Double Annulation Route to Fused Bicyclic Compounds with Three Adjacent Quaternary Centers.

Robert B. Grossman, Aaron J. Skaggs, Arlene E. Kray, and Brian O. Patrick

Supporting Information

Detailed experimental procedures for the preparation and characterization of **1c-e**, **2c,e**, **3a,b**, **4a-c**, and **5a,b**, and 2-amino-2-cyclopentene-1,1,3-tricarbonitrile, and crystallographic information for **3a**, **4a**, and **5b** (29 pages).

(*E,E*)-3,9-Diethyl-2,9-undecadiene-4,4,8,8-tetracarbonitrile. A modification of the literature procedure was used.[40] An excess of (3-pentylidene)malononitrile (23.5 mL, 165 mmol) was added slowly to a suspension of NaH (7.37 g of 60% suspension in mineral oil, 180 mmol, washed with petroleum ether) in dry DMF (300 mL), and 1,3-dibromopropane (7.5 mL, 75 mmol) was added. When the reaction was judged to be complete (GC), acetic acid (ca. 2 mL) was added. The DMF and excess acetic acid were then removed by distillation. The residue was diluted with ether and washed with water and brine. After evaporation, excess starting material was removed by Kugelrohr distillation. The residue was dissolved in a solution of 50% EtOAc in petroleum ether and passed through a plug of silica gel, and the solvent was evaporated again. The material thus obtained (19.9 g, 64.5 mmol, 86% yield, 96% pure by GC) was generally carried on to the next step without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.06 (q, 1.0 Hz, 1H), 2.26 (q, 7.7 Hz, 2H), 2.14 (m, 2H), 1.90 (m, 1H), 1.79 (d, 6.6 Hz, 3H), 1.17 (t, 7.3 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 131.3, 128.3, 114.4, 43.3, 36.8, 21.2, 21.1, 13.7, 13.6. IR (neat): 2249, 1735, 1460 cm^{-1}. Anal. Calcd for $C_{19}H_{24}N_4$: C, 73.99; H, 7.84. Found: C, 73.77; H, 7.85.

1,1,5,5-Pentanetetracarbonitrile (1c). Ozonolysis and acidic alcoholysis of (*E,E*)-3,9-diethyl-2,9-undecadiene-4,4,8,8-tetracarbonitrile (19.9 g, 64.5 mmol) were carried out as described previously.[40] The title compound (6.74 g, 39.6 mmol, 61% yield) was obtained as white microcrystals, mp 87-88.5 °C, by recrystallization from the crude reaction mixture. ^{1}H NMR (200 MHz, DMSO): δ 4.91 (t, 6.8 Hz, 1H), 2.13 (m, 2H), 1.66 (m, 1H). ^{13}C{H} NMR (50 MHz, DMSO): δ 114.3, 28.1, 23.2, 21.9. IR (KBr): 2257, 1456 cm^{-1}. Anal. Calcd for $C_9H_8N_4$: C, 62.78; H, 4.68. Found: C, 62.50; H, 4.80.

(*E,E*)-3,9-Diethyl-6-methyl-2,9-undecadiene-4,4,8,8-tetracarbonitrile. Prepared from (3-pentylidene)malononitrile (16.0 mL, 113 mmol) and 1,3-dibromo-2-methylpropane (10.8 mL, 50.0 mmol) as described above. The crude product that was obtained after extraction with ether (12.17 g, ca. 87% pure by GC–MS, 66% yield) was carried on to the next step without further purification. A small portion was subjected to flash chromatography (7.5%, then 12.5% EtOAc in petroleum ether as eluant) for purposes of characterization to give a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$):

δ 6.08 (q, 6.8 Hz, 2H), 2.24 (m, 7H), 1.99 (dd, 6.9 Hz, 13.8 Hz, 2H), 1.79 (d, 7.0 Hz, 6H), 1.35 (d, 6.6 Hz, 3H), 1.16 (t, 7.6 Hz, 6H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 132.2, 127.9, 115.1, 114.6, 44.5, 41.9, 29.1, 21.2, 20.5, 13.8, 13.6. IR (neat): 2244, 1469 cm^{-1}. Anal. Calcd for $C_{20}H_{26}N_4$: C, 74.50; H, 8.13. Found: C, 74.24; H, 8.30.

3-Methyl-1,1,5,5-pentanetetracarbonitrile (1d). Ozonolysis and acidic alcoholysis of (*E,E*)-3,9-diethyl-6-methyl-2,9-undecadiene-4,4,8,8-tetracarbonitrile (9.67 g, 30.0 mmol) were carried out as described previously.[40] The title compound (3.29 g, 17.7 mmol, 59% yield) was obtained as white microcrystals, mp 85 °C, by recrystallization from the crude reaction mixture. ^1H NMR (200 MHz, $CDCl_3$): δ 3.84 (dd, 8.4 Hz, 6.2 Hz, 2H), 2.21 (m, 3H), 2.02 (m, 2H), 1.20 (d, 6.6 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 114.4, 114.2, 29.0, 20.3, 17.1. IR (KBr): 2257, 1469 cm^{-1}. Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41. Found: C, 64.69; H, 5.51.

(*E,E*)-*o*-Xylylenebis[(2-penten-3-yl)malononitrile]. Prepared from (3-pentylidene)malononitrile (9.8 mL, 69 mmol) and *o*-xylylene dibromide[45] (7.93 g, 30.0 mmol) as described above, except that the reaction was carried out in THF. The crude product that was obtained after extraction with ether (12.93 g, ca. 75% pure by GC–MS) was carried on to the next step without further purification. A small portion was recrystallized from hot toluene for purposes of characterization: mp 95-96 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 7.44 (s, 2H), 5.99 (q, 4.6 Hz, 1H), 3.46 (s, 2H), 2.33 (q, 7.6 Hz, 2H), 1.80 (d, 7.0 Hz, 3H), 1.24 (t, 7.7 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 132.4, 132.2, 131.8, 129.2, 129.2, 114.5, 45.5, 40.9, 21.8, 13.8, 13.7. IR (KBr): 2244, 1491, 1465 cm^{-1}. Anal. Calcd for $C_{24}H_{26}N_4$: C, 77.80; H, 7.07. Found: C, 77.56; H, 6.87.

***o*-Xylylenebis(malononitrile) (1e).** Ozonolysis and acidic alcoholysis of (*E,E*)-*o*-xylylenebis[(2-penten-3-yl)malononitrile] (12.93 g of ca. 75% pure material) were carried out as described previously.[40] The title compound (3.30 g, 14.1 mmol, 47% yield over two steps) was obtained as white crystals, mp 137-140 °C. ^1H NMR (200 MHz, DMSO): δ 7.40 (m, 2H), 4.98 (t, 7.7 Hz, 1H), 3.53 (d, 7.7 Hz, 2H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 134.1, 131.0, 128.4, 114.2,

30.9, 24.1. IR (KBr): 2254, 1941, 1742 (w), 1501, 1443 cm^{-1}. Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30. Found: C , 71.92; H, 4.27.

(*E,E*)-3,8-Diethyl-2,8-decadiene-4,4,7,7-tetracarbonitrile. Prepared from (3-pentylidene)malononitrile (7.8 mL, 55 mmol) and 1,2-dibromopropane (2.2 mL, 25 mmol) as described above. The crude material was purified further by flash chromatography (15% EtOAc in petroleum ether as eluant) to provide the title compound (1.92 g, 6.52 mmol, 26% yield) as a white solid. ^1H NMR (200 MHz, $CDCl_3$): δ 6.08 (q, 6.9 Hz, 1H), 2.30 (m, 4H), 1.82 (d, 6.6 Hz, 3H), 1.20 (t, 7.5 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 131.0, 128.8, 113.9, 42.7, 34.1, 21.2, 13.8, 13.6. Anal. Calcd for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53. Found: C, 73.30; H 7.42.

2-Amino-2-cyclopentene-1,1,3-tricarbonitrile. Prepared in the same way from (*E,E*)-3,8-diethyl-2,8-decadiene-4,4,7,7-tetracarbonitrile (2.14 g, 7.27 mmol) to give the title compound (0.425 g, 2.69 mmol, 37% yield) as white crystals, mp 133-134.5 °C. ^1H NMR (200 MHz, DMSO): δ 7.51 (s, 1H), 2.75 (m, 1H), 2.64 (m, 1H). $^{13}C\{H\}$ NMR (50 MHz, DMSO): δ 153.4, 117.3, 114.7, 76.8, 42.0, 37.6, 29.5. IR (KBr): 3430, 3336, 2204 (s), 1654 (s), 1617, 1508, 1442 cm^{-1}. Anal. Calcd for $C_8H_6N_4$: C, 60.75; H, 3.82. Found: C, 60.64; H, 3.53.

2-(2-Oxopropyl)cyclohexane-1,1,3,3-tetracarbonitrile (2c). The following procedure is representative. Bis(malononitrile) **1c** (348 mg, 2.02 mmol) was added to a suspension of NaH (a small amount, 60% suspension in mineral oil) in THF (30 mL), and the mixture was allowed to stir for 15 min. The solution was cooled to 0 °C, and 3-butyn-2-one (160 μL, 2.04 mmol) was added. The reaction mixture was allowed to stir until the reaction was judged to be complete by GC or TLC. The reaction was quenched with 1 N HCl, and the THF was evaporated. The residue was taken up in water and extracted with ether. The organic layer was shaken with brine, dried over $MgSO_4$, and evaporated, and the residue was recrystallized from hot EtOH to afford the title compound (325 mg, 1.35 mmol, 67% yield) as a white microcrystalline solid, mp 222-224 °C. ^1H NMR (400 MHz, DMSO): δ 3.76 (t, 4.9 Hz, 1H), 3.25 (d, 4.6 Hz, 2H), 2.63 (dm, J_d = 3 Hz, 2H), 2.39 (td, J_t = 13.5 Hz, J_d = 3.2 Hz, 2H), 2.31 (s, 3H), 2.20 (dt, J_d = 15.4 Hz, J_t = 3.4 Hz, 1H), 1.58 (qm, $J_q \approx$ 15 Hz, 1H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 202.9, 114.7, 112.9, 44.0, 37.2, 36.6,

31.9, 29.6, 17.6. IR (KBr): 2249, 1725 (s), 1446 cm^{-1}. Anal. Calcd for $C_{13}H_{12}N_4O$: C, 64.99; H, 5.03. Found: C, 64.62; H, 4.98.

2-(2-Oxopropyl)-5-benzocycloheptene-1,1,3,3-tetracarbonitrile (2e). Bis(malononitrile) **1e** (240 mg, 1.02 mmol) and 3-butyn-2-one (90 μL, 1.2 mmol) were combined according to the standard procedure to afford the title compound (204 mg, 0.675 mmol, 66% yield) as a white solid, mp 269–270 °C. ^{1}H NMR (400 MHz, DMSO): δ 7.40 (m, 4H), 4.16 (m, 3H), 3.74 (d, 14.5 Hz, 2H), 3.30 (d, 4.1 Hz, 2H), 2.31 (s, 3H). ^{13}C{H} NMR (50 MHz, DMSO): δ 202.6, 134.0, 131.3, 129.2, 115.0, 111.3, 46.0, 42.2, 39.3, 38.5, 29.3. IR (KBr): 2249, 1722 (s), 1461 cm^{-1}. Anal. Calcd for $C_{18}H_{14}N_4O$: C, 71.51; H, 4.67. Found: C, 71.36; H, 4.59.

(*1R*,6R*)-10-Amino-6,9-dimethylbicyclo[4.4.0]dec-9-en-8-one-1,5,5-tricarbonitrile (3a). Bis(malononitrile) **1c** (186 mg, 1.00 mmol), 4-hexyn-3-one (120 μL, 1.11 mmol), and NaH (40 mg, 1.0 mmol) were combined according to the standard procedure. After evaporation of the solvent, the residue was triturated with EtOH and filtered to afford the title compound (138 mg, 0.515 mmol, 48% yield) as a white microcrystalline solid, mp 285–287 °C. Crystals suitable for X-ray analysis were grown from a solution of EtOH into which water was allowed to diffuse. ^{1}H NMR (400 MHz, DMSO): δ 6.98 (s, 2H), 2.88 (d, 16.3 Hz, 1H), 2.55 (m, obscured by residual DMSO, 3H), 2.43 (d, 16.4 Hz, 1H), 2.10 (m, 1H), 1.88 (m, 2H), 1.65 (s, 3H), 1.29 (s, 3H). ^{13}C{H} NMR (50 MHz, DMSO): δ 186.8, 156.2, 118.8, 114.8, 114.1, 108.8, 45.8, 43.9, 41.5, 40.2, 29.1, 24.6, 18.9, 17.0, 8.9. IR (KBr): 3353, 3195, 2244, 2233, 1666, 1551 (s), 1456 cm^{-1}. Anal. Calcd for $C_{15}H_{16}N_4O$: C, 67.15; H, 6.01. Found: C, 66.93; H, 6.03.

(*1R*,3R,6R*)-10-Amino-3,6,9-trimethylbicyclo[4.4.0]dec-9-en-8-one-1,5,5-tricarbonitrile (3b). Prepared in the same way as **3a** from **1d** (373 mg, 2.00 mmol), 4-hexyn-3-one (250 μL, 2.31 mmol), and NaH (80 mg, 2.0 mmol) to afford the product (275 mg, 0.974 mmol, 49% yield) as a white solid, mp 271–273 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (s, 2H), 2.87 (dd, 1.1 Hz, 16.3 Hz, 1H), 2.59 (dd, 2.5 Hz, 14.0 Hz, 1H), 2.51 (dd, obscured by residual DMSO, 1H), 2.44 (d, 15.3 Hz, 1H), 2.22 (t, 13.2 Hz, 1H), 2.13 (m, 1H), 1.63 (s + dd, 4H), 1.27 (d, 1.0 Hz, 3H), 1.13 (d, 6.3 Hz, 3H). ^{13}C{H} NMR (50 MHz): δ 188.1, 155.8, 119.3, 115.5, 114.9,

104.9, 46.7, 45.1, 43.0, 41.2, 37.7, 33.7, 27.4, 20.4, 17.7, 8.9. IR (KBr): 3440, 3411, 3350, 3275, 3242, 2250, 2233, 1654, 1623, 1599, 1548 (s), 1394 cm^{-1}. Anal. Calcd for $C_{16}H_{18}N_4O$: C, 68.06; H, 6.43. Found: C, 67.94; H, 6.60.

(*1R*,6S*)-6-Ethyl-8-methyl-9-oxabicyclo[4.4.0]dec-7-en-10-one-1,5,5-tricarbonitrile (4a). Prepared in the same way as **3a** from **1c** (2.06 g, 12.0 mmol) and 3-hexyn-2-one (1.31 mL, 12.0 mmol) to afford the title compound (2.54 g, 9.43 mmol, 79% yield) as a white microcrystalline solid, mp 220-221 °C. Crystals suitable for X-ray analysis were grown from a solution of $CHCl_3$ into which petroleum ether (30–60 °C fraction) was allowed to diffuse. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (d, 1.0 Hz, 1H), 2.53 (dm, $J_d \approx 12$ Hz, 1H), 2.39 (m, 1H), 2.28 (dm, $J_d \approx 14$ Hz, 1H), 2.10 (m, 8H), 1.05 (t, 7.5 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 162.8, 152.2, 114.3, 114.1, 112.3, 96.9, 46.5, 45.2, 41.4, 32.4, 31.5, 30.7, 18.7, 17.8, 7.7. IR (KBr): 2249, 1766 (s), 1706, 1465, 1447 cm^{-1}. Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.90; H, 5.61. Found: C, 66.58; H, 5.52.

(*1R*,3R,6S*)-6-Ethyl-3,8-dimethyl-9-oxabicyclo[4.4.0]dec-7-en-10-one-1,5,5-tricarbonitrile (4b). Prepared in the same way as **3a** from **1d** (373 mg, 2.00 mmol) and 3-hexyn-2-one (245 μL, 2.25 mmol) to afford the product (164 mg, 0.579 mmol, 29% yield) as a white solid, mp 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (q, 1.1 Hz, 1H), 2.44 (ddd, 2.0 Hz, 3.0 Hz, 13.0 Hz, 1H), 2.38 (dq, $J_q = 7.1$ Hz, $J_d = 14.3$ Hz, 1H), 2.33 (m, 1H), 2.21 (ddd, 2.1 Hz, 3.0 Hz, 11.6 Hz, 1H), 2.08 (d, 1.1 Hz, 3H), 2.06 (dq, partly obscured, $J_q = 7.2$ Hz, $J_q = 14.4$ Hz, 1H), 1.84 (dd, 12.5 Hz, 13.7 Hz, 1H), 1.56 (dd, 12.4 Hz, 13.7 Hz, 1H), 1.12 (d, 3.1 Hz, 3H), 1.04 (t, 7.4 Hz, 3H). ^{13}C{H} NMR (50 MHz, $CDCl_3$): δ 162.6, 152.2, 114.3, 114.2, 112.5, 96.9, 47.0, 44.9, 42.0, 39.5, 38.2, 31.3, 24.8, 19.8, 18.7, 7.8. IR (KBr): 2249, 1771 (s), 1709, 1429 cm^{-1}. Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05. Found: C, 67.79; H, 5.97.

(*1R*,6S*)-6,8-Diethyl-9-oxabicyclo[4.4.0]dec-7-en-10-one-1,5,5-tricarbonitrile (4c). Prepared in the same way as **3a** from **1c** (173 mg, 1.00 mmol) and 4-heptyn-3-one (140 μL, 1.09 mmol) to afford the product (126 mg, 0.445 mmol, 45% yield) as a white solid, mp 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.96 (t, 0.9 Hz, 1H), 2.52 (dm, 1H), 2.39 (dq, $J_q = 7.3$ Hz, $J_d =$

14.4 Hz, 1H), 2.35 (dq, J_q= 3.3 Hz, J_d = 1.0 Hz, 2H), 2.28 (dm, 1H), 2.10 (m, 4H), 1.88 (m, 1H), 1.19 (t, 7.5 Hz, 3H), 1.04 (t, 7.4 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 162.9, 157.1, 114.3, 114.2, 112.4, 95.4, 46.5, 44.9, 41.5, 32.3, 31.5, 30.7, 25.9, 17.8, 10.8, 7.6. IR (KBr): 2254, 1772 (s), 1701, 1460, 1447 cm^{-1}. Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05. Found: C, 67.52; H, 6.07.

(*1R*,11S*)-14-Ethyl-1-methyl-13-oxatricyclo[10.4.0.0^{4,9}]pentadeca-4,6,8,14-tetraen-12-one-2,2,11-tricarbonitrile (5a). Prepared in the same way as **3a** from **1e** (236 mg, 1.01 mmol) and 4-hexyn-3-one (103 μL, 1.07 mmol) to afford the title compound (101 mg, 0.30 mmol, 30% yield) as a white microcrystalline solid, mp 194–196 °C. ^1H NMR (400 MHz, DMSO): δ 7.45 (m, 4H), 5.56 (s, 1H), 3.91 (d, 14.6 Hz, 1H), 3.82 (d, 14.5 Hz, 1H), 3.73 (d, 14.9 Hz, 1H), 3.09 (d, 14.5 Hz, 1H), 2.40 (m, partly obscured by residual DMSO, 2H), 1.61 (s, 3H), 1.10 (t, 7.4 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 161.8, 157.0, 133.3, 132.6, 131.5, 130.3, 129.8, 114.6, 112.6, 110.3, 99.3, 51.9, 45.1, 43.3, 39.5, 36.3, 25.8, 25.5, 10.6. IR (KBr): 2254, 1765 (s), 1701, 1455 cm^{-1}. Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17. Found: C, 72.22; H, 5.19.

(*1R*,11S*)-1-Ethyl-14-methyl-13-oxatricyclo[10.4.0.0^{4,9}]pentadeca-4,6,8,14-tetraen-12-one-2,2,11-tricarbonitrile (5b). Prepared in the same way as **3a** from **1d** (235 mg, 1.00 mmol) and 3-hexyn-2-one (110 μL, 1.01 mmol) to afford the title compound (122 mg, 0.37 mmol, 37% yield) as a white microcrystalline solid, mp 252 °C (dec). Crystals suitable for X-ray analysis were grown from a solution of EtOH into which water was allowed to diffuse. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 2H), 7.35 (m, 2H), 5.17 (q, 1.0 Hz, 1H), 3.79 (d, 14.7 Hz, 1H), 3.66 (d, 14.3 Hz, 1H), 3.34 (d, 14.8 Hz, 1H), 2.95 (d, 14.3 Hz, 1H), 2.41 (m, 1H), 2.18 (m, 4H), 1.08 (t, 7.4 Hz, 3H). $^{13}C\{H\}$ NMR (50 MHz, $CDCl_3$): δ 162.8, 153.1, 133.2, 132.9, 131.4, 131.1, 130.2, 129.8, 115.1, 112.6, 110.5, 97.3, 49.9, 49.7, 43.9, 40.0, 38.0, 32.8, 18.7, 8.3. IR (KBr): 2249, 1771 (s), 1700, 1448 cm^{-1}. Anal. Calcd for $C_{20}H_{17}N_3O_2$: C, 72.49; H, 5.17. Found: C, 72.12; H, 5.23.

Crystallographic Information. X-ray crystallographic data for **3a**, **4a**, and **5b** were collected at room temperature on a Nonius KappaCCD diffractometer. Reflections were indexed and scaled using the Denzo-SMN software package (Otwinowski & Minor, 1997). The structure was solved

with SHELXTL-PC (Sheldrick, 1990) and refined with SHELXL-93 (Sheldrick, 1993). Crystallographic data appear in Table 1. Hydrogen atoms were placed in calculated positions. Disorder was evident in the Et group of **5b** and was modelled; nothing was found that would call into question the stereochemistry of this compound.

References.

Otwinowski, Z. and Minor, W. (1997). *Methods of Enzymology*, Vol. 276: Macromolecular Crystallography, part A, edited by C. W. Carter, Jr. & R. M. Sweet, pp.307-326. Academic Press.

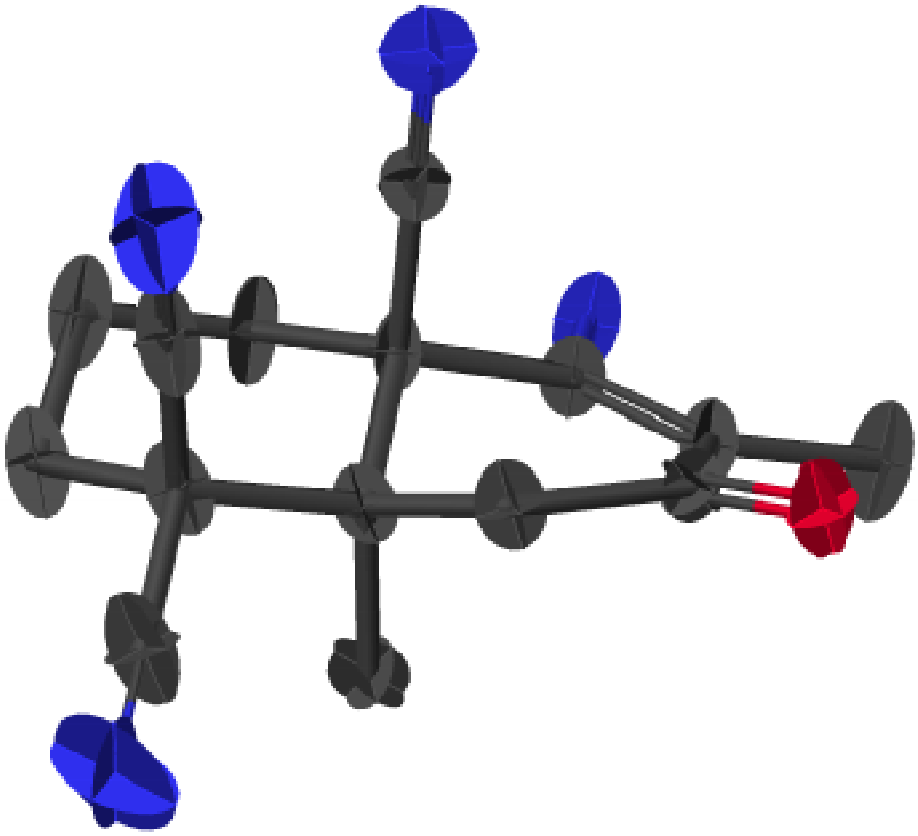
Sheldrick, G. M. (1990). *SHELXTL-PC*, Release 4.1. Siemens Analytical Instruments, Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

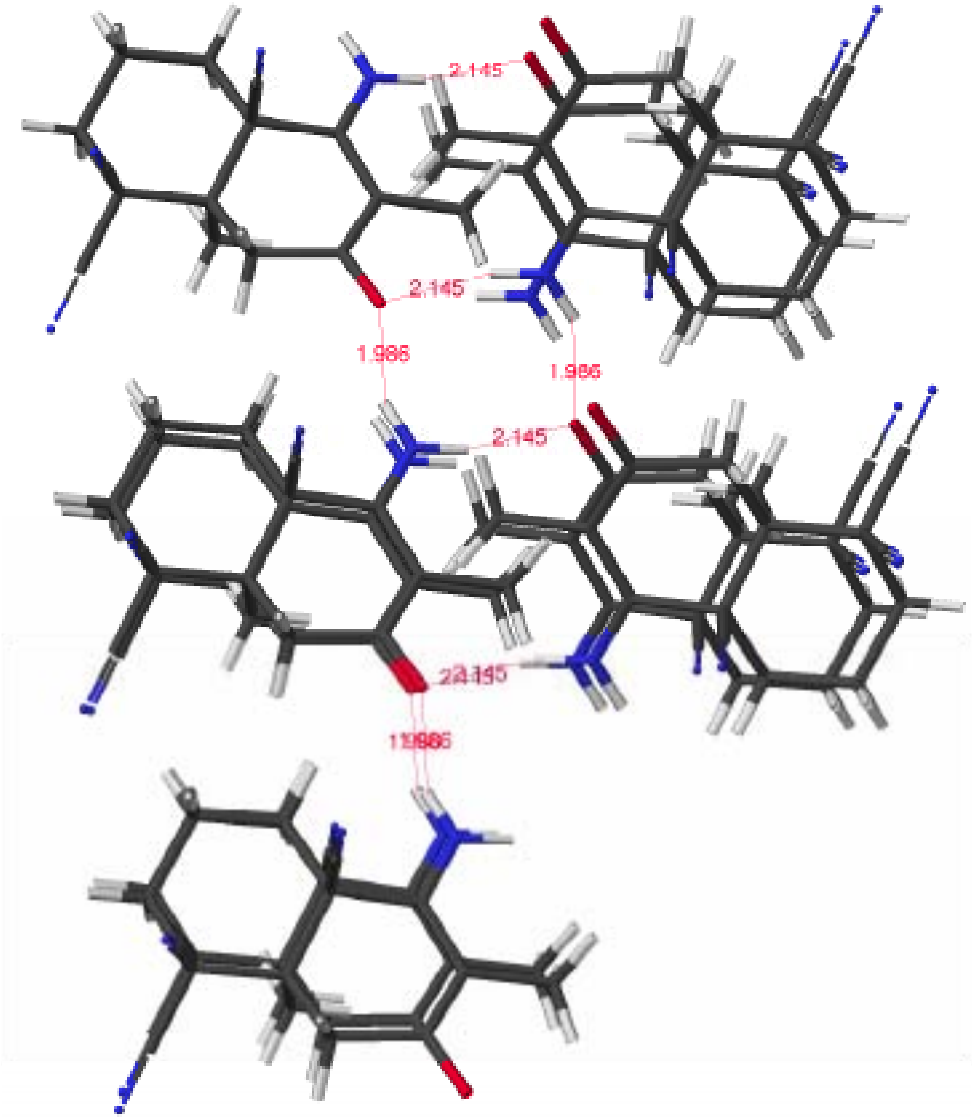
Table 1. Crystal data for **3a**, **4a**, and **5b**.

	3a	**4a**	**5b**
empirical formula	$C_{15}H_{16}N_4O$	$C_{15}H_{15}N_3O_2$	$C_{20}H_{17}N_3O_2$
fw	268.32	269.30	331.37
crystal system	orthorhombic	monoclinic	monoclinic
space group	$C222_1$	$P2_1/n$	$P2_1/c$
a (Å)	7.132(1)	7.438(1)	14.066(3)
b (Å)	13.017(1)	18.505(4)	8.067(2)
c (Å)	31.005(1)	10.101(2)	15.800(3)
α (deg)	90	90	90
β (deg)	90	93.01(3)	106.20(3)
γ (deg)	90	90	90
V (Å^3)	2878.4(5)	1390.3(4)	1721.7(6)
Z	8	4	4
Dcalc(g/cm^3)	1.248	1.298	1.283
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.082	0.088	0.085
temp (K)	293(2)	293(2)	293(2)
Θ range (deg)	3.33 to 27.89	2.20 to 27.90	3.06 to 20.70
$R(F_o^2)^a$	0.0403	0.0465	0.0744
$Rw(F_o^2)^b$	0.1009	0.1208	0.1805

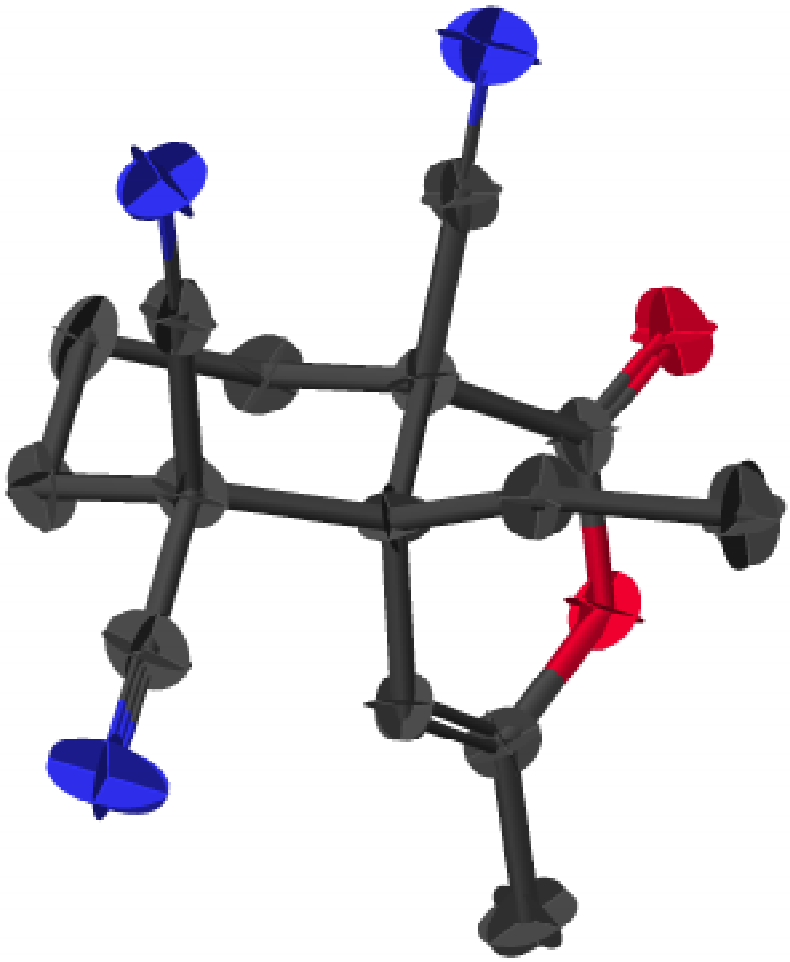
$^aR = \_\_F_o - \_F_c\_/\_\_F_o\_$. $^bRw = [\_\ w(F_o^2 - F_c^2)^2/\_\ wF_o^4]^{-}$



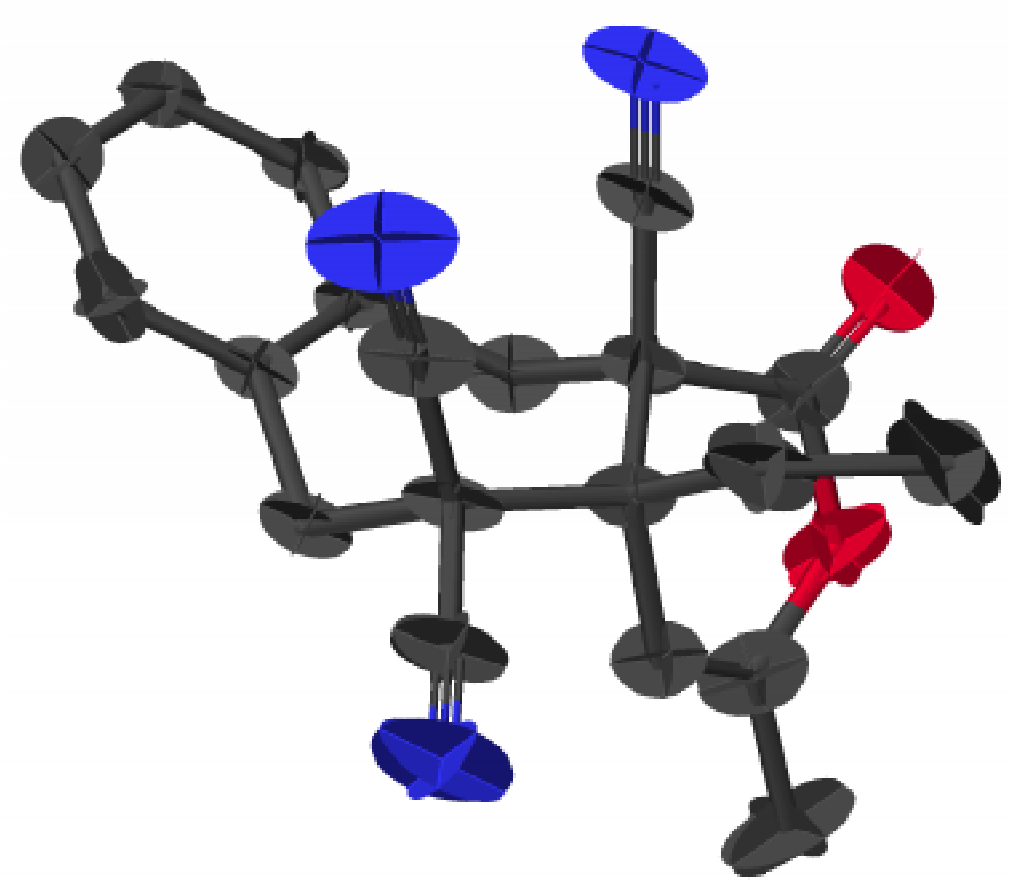
Thermal ellipsoid plot of **3a** (50% probability ellipsoids).



Plot of **3a** showing the packing and the hydrogen-bonding network.



Thermal ellipsoid plot of **4a** (50% probability ellipsoids).



Thermal ellipsoid plot of the major conformer of **5b** (30% probability ellipsoids).

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(4)	5609(2)	4087(1)	5496(1)	45(1)
N(2)	9032(3)	1032(1)	5403(1)	47(1)
N(11)	4150(3)	781(2)	6011(1)	72(1)
N(14)	7636(5)	3967(2)	7290(1)	105(1)
N(15)	3598(3)	1874(2)	6956(1)	75(1)
C(1)	7577(2)	1496(1)	6089(1)	32(1)
C(2)	8138(2)	1760(1)	5621(1)	33(1)
C(3)	7608(3)	2673(1)	5435(1)	35(1)
C(4)	6491(2)	3379(1)	5673(1)	33(1)
C(5)	6326(3)	3282(2)	6158(1)	39(1)
C(6)	7683(3)	2507(1)	6357(1)	33(1)
C(7)	7153(3)	2289(2)	6845(1)	42(1)
C(8)	8342(3)	1397(2)	7035(1)	51(1)
C(9)	8172(4)	436(2)	6761(1)	55(1)
C(10)	8745(3)	629(2)	6293(1)	48(1)
C(11)	5612(3)	1114(2)	6050(1)	44(1)
C(12)	8085(4)	2916(2)	4974(1)	56(1)
C(13)	9695(3)	2937(2)	6347(1)	49(1)
C(14)	7440(4)	3238(2)	7098(1)	62(1)
C(15)	5139(3)	2039(2)	6899(1)	51(1)

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

O(4)-C(4)	1.240(2)
N(2)-C(2)	1.326(2)
N(11)-C(11)	1.134(3)
N(14)-C(14)	1.128(4)
N(15)-C(15)	1.132(3)
C(1)-C(11)	1.490(3)
C(1)-C(10)	1.537(2)
C(1)-C(2)	1.542(2)
C(1)-C(6)	1.557(2)
C(2)-C(3)	1.371(2)
C(3)-C(4)	1.420(2)
C(3)-C(12)	1.502(3)
C(4)-C(5)	1.513(2)
C(5)-C(6)	1.527(2)
C(6)-C(13)	1.539(3)
C(6)-C(7)	1.583(2)
C(7)-C(14)	1.475(3)
C(7)-C(15)	1.481(3)
C(7)-C(8)	1.552(3)
C(8)-C(9)	1.515(4)
C(9)-C(10)	1.528(3)
C(11)-C(1)-C(10)	107.3(2)
C(11)-C(1)-C(2)	104.01(13)
C(10)-C(1)-C(2)	114.18(14)
C(11)-C(1)-C(6)	111.71(14)
C(10)-C(1)-C(6)	111.9(2)
C(2)-C(1)-C(6)	107.55(13)
N(2)-C(2)-C(3)	122.5(2)
N(2)-C(2)-C(1)	116.36(14)
C(3)-C(2)-C(1)	120.97(14)
C(2)-C(3)-C(4)	119.8(2)
C(2)-C(3)-C(12)	121.2(2)
C(4)-C(3)-C(12)	118.9(2)
O(4)-C(4)-C(3)	122.4(2)
O(4)-C(4)-C(5)	117.4(2)
C(3)-C(4)-C(5)	120.2(2)
C(4)-C(5)-C(6)	114.1(2)
C(5)-C(6)-C(13)	109.9(2)
C(5)-C(6)-C(1)	108.08(14)
C(13)-C(6)-C(1)	109.9(2)
C(5)-C(6)-C(7)	110.66(14)
C(13)-C(6)-C(7)	107.9(2)
C(1)-C(6)-C(7)	110.33(14)
C(14)-C(7)-C(15)	104.9(2)
C(14)-C(7)-C(8)	110.3(2)
C(15)-C(7)-C(8)	108.8(2)
C(14)-C(7)-C(6)	108.9(2)
C(15)-C(7)-C(6)	112.3(2)
C(8)-C(7)-C(6)	111.5(2)
C(9)-C(8)-C(7)	111.1(2)

C(8)-C(9)-C(10)	112.1(2)
C(9)-C(10)-C(1)	111.5(2)
N(11)-C(11)-C(1)	176.7(2)
N(14)-C(14)-C(7)	179.1(3)
N(15)-C(15)-C(7)	177.1(2)

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3a**. 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
O(4)	58(1)	36(1)	40(1)	0(1)	-7(1)	19(1)
N(2)	69(1)	38(1)	34(1)	6(1)	13(1)	22(1)
N(11)	68(1)	87(2)	62(1)	7(1)	-6(1)	-30(1)
N(14)	150(3)	98(2)	67(1)	-40(1)	-9(2)	-2(2)
N(15)	51(1)	124(2)	51(1)	14(1)	14(1)	13(1)
C(1)	37(1)	32(1)	28(1)	4(1)	2(1)	9(1)
C(2)	37(1)	34(1)	30(1)	2(1)	4(1)	8(1)
C(3)	41(1)	35(1)	30(1)	5(1)	4(1)	10(1)
C(4)	35(1)	29(1)	35(1)	1(1)	-4(1)	5(1)
C(5)	45(1)	38(1)	34(1)	-3(1)	-2(1)	15(1)
C(6)	34(1)	39(1)	27(1)	-1(1)	-3(1)	7(1)
C(7)	43(1)	56(1)	28(1)	-2(1)	-2(1)	11(1)
C(8)	49(1)	75(2)	29(1)	9(1)	-2(1)	17(1)
C(9)	69(2)	58(1)	37(1)	18(1)	7(1)	22(1)
C(10)	64(1)	43(1)	37(1)	10(1)	7(1)	24(1)
C(11)	55(1)	43(1)	33(1)	3(1)	0(1)	-6(1)
C(12)	68(2)	59(1)	40(1)	18(1)	17(1)	25(1)
C(13)	41(1)	60(1)	47(1)	2(1)	-9(1)	-3(1)
C(14)	75(2)	74(2)	37(1)	-13(1)	-6(1)	11(1)
C(15)	49(1)	75(1)	29(1)	6(1)	4(1)	17(1)

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

	x	y	z	U(eq)
H(2A)	9378(36)	455(22)	5527(8)	60(7)
H(2B)	9350(39)	1114(20)	5127(9)	64(7)
H(5A)	4978(36)	3052(16)	6208(7)	43(5)
H(5B)	6633(36)	3984(21)	6256(8)	62(7)
H(8A)	9698(42)	1638(20)	7039(8)	64(7)
H(8B)	7919(32)	1265(17)	7322(7)	46(6)
H(9A)	6872(46)	186(24)	6772(9)	66(7)
H(9B)	8966(42)	-95(24)	6876(9)	67(7)
H(10A)	8515(34)	-18(22)	6122(8)	57(6)
H(10B)	10091(39)	860(18)	6267(7)	47(6)
H(12A)	7774(38)	3624(22)	4908(9)	64(7)
H(12B)	7361(45)	2405(24)	4755(9)	77(9)
H(12C)	9362(46)	2789(23)	4933(10)	73(8)
H(13A)	10648(50)	2434(27)	6454(11)	87(10)
H(13B)	9785(49)	3554(30)	6503(11)	97(10)
H(13C)	9995(50)	3067(24)	6062(10)	82(9)

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	789(1)	8429(1)	5729(1)	49(1)
O(2)	29(1)	9484(1)	6512(1)	43(1)
N(1)	-2290(2)	7136(1)	6222(1)	53(1)
N(2)	-6126(2)	7394(1)	8038(1)	47(1)
N(3)	-6916(2)	9566(1)	9040(1)	56(1)
C(1)	-1580(1)	8406(1)	7258(1)	29(1)
C(2)	-195(2)	8764(1)	6395(1)	35(1)
C(3)	-1146(2)	9903(1)	7248(1)	38(1)
C(4)	-2662(2)	9638(1)	7655(1)	34(1)
C(5)	-3309(1)	8882(1)	7363(1)	28(1)
C(6)	-528(2)	8286(1)	8616(1)	36(1)
C(7)	-1724(2)	8004(1)	9671(1)	39(1)
C(8)	-3262(2)	8520(1)	9867(1)	37(1)
C(9)	-4423(2)	8612(1)	8568(1)	30(1)
C(10)	-426(3)	10647(1)	7428(2)	55(1)
C(11)	-1999(2)	7694(1)	6662(1)	35(1)
C(12)	-5375(2)	7921(1)	8246(1)	33(1)
C(13)	-5860(2)	9149(1)	8811(1)	38(1)
C(14)	-4565(2)	8865(1)	6090(1)	38(1)
C(15)	-3736(2)	9088(1)	4810(1)	53(1)

Table 7. Bond lengths [Å] and angles [deg] for **4a.**

O(1)-C(2)	1.1920(14)
O(2)-C(2)	1.345(2)
O(2)-C(3)	1.406(2)
N(1)-C(11)	1.140(2)
N(2)-C(12)	1.136(2)
N(3)-C(13)	1.132(2)
C(1)-C(11)	1.472(2)
C(1)-C(2)	1.532(2)
C(1)-C(6)	1.557(2)
C(1)-C(5)	1.565(2)
C(3)-C(4)	1.313(2)
C(3)-C(10)	1.484(2)
C(4)-C(5)	1.503(2)
C(5)-C(14)	1.547(2)
C(5)-C(9)	1.587(2)
C(6)-C(7)	1.514(2)
C(7)-C(8)	1.509(2)
C(8)-C(9)	1.540(2)
C(9)-C(13)	1.486(2)
C(9)-C(12)	1.488(2)
C(14)-C(15)	1.517(2)

C(2)-O(2)-C(3)	120.87(9)
C(11)-C(1)-C(2)	106.74(9)
C(11)-C(1)-C(6)	108.53(10)
C(2)-C(1)-C(6)	103.90(9)
C(11)-C(1)-C(5)	111.91(9)
C(2)-C(1)-C(5)	111.93(9)
C(6)-C(1)-C(5)	113.32(9)
O(1)-C(2)-O(2)	119.08(11)
O(1)-C(2)-C(1)	123.08(11)
O(2)-C(2)-C(1)	117.47(10)
C(4)-C(3)-O(2)	121.77(11)
C(4)-C(3)-C(10)	128.01(13)
O(2)-C(3)-C(10)	110.20(11)
C(3)-C(4)-C(5)	123.73(11)
C(4)-C(5)-C(14)	110.78(9)
C(4)-C(5)-C(1)	106.32(9)
C(14)-C(5)-C(1)	113.18(10)
C(4)-C(5)-C(9)	108.42(9)
C(14)-C(5)-C(9)	108.27(9)
C(1)-C(5)-C(9)	109.78(9)
C(7)-C(6)-C(1)	112.44(9)
C(8)-C(7)-C(6)	110.57(10)
C(7)-C(8)-C(9)	110.63(10)
C(13)-C(9)-C(12)	105.76(9)
C(13)-C(9)-C(8)	107.99(10)
C(12)-C(9)-C(8)	109.20(10)
C(13)-C(9)-C(5)	108.96(10)
C(12)-C(9)-C(5)	111.28(9)
C(8)-C(9)-C(5)	113.31(9)

N(1)-C(11)-C(1)	178.31(14)
N(2)-C(12)-C(9)	177.77(12)
N(3)-C(13)-C(9)	177.24(14)
C(15)-C(14)-C(5)	116.55(11)

Table 8. Anisotropic displacement parameters (A^2 x 10^3) for **4a.** 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
O(1)	43(1)	52(1)	53(1)	-4(1)	20(1)	3(1)
O(2)	42(1)	38(1)	50(1)	1(1)	16(1)	-8(1)
N(1)	53(1)	41(1)	68(1)	-13(1)	18(1)	-4(1)
N(2)	47(1)	43(1)	51(1)	-4(1)	9(1)	-10(1)
N(3)	41(1)	52(1)	77(1)	-15(1)	10(1)	7(1)
C(1)	26(1)	29(1)	33(1)	1(1)	4(1)	-1(1)
C(2)	32(1)	38(1)	35(1)	0(1)	4(1)	-1(1)
C(3)	45(1)	31(1)	38(1)	1(1)	5(1)	-3(1)
C(4)	36(1)	29(1)	38(1)	-1(1)	6(1)	1(1)
C(5)	26(1)	27(1)	32(1)	0(1)	2(1)	1(1)
C(6)	28(1)	41(1)	39(1)	5(1)	-1(1)	2(1)
C(7)	35(1)	46(1)	36(1)	11(1)	-2(1)	-1(1)
C(8)	35(1)	46(1)	31(1)	-1(1)	5(1)	-6(1)
C(9)	26(1)	30(1)	35(1)	-3(1)	4(1)	-1(1)
C(10)	63(1)	36(1)	68(1)	0(1)	12(1)	-14(1)
C(11)	30(1)	34(1)	42(1)	-2(1)	10(1)	1(1)
C(12)	28(1)	36(1)	35(1)	-1(1)	7(1)	0(1)
C(13)	31(1)	38(1)	46(1)	-8(1)	7(1)	-3(1)
C(14)	36(1)	41(1)	38(1)	2(1)	-5(1)	3(1)
C(15)	56(1)	66(1)	36(1)	7(1)	-4(1)	6(1)

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

	x	y	z	U(eq)
H(4)	-3375	9936	8153	41
H(6A)	441	7944	8499	43
H(6B)	8	8741	8912	43
H(7A)	-2199	7534	9408	47
H(7B)	-1018	7947	10501	47
H(8A)	-2787	8986	10154	45
H(8B)	-4003	8335	10555	45
H(10D)	1022(58)	10660(19)	7478(54)	53(13)
H(10E)	-871(63)	10878(18)	8257(48)	41(13)
H(10F)	-902(105)	10963(27)	6671(54)	87(18)
H(10A)	-1483(66)	10944(18)	7829(47)	43(12)
H(10B)	-116(54)	10860(16)	6564(31)	26(12)
H(10C)	742(52)	10607(17)	8024(51)	45(13)
H(14A)	-5031	8377	5978	46
H(14B)	-5584	9180	6226	46
H(15A)	-4630	9057	4089	80
H(15B)	-2750	8771	4640	80
H(15C)	-3304	9576	4889	80

Table 10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **5b.** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(4)	8603(3)	-2102(7)	11566(2)	131(2)
O(5)	8125(3)	-4682(6)	11258(3)	146(2)
N(16)	8445(5)	1815(7)	8454(4)	157(2)
N(17)	6728(5)	-2285(7)	7498(3)	146(2)
N(18)	6821(4)	-5278(6)	9148(4)	124(2)
C(1)	8007(3)	-1420(5)	9721(3)	74(1)
C(2)	8429(4)	-137(6)	10442(4)	97(2)
C(3)	8683(4)	-502(9)	11264(5)	117(2)
C(5)	8087(4)	-3292(9)	11011(4)	105(2)
C(6)	7406(3)	-2664(5)	10128(3)	72(1)
C(7)	6467(4)	-1968(5)	10358(3)	79(1)
C(8)	5564(3)	-1792(5)	9590(2)	62(1)
C(9)	4744(4)	-2768(5)	9520(3)	78(1)
C(10)	3916(4)	-2646(5)	8803(4)	84(1)
C(11)	3905(4)	-1521(7)	8156(3)	95(2)
C(12)	4728(4)	-526(6)	8229(4)	95(2)
C(13)	5551(3)	-640(5)	8942(3)	68(1)
C(14)	6425(4)	482(5)	9012(3)	86(1)
C(15)	7347(3)	-451(5)	8900(3)	74(1)
C(16)	7991(4)	836(7)	8645(4)	108(2)
C(17)	7009(4)	-1513(6)	8116(3)	93(2)
C(18)	7090(4)	-4135(6)	9567(3)	87(2)
C(19)	8857(5)	-2279(8)	9457(5)	127(2)
C(21)	9128(6)	699(11)	12006(5)	182(4)
C(20A)	9643(7)	-3243(13)	10111(10)	213(8)
C(20B)	9576(38)	-1946(61)	8909(39)	213(8)
C(20C)	8970(38)	-3417(53)	8714(25)	213(8)

Table 11. Bond lengths [Å] and angles [deg] for **5b.**

O(4)-C(5)	1.363(7)
O(4)-C(3)	1.391(7)
O(5)-C(5)	1.183(6)
N(16)-C(16)	1.108(6)
N(17)-C(17)	1.131(6)
N(18)-C(18)	1.135(6)
C(1)-C(2)	1.529(6)
C(1)-C(19)	1.535(7)
C(1)-C(6)	1.559(6)
C(1)-C(15)	1.575(6)
C(2)-C(3)	1.279(8)
C(2)-H(2)	0.930(5)
C(3)-C(21)	1.513(8)
C(5)-C(6)	1.539(7)
C(6)-C(18)	1.472(7)
C(6)-C(7)	1.566(6)
C(7)-C(8)	1.497(6)
C(7)-H(7A)	0.970(4)
C(7)-H(7B)	0.970(4)
C(8)-C(9)	1.373(6)
C(8)-C(13)	1.378(5)
C(9)-C(10)	1.381(6)
C(9)-H(9)	0.930(4)
C(10)-C(11)	1.361(7)
C(10)-H(10)	0.930(4)
C(11)-C(12)	1.384(7)
C(11)-H(11)	0.930(5)
C(12)-C(13)	1.373(6)
C(12)-H(12)	0.930(5)
C(13)-C(14)	1.504(6)
C(14)-C(15)	1.549(6)
C(14)-H(14A)	0.970(5)
C(14)-H(14B)	0.970(4)
C(15)-C(17)	1.469(7)
C(15)-C(16)	1.503(7)
C(19)-C(20A)	1.501(9)
C(19)-C(20B)	1.526(11)
C(19)-C(20C)	1.530(11)
C(19)-H(19A)	0.970(6)
C(19)-H(19B)	0.970(6)
C(21)-H(21A)	0.960(9)
C(21)-H(21B)	0.960(9)
C(21)-H(21C)	0.960(8)
C(20A)-H(20A)	0.960(13)
C(20A)-H(20B)	0.960(11)
C(20A)-H(20C)	0.96(2)
C(20B)-H(20D)	0.96(4)
C(20B)-H(20E)	0.96(6)
C(20B)-H(20F)	0.96(6)
C(20C)-H(20G)	0.96(5)

C(20C)-H(20H)	0.96(5)
C(20C)-H(20I)	0.96(5)

C(5)-O(4)-C(3)	120.7(5)
C(2)-C(1)-C(19)	109.7(4)
C(2)-C(1)-C(6)	105.7(3)
C(19)-C(1)-C(6)	111.9(4)
C(2)-C(1)-C(15)	107.1(4)
C(19)-C(1)-C(15)	108.9(4)
C(6)-C(1)-C(15)	113.3(3)
C(3)-C(2)-C(1)	122.7(5)
C(3)-C(2)-H(2)	118.7(6)
C(1)-C(2)-H(2)	118.7(6)
C(2)-C(3)-O(4)	122.3(5)
C(2)-C(3)-C(21)	125.2(7)
O(4)-C(3)-C(21)	112.5(7)
O(5)-C(5)-O(4)	119.1(5)
O(5)-C(5)-C(6)	124.7(5)
O(4)-C(5)-C(6)	115.8(5)
C(18)-C(6)-C(5)	106.7(4)
C(18)-C(6)-C(1)	112.2(3)
C(5)-C(6)-C(1)	108.2(4)
C(18)-C(6)-C(7)	107.2(4)
C(5)-C(6)-C(7)	105.0(4)
C(1)-C(6)-C(7)	116.9(3)
C(8)-C(7)-C(6)	115.1(3)
C(8)-C(7)-H(7A)	108.5(4)
C(6)-C(7)-H(7A)	108.5(4)
C(8)-C(7)-H(7B)	108.5(4)
C(6)-C(7)-H(7B)	108.5(4)
H(7A)-C(7)-H(7B)	107.5(4)
C(9)-C(8)-C(13)	119.2(4)
C(9)-C(8)-C(7)	120.9(4)
C(13)-C(8)-C(7)	119.9(4)
C(8)-C(9)-C(10)	121.4(4)
C(8)-C(9)-H(9)	119.3(5)
C(10)-C(9)-H(9)	119.3(5)
C(11)-C(10)-C(9)	119.5(4)
C(11)-C(10)-H(10)	120.3(6)
C(9)-C(10)-H(10)	120.3(5)
C(10)-C(11)-C(12)	119.2(5)
C(10)-C(11)-H(11)	120.4(6)
C(12)-C(11)-H(11)	120.4(6)
C(13)-C(12)-C(11)	121.5(4)
C(13)-C(12)-H(12)	119.3(6)
C(11)-C(12)-H(12)	119.3(6)
C(12)-C(13)-C(8)	119.1(4)
C(12)-C(13)-C(14)	120.3(4)
C(8)-C(13)-C(14)	120.6(4)
C(13)-C(14)-C(15)	113.0(3)
C(13)-C(14)-H(14A)	109.0(4)
C(15)-C(14)-H(14A)	109.0(4)
C(13)-C(14)-H(14B)	109.0(4)
C(15)-C(14)-H(14B)	109.0(4)

H(14A)-C(14)-H(14B)	107.8(4)
C(17)-C(15)-C(16)	104.7(4)
C(17)-C(15)-C(14)	107.1(4)
C(16)-C(15)-C(14)	106.3(4)
C(17)-C(15)-C(1)	112.4(4)
C(16)-C(15)-C(1)	107.6(4)
C(14)-C(15)-C(1)	117.7(3)
N(16)-C(16)-C(15)	178.1(7)
N(17)-C(17)-C(15)	177.5(6)
N(18)-C(18)-C(6)	177.7(5)
C(20A)-C(19)-C(1)	121.7(7)
C(20B)-C(19)-C(1)	140(2)
C(20C)-C(19)-C(1)	137(2)
C(20A)-C(19)-H(19A)	106.9(8)
C(1)-C(19)-H(19A)	106.9(5)
C(20A)-C(19)-H(19B)	106.9(7)
C(1)-C(19)-H(19B)	106.9(5)
H(19A)-C(19)-H(19B)	106.7(7)
C(3)-C(21)-H(21A)	109.5(8)
C(3)-C(21)-H(21B)	109.5(6)
H(21A)-C(21)-H(21B)	109.5(8)
C(3)-C(21)-H(21C)	109.5(7)
H(21A)-C(21)-H(21C)	109.5(7)
H(21B)-C(21)-H(21C)	109.5(9)
C(19)-C(20A)-H(20A)	109.5(12)
C(19)-C(20A)-H(20B)	109.5(9)
H(20A)-C(20A)-H(20B)	109.5(11)
C(19)-C(20A)-H(20C)	109.5(9)
H(20A)-C(20A)-H(20C)	109.5(10)
H(20B)-C(20A)-H(20C)	110(2)
C(19)-C(20B)-H(20D)	110(3)
C(19)-C(20B)-H(20E)	110(4)
H(20D)-C(20B)-H(20E)	110(5)
C(19)-C(20B)-H(20F)	110(4)
H(20D)-C(20B)-H(20F)	110(5)
H(20E)-C(20B)-H(20F)	110(4)
C(19)-C(20C)-H(20G)	110(3)
C(19)-C(20C)-H(20H)	110(3)
H(20G)-C(20C)-H(20H)	110(4)
C(19)-C(20C)-H(20I)	110(3)
H(20G)-C(20C)-H(20I)	110(4)
H(20H)-C(20C)-H(20I)	110(4)

Table 12. Anisotropic displacement parameters ($Å^2$ x 10^3) for **5b.** 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
O(4)	125(3)	162(4)	87(3)	3(3)	-1(2)	-43(3)
O(5)	142(4)	120(3)	156(4)	52(3)	10(3)	-23(3)
N(16)	182(5)	107(4)	219(6)	22(4)	116(5)	-43(4)
N(17)	226(6)	156(5)	81(3)	-31(3)	83(4)	-64(4)
N(18)	192(5)	61(3)	133(4)	-14(3)	67(4)	-28(3)
C(1)	88(3)	60(3)	82(3)	-17(2)	38(3)	-16(2)
C(2)	95(4)	88(4)	108(4)	-13(3)	31(3)	-22(3)
C(3)	118(5)	128(5)	107(5)	-24(4)	33(4)	-34(4)
C(5)	97(4)	120(5)	89(4)	5(4)	14(3)	-20(4)
C(6)	94(3)	63(3)	62(3)	-5(2)	25(2)	-8(2)
C(7)	106(4)	87(3)	55(3)	-8(2)	40(3)	-22(3)
C(8)	83(3)	55(2)	51(2)	-7(2)	27(2)	-11(2)
C(9)	97(4)	64(3)	77(3)	4(2)	32(3)	-13(3)
C(10)	88(3)	64(3)	101(4)	-8(3)	31(3)	-16(2)
C(11)	96(4)	87(3)	95(4)	0(3)	13(3)	-1(3)
C(12)	109(4)	79(3)	100(4)	31(3)	36(3)	10(3)
C(13)	90(3)	49(2)	69(3)	0(2)	31(3)	-5(2)
C(14)	107(4)	58(3)	100(3)	5(2)	43(3)	-12(3)
C(15)	104(3)	55(2)	80(3)	-12(2)	53(3)	-23(2)
C(16)	130(4)	78(4)	139(5)	0(3)	74(4)	-27(3)
C(17)	134(4)	93(4)	74(3)	-6(3)	65(3)	-30(3)
C(18)	120(4)	52(3)	98(4)	3(3)	45(3)	-10(3)
C(19)	131(5)	99(4)	177(6)	-28(4)	82(5)	3(4)
C(21)	164(6)	219(8)	141(6)	-101(6)	6(5)	-57(6)
C(20A)	131(9)	113(8)	422(22)	54(11)	119(12)	27(7)
C(20B)	131(9)	113(8)	422(22)	54(11)	119(12)	27(7)
C(20C)	131(9)	113(8)	422(22)	54(11)	119(12)	27(7)

Table 13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **5b.**

	x	y	z	U(eq)
H(2)	8504	952	10277	116
H(7A)	6310	-2698	10789	95
H(7B)	6629	-889	10633	95
H(9)	4746	-3527	9964	93
H(10)	3371	-3327	8762	100
H(11)	3352	-1423	7671	114
H(12)	4722	238	7786	114
H(14A)	6597	1023	9583	103
H(14B)	6239	1337	8563	103
H(19A)	8555	-3031	8977	153
H(19B)	9193	-1429	9214	153
H(21A)	9254	132	12562	273
H(21B)	8673	1595	11991	273
H(21C)	9738	1133	11937	273
H(20A)	10107	-3685	9823	320
H(20B)	9342	-4137	10345	320
H(20C)	9984	-2523	10583	320
H(20D)	9998	-2893	8936	320
H(20E)	9973	-992	9140	320
H(20F)	9209	-1743	8307	320
H(20G)	9658	-3674	8803	320
H(20H)	8717	-2866	8157	320
H(20I)	8606	-4424	8717	320