)-H(54A)	108.9
C(53)-C(54)-H(54B)	108.9
C(55)-C(54)-H(54B)	108.9
H(54A)-C(54)-H(54B)	107.7
C(54)-C(55)-H(55A)	109.5
C(54)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(54)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters (A^2 x 10^3) for **4**.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	13(2)	15(2)	28(2)	0(1)	-1(1)	-6(1)
C(2)	15(2)	17(2)	27(2)	-3(1)	-3(1)	-3(1)
C(3)	17(2)	18(2)	24(2)	0(1)	-1(1)	-3(1)
C(4)	15(2)	14(2)	29(2)	1(1)	-3(1)	-6(1)
C(5)	16(2)	15(2)	27(2)	-2(1)	-2(1)	-4(1)
C(6)	17(2)	16(2)	22(2)	0(1)	-3(1)	-5(1)
C(7)	12(2)	17(2)	28(2)	-2(1)	-4(1)	-2(1)
O(8)	26(1)	29(1)	23(1)	-6(1)	1(1)	-15(1)
N(9)	16(1)	21(1)	21(1)	-3(1)	2(1)	-9(1)
C(10)	12(2)	16(2)	24(2)	-1(1)	-1(1)	-4(1)
C(11)	13(2)	19(2)	21(2)	-2(1)	-1(1)	-3(1)
C(12)	19(2)	18(2)	21(2)	-4(1)	-4(1)	-4(1)
C(13)	14(2)	16(2)	27(2)	-2(1)	1(1)	-5(1)
C(14)	15(2)	17(2)	22(2)	-3(1)	-1(1)	-4(1)
C(15)	16(2)	16(2)	24(2)	-4(1)	-4(1)	-4(1)
C(16)	16(2)	18(2)	23(2)	-2(1)	-3(1)	-3(1)
O(17)	30(1)	25(1)	23(1)	-6(1)	1(1)	-14(1)
N(18)	22(2)	21(1)	21(1)	-3(1)	4(1)	-11(1)
C(19)	19(2)	24(2)	21(2)	0(1)	0(1)	-7(1)
C(20)	22(2)	23(2)	24(2)	-1(1)	-3(1)	-9(2)
C(21)	24(2)	28(2)	26(2)	6(2)	-4(1)	-14(2)
C(22)	27(2)	40(2)	19(2)	2(2)	2(1)	-12(2)
C(23)	33(2)	33(2)	24(2)	-6(2)	0(2)	-6(2)
C(24)	25(2)	23(2)	23(2)	0(1)	-1(1)	-8(2)

O(25)	41(2)	28(1)	25(1)	-5(1)	1(1)	-23(1)
C(26)	51(3)	30(2)	36(2)	-3(2)	-2(2)	-25(2)
O(27)	24(1)	22(1)	25(1)	-5(1)	-1(1)	-16(1)
C(28)	22(2)	23(2)	31(2)	-4(1)	-6(1)	-14(2)
O(29)	27(1)	27(1)	18(1)	-3(1)	2(1)	-15(1)
C(30)	36(2)	37(2)	21(2)	-6(2)	-1(2)	-20(2)
N(31)	19(2)	21(1)	27(2)	-2(1)	-5(1)	-8(1)
O(32)	56(2)	50(2)	27(2)	-10(1)	4(1)	-36(2)
O(33)	58(2)	40(2)	34(2)	-2(1)	-4(1)	-39(1)
O(34)	26(1)	24(1)	26(1)	0(1)	0(1)	-15(1)
C(35)	21(2)	24(2)	25(2)	-2(1)	0(1)	-11(2)
C(36)	23(2)	24(2)	27(2)	0(1)	-4(1)	-10(2)
C(37)	22(2)	27(2)	29(2)	2(2)	-1(1)	-11(2)
C(38)	22(2)	29(2)	25(2)	1(1)	-4(1)	-12(2)
C(39)	22(2)	31(2)	28(2)	-2(2)	-2(1)	-9(2)
C(40)	22(2)	33(2)	21(2)	2(1)	0(1)	-11(2)
C(41)	30(2)	29(2)	24(2)	0(2)	2(2)	-9(2)
C(42)	29(2)	38(2)	26(2)	2(2)	4(2)	-12(2)
C(43)	39(2)	34(2)	41(2)	6(2)	14(2)	-8(2)
C(44)	51(3)	53(3)	61(3)	12(2)	17(2)	-21(2)
O(45)	25(1)	22(1)	22(1)	-2(1)	-1(1)	-12(1)
C(46)	34(2)	30(2)	26(2)	5(2)	-6(2)	-16(2)
C(47)	55(3)	50(2)	31(2)	7(2)	-16(2)	-30(2)
C(48)	88(4)	86(4)	66(4)	-11(3)	-15(3)	-32(4)
C(49)	102(5)	85(4)	74(4)	-1(3)	-9(4)	5(4)
C(50)	113(5)	116(5)	46(3)	29(3)	26(3)	49(4)
C(51)	72(4)	66(3)	70(4)	-8(3)	-2(3)	-12(3)
C(52)	72(4)	49(3)	69(3)	-4(2)	1(3)	-21(3)
C(53)	41(3)	52(3)	75(3)	13(2)	-5(2)	-23(2)

C(54)	54(3)	73(3)	67(3)	26(3)	-8(2)	-28(3)
C(55)	213(8)	85(4)	47(3)	5(3)	-36(4)	-63(5)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **4**.

	x	y	z	U(eq)
H(3A)	4071	876	3461	24
H(6A)	2562	429	5905	22
H(9A)	1253	-1499	4407	22
H(12A)	-1359	-4119	4336	23
H(15A)	-237	-2192	6170	22
H(18A)	-2722	-4712	6682	25
H(21A)	-5279	-6300	8471	30
H(22A)	-5557	-5169	9418	34
H(23A)	-4520	-3616	9294	36
H(24A)	-3179	-3176	8217	28
H(26A)	-4145	-7353	6785	55
H(26B)	-5433	-6837	7325	55
H(26C)	-3966	-7500	7630	55
H(28A)	-3505	-5829	5258	35
H(28B)	-2091	-5651	4767	35
H(28C)	-3532	-4756	4731	35
H(30A)	375	-2952	2806	44
H(30B)	-1132	-3073	3229	44
H(30C)	266	-3986	3353	44
H(35A)	4952	2382	3136	27
H(35B)	6380	1560	3377	27

H(36A)	7234	3061	3793	29
H(36B)	5860	3857	3482	29
H(37A)	6721	3326	2287	30
H(37B)	8144	2631	2618	30
H(38A)	7373	4939	2633	29
H(38B)	8821	4231	2928	29
H(39A)	9700	3818	1747	31
H(39B)	8223	4452	1438	31
H(40A)	10252	5456	2043	30
H(40B)	8751	6103	1770	30
H(41A)	9554	5740	563	33
H(41B)	11038	5045	827	33
H(42A)	10189	7348	860	37
H(42B)	11606	6685	1213	37
H(43A)	11214	6838	-300	48
H(43B)	12643	6209	59	48
H(44A)	13027	7918	-483	84
H(44B)	13135	7881	364	84
H(44C)	11704	8510	7	84
H(46A)	3398	-344	2727	35
H(46B)	2178	693	2871	35
H(47A)	1542	-1361	2625	51
H(47B)	342	-307	2744	51
H(48A)	776	-623	1534	93
H(48B)	2419	-525	1566	93
H(49A)	-27	1247	1598	108
H(49B)	1507	1401	1814	108
H(50A)	1054	851	425	127
H(50B)	968	2061	597	127

H(51A)	3547	484	606	83
H(51B)	3448	1710	755	83
H(52A)	2815	2239	-472	75
H(52B)	4414	1552	-418	75
H(53A)	1969	723	-725	66
H(53B)	3511	-17	-610	66
H(54A)	4498	883	-1671	77
H(54B)	2947	1612	-1788	77
H(55A)	3363	181	-2569	164
H(55B)	2031	34	-2008	164
H(55C)	3586	-694	-1894	164

Table 13. Torsion angles [deg] for **4**.

C(6)-C(1)-C(2)-O(45)	-175.6(3)
C(7)-C(1)-C(2)-O(45)	2.3(5)
C(6)-C(1)-C(2)-C(3)	4.3(4)
C(7)-C(1)-C(2)-C(3)	-177.7(3)
O(45)-C(2)-C(3)-C(4)	175.6(3)
C(1)-C(2)-C(3)-C(4)	-4.4(5)
C(2)-C(3)-C(4)-O(34)	-178.1(3)
C(2)-C(3)-C(4)-C(5)	1.4(5)
O(34)-C(4)-C(5)-C(6)	-179.1(3)
C(3)-C(4)-C(5)-C(6)	1.4(4)
O(34)-C(4)-C(5)-N(31)	0.7(5)
C(3)-C(4)-C(5)-N(31)	-178.8(3)
C(2)-C(1)-C(6)-C(5)	-1.5(5)
C(7)-C(1)-C(6)-C(5)	-179.8(3)
C(4)-C(5)-C(6)-C(1)	-1.3(5)
N(31)-C(5)-C(6)-C(1)	178.9(3)

C(6)-C(1)-C(7)-O(8)	0.8(4)
C(2)-C(1)-C(7)-O(8)	-177.2(3)
C(6)-C(1)-C(7)-N(9)	-177.8(3)
C(2)-C(1)-C(7)-N(9)	4.2(5)
O(8)-C(7)-N(9)-C(10)	1.3(5)
C(1)-C(7)-N(9)-C(10)	179.9(3)
C(7)-N(9)-C(10)-C(15)	-1.0(5)
C(7)-N(9)-C(10)-C(11)	178.2(3)
C(15)-C(10)-C(11)-O(29)	179.2(3)
N(9)-C(10)-C(11)-O(29)	-0.1(4)
C(15)-C(10)-C(11)-C(12)	-1.8(4)
N(9)-C(10)-C(11)-C(12)	178.9(3)
O(29)-C(11)-C(12)-C(13)	179.9(3)
C(10)-C(11)-C(12)-C(13)	1.0(4)
C(11)-C(12)-C(13)-O(27)	-178.7(3)
C(11)-C(12)-C(13)-C(14)	0.9(5)
O(27)-C(13)-C(14)-C(15)	177.7(3)
C(12)-C(13)-C(14)-C(15)	-1.8(4)
O(27)-C(13)-C(14)-C(16)	-6.9(5)
C(12)-C(13)-C(14)-C(16)	173.5(3)
C(11)-C(10)-C(15)-C(14)	0.8(4)
N(9)-C(10)-C(15)-C(14)	-179.9(3)
C(13)-C(14)-C(15)-C(10)	1.0(4)
C(16)-C(14)-C(15)-C(10)	-174.9(3)
C(13)-C(14)-C(16)-O(17)	-168.6(3)
C(15)-C(14)-C(16)-O(17)	6.9(4)
C(13)-C(14)-C(16)-N(18)	10.0(5)
C(15)-C(14)-C(16)-N(18)	-174.5(3)
O(17)-C(16)-N(18)-C(19)	2.8(5)

C(14)-C(16)-N(18)-C(19)	-175.8(3)
C(16)-N(18)-C(19)-C(24)	4.4(5)
C(16)-N(18)-C(19)-C(20)	-176.5(3)
C(24)-C(19)-C(20)-O(25)	-179.1(3)
N(18)-C(19)-C(20)-O(25)	1.8(4)
C(24)-C(19)-C(20)-C(21)	1.9(5)
N(18)-C(19)-C(20)-C(21)	-177.3(3)
O(25)-C(20)-C(21)-C(22)	179.7(3)
C(19)-C(20)-C(21)-C(22)	-1.3(5)
C(20)-C(21)-C(22)-C(23)	0.4(5)
C(21)-C(22)-C(23)-C(24)	0.1(5)
C(20)-C(19)-C(24)-C(23)	-1.4(5)
N(18)-C(19)-C(24)-C(23)	177.6(3)
C(22)-C(23)-C(24)-C(19)	0.5(5)
C(21)-C(20)-O(25)-C(26)	-1.6(5)
C(19)-C(20)-O(25)-C(26)	179.4(3)
C(12)-C(13)-O(27)-C(28)	-7.1(4)
C(14)-C(13)-O(27)-C(28)	173.4(3)
C(12)-C(11)-O(29)-C(30)	1.6(4)
C(10)-C(11)-O(29)-C(30)	-179.4(3)
C(6)-C(5)-N(31)-O(33)	-174.7(3)
C(4)-C(5)-N(31)-O(33)	5.5(5)
C(6)-C(5)-N(31)-O(32)	3.4(4)
C(4)-C(5)-N(31)-O(32)	-176.4(3)
C(3)-C(4)-O(34)-C(35)	-7.3(4)
C(5)-C(4)-O(34)-C(35)	173.2(3)
C(4)-O(34)-C(35)-C(36)	176.8(3)
O(34)-C(35)-C(36)-C(37)	174.9(3)
C(35)-C(36)-C(37)-C(38)	174.4(3)

C(36)-C(37)-C(38)-C(39)	-177.3(3)
C(37)-C(38)-C(39)-C(40)	176.1(3)
C(38)-C(39)-C(40)-C(41)	-177.5(3)
C(39)-C(40)-C(41)-C(42)	-177.5(3)
C(40)-C(41)-C(42)-C(43)	173.6(3)
C(41)-C(42)-C(43)-C(44)	178.2(3)
C(1)-C(2)-O(45)-C(46)	164.7(3)
C(3)-C(2)-O(45)-C(46)	-15.3(4)
C(2)-O(45)-C(46)-C(47)	-161.2(3)
O(45)-C(46)-C(47)-C(48)	-178.1(4)
C(46)-C(47)-C(48)-C(49)	-62.6(6)
C(47)-C(48)-C(49)-C(50)	167.0(5)
C(48)-C(49)-C(50)-C(51)	-70.3(8)
C(49)-C(50)-C(51)-C(52)	178.3(5)
C(50)-C(51)-C(52)-C(53)	-67.7(6)
C(51)-C(52)-C(53)-C(54)	-175.0(4)
C(52)-C(53)-C(54)-C(55)	179.3(5)

Symmetry transformations used to generate equivalent atoms:

Table 14. Hydrogen bonds for **4** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(9)-H(9A)...O(29)	0.86	2.226	2.623	108.0
N(9)-H(9A)...O(45)	0.86	2.021	2.722	137.98
N(18)-H(18A)...O(25)	0.86	2.162	2.582	109.6
N(18)-H(18A)...O(27)	0.86	1.960	2.668	138.80