Highly Efficient Synthesis and Solid-State Characterization of 1,2,4,5-Tetrakis(alkyl- and arylamino)benzenes and Cyclization to their Respective Benzobis(imidazolium) Salts

Dimitri M. Khramov, Andrew. J. Boydston, and Christopher W. Bielawski*

*The University of Texas at Austin, Department of Chemistry and Biochemistry,
Austin, TX 78712 USA; email: bielawski@cm.utexas.edu*

SUPPORTING INFORMATION

General Considerations: All reactions were conducted under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glove-box. CHCl_3 was degassed by two freeze-pump-thaw cycles and stored over 4Å molecular sieves and K_2CO_3 . Hexanes were distilled from CaH_2 and degassed by two freeze-pump-thaw cycles. THF and toluene were freshly distilled from Na/benzophenone and degassed by two freeze-pump-thaw cycles. All reagents were purchased from Aldrich or Acros and were used without further purification. ^1H NMR spectra were recorded using a Varian Gemini (300 MHz or 400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protonated solvent as an internal standard (CDCl_3 , 7.24 ppm; C_6D_6 , 7.15 ppm; $\text{DMSO}-d_6$, 2.49 ppm). ^{13}C NMR spectra were recorded using a Varian Gemini (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as an internal standard (CDCl_3 , 77.0 ppm; C_6D_6 , 128 ppm; $\text{DMSO}-d_6$, 39.5 ppm). ^{13}C NMR spectra were routinely run with broadband decoupling. High-resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E or a Karatos MS9 instrument and are reported as m/z (relative intensity).

1,2,4,5-Tetrakis-N-tert-butylaminobenzene (4). A catalyst for mediating aryl-amination coupling reaction was prepared by charging a 20 mL vial with 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.085 g, 0.2 mmol), NaOtBu (0.03 g, 0.3 mmol), $\text{Pd}(\text{OAc})_2$ (0.025 g, 0.1 mmol), toluene (5 mL), and a stir bar followed by stirring this mixture at 80 °C for 10 minutes. The catalyst solution was added to a 250 mL flask containing 1,2,4,5-tetrabromobenzene (2.22 g, 5.64 mmol) suspended in toluene (100 mL). *tert*-Butyl amine (1.73 g, 23.7 mmol) and NaOtBu (2.65 g, 27.6 mmol) were then added and the resulting mixture was sealed and stirred at 110 °C overnight. After cooling to ambient temperature, precipitated solids were collected by filtration under a cone of nitrogen, dissolved in degassed CHCl_3 (100 mL), and filtered to remove residual NaBr salts. Solvent was then removed under reduced pressure to afford 1.96 g (96% yield) of the desired product as a gray solid. Note: the product slowly oxidizes to the corresponding benzoquinonediimine over several days in aerated solutions. As a solid, the product is bench stable for >months. ^1H NMR (CDCl_3): δ 6.53 (s, 2H), 3.73 (br, 4H), 1.22 (s, 36H). ^{13}C NMR (CDCl_3): δ 131.7, 115.5, 52.0, 30.0. HRMS: $[\text{M}]^+$ calcd for $\text{C}_{22}\text{H}_{42}\text{N}_4$: 362.3409; Found, 362.3406.

N,N',N'',N'''-tetra(*tert*-butyl)-2,5-diamino-1,4-benzoquinonediimine (5). Compound **4** (0.1 g, 0.28 mmol) was dissolved in CHCl₃ (3 mL) and stirred under a balloon of oxygen for 24 h followed by removal of solvent to obtain a yellow powder (0.1 g) in quantitative yield. Alternatively, oxidations can be accomplished in less than 5 minutes by adding an excess of H₂O₂. ¹H NMR (CDCl₃): δ 5.53 (s, 2H), 1.35 (s, 36H). ¹³C NMR (CDCl₃): δ 138, 90.8, 52.0, 29.8. HRMS: [M]⁺ calcd for C₂₄H₄₁N₄; 361.3331; Found: 361.3326.

1,2,4,5-Tetrakis-N-adamantylaminobenzene (6). The aryl amination was performed in a manner analogous to the synthesis of **4** using 1,2,4,5-tetrabromobenzene (13.97 g, 35.5 mmol) and adamantyl amine (22.5 g, 149 mol). Upon completion, the cooled reaction mixture was filtered in a drybox to afford a beige solid. The solids were rinsed with toluene and extracted with degassed CHCl₃ and the extract was concentrated under reduced pressure to afford 21.5 g (90% yield) of the desired product as a white powder. Note: the product slowly oxidizes to the corresponding benzoquinone-diimine over several days in aerated solutions. As a solid, the product is bench stable for >months. ¹H NMR (CDCl₃): δ 6.59 (s, 2H), 2.06 (br, 12H), 1.81 (br, 24H), 1.66-1.58 (br, 24H). ¹³C NMR (CDCl₃): δ 131.3, 117.8, 52.5, 43.7, 36.6, 29.8. HRMS: [M]⁺ calcd for C₄₆H₆₆N₄; 674.5287; Found, 674.5286.

N,N',N'',N'''-tetra(adamantyl)-2,5-diamino-1,4-benzoquinone-diimine. Compound **4** (0.1 g, 0.15 mmol) was dissolved in CH₂Cl₂ (3 mL) and stirred under a balloon of oxygen for 24 h followed by removal of solvent to obtain a yellow powder (0.1 g) in quantitative yield. ¹H NMR (CDCl₃): δ 6.69 (br, 2H), 5.77 (s, 2H), 2.10 (br, 12H), 1.97 (br, 24H), 1.68 (br, 24H). ¹³C NMR (CDCl₃): δ 138, 92.2, 52.7, 42.6, 36.9, 29.8. HRMS: [M+H]⁺ calcd for C₄₆H₆₄N₄; 673.5209; Found, 673.5209.

1,2,4,5-Tetrakis-N-phenylbenzene (7). The aryl amination was performed in a manner analogous to the synthesis of **4** using 1,2,4,5-tetrabromobenzene (2.39 g, 5.84 mol) and aniline (2.8 g, 30 mol). Upon completion, the cooled reaction mixture was filtered in a drybox to afford a beige solid. The solids were rinsed with excess hexanes and extracted with degassed CHCl₃. The extract was then concentrated under reduced pressure to afford 1.78 g (76 %) of the desired product as a light pink powder. ¹H NMR (CDCl₃): δ 7.24-7.19 (br m, 12H), 6.9-6.84 (br, 12H), 5.56 (s, 2H). ¹³C NMR (CDCl₃): δ 144.5, 130.6, 129.3, 120.2, 116.6, 113.9. HRMS: [M]⁺ calcd for C₃₀H₂₅N₄; 441.2074; Found: 441.2074.

1,2,4,5-Tetrakis(2,4,6-trimethylphenylamino)benzene (8). The aryl amination was performed in a manner analogous to the synthesis of **4** using 1,2,4,5-tetrabromobenzene (2.00 g, 5.1 mmol) and mesityl amine (7 mL, 51 mmol). Upon completion, the cooled reaction mixture was filtered in a drybox to afford a beige solid. The solids were rinsed with toluene and extracted with degassed CHCl₃. The extract was then concentrated under reduced pressure to afford 2.71 g (94%) of the desired product as a white powder. ¹H NMR (CDCl₃): δ 6.75 (s, 8H), 5.40 (s, 2H), 4.86 (br s, 4H), 2.22 (s, 12H), 2.05 (s, 24 H). ¹³C NMR (CDCl₃): δ 137.9, 132.6,

132.1, 129.4, 129.0, 105.3, 20.6, 18.2. HRMS: $[M]^+$ calcd for $C_{42}H_{49}N_4$, 609.3978; Found: 609.3952.

Mesityl-derived azophenine (9). The tetraamine **8** (0.1 g, 0.164 mmol) was stirred in aerated $CHCl_3$ (3 mL) for 2 h. The mixture was concentrated to give an orange-red solid (0.1 g) in quantitative yield. 1H NMR ($CDCl_3$): δ 6.79 (s, 4H), 6.75 (s, 4H), 5.40 (s, 2H), 4.61 (s, 2H), 2.23 (s, 12H), 2.07 (s, 12H), 2.05 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 137.9, 132.6, 132.1, 129.4, 129.0, 128.6, 88.9, 20.8, 20.6, 18.2, 18.0. HRMS: $[M]^+$ calcd for $C_{42}H_{49}N_4$, 609.3956; Found: 609.3952.

1,2,4,5-Tetrakis(2-methoxyphenylamino)benzene (10). The aryl amination was performed in a manner analogous to the synthesis of **4** using 1,2,4,5-tetrabromobenzene (4.00 g, 10.2 mmol) and *o*-anisidine (11.5 mL, 100.6 mmol). Upon completion, the cooled reaction mixture was filtered in a drybox to afford a beige solid. The solids were rinsed with toluene and extracted with degassed $CHCl_3$ and the extract was concentrated under reduced pressure to afford 6.92 g (96%) of the desired product as an off-white powder. Alternatively, the cooled reaction mixture was opened under a cone of nitrogen and HCl (2 mL) in MeOH (10 mL) was added quickly to produce a deep purple slurry. The mixture was poured into H_2O (25 mL) and the solids were collected via vacuum filtration, rinsed with H_2O and Et_2O , and dried under vacuum to provide the tetrahydrochloride salt as a light purple solid in nearly quantitative yield. 1H NMR of free base ($CDCl_3$): δ 7.33 (s, 2H), 7.06-7.04 (m, 4H), 6.86-6.76 (m, 12H), 6.02 (br s, 4H), 3.82 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 148.2, 134.4, 130.5, 121.0, 119.1, 114.4, 110.3, 114.2, 55.5. HRMS: $[M]^+$ calcd for $C_{34}H_{35}N_4O_4$, 563.2606; Found 563.2653.

1,2,4,5-Tetrakis(*tert*-butylamino)-*para*-xylene (11). The aryl amination was performed in a manner analogous to the synthesis of **4** using 2,3,5,6-tetrabromoxylene (3.0 g, 7.11 mol) and *tert*-butyl amine (2.13 g, 29.2 mmol). Upon completion, the cool reaction mixture was filtered over Celite under a cone of nitrogen with the aid of degassed toluene. The filtrate was concentrated under reduced pressure to afford 2.7g (99%) of the desired product as a brown solid. It should be noted that the product is bench stable in aerated solutions for >months. 1H NMR ($CDCl_3$): δ 3.39 (br, 4H), 2.28 (s, 6H), 1.06 (s, 36H). ^{13}C NMR ($CDCl_3$): δ 138.1, 128.2, 55.3, 30.7, 18.6. HRMS: $[M]^+$ calcd for $C_{24}H_{46}N_4$, 390.3722; Found, 390.3719.

3,3',4,4'-Tetrakis(2,4,6-trimethylphenylamino)biphenyl (13). A catalyst for mediating aryl-amination coupling reactions was prepared by charging a 10 mL vial with 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (86 mg, 0.02 mmol), NaOtBu (3 mg, 0.03 mmol), $Pd(OAc)_2$ (30 mg, 0.01 mmol), toluene (3 mL), and a stir bar followed by stirring this mixture at 23 °C for 10 minutes. 2-Bromomesitylene (410 mg, 2.05 mmol) was added to the catalyst solution. 3,3'-diaminobenzidine (110 mg, 0.5 mmol) and NaOtBu (0.20 g, 2.05 mmol) were then added and the resulting mixture was sealed and stirred at 110 °C overnight. After cooling to ambient temperature, precipitated solids (NaBr) were removed by filtration under a cone of nitrogen. Solvent was removed under reduced pressure. Analysis of the crude product indicated that the

reaction was >98% complete. The crude product was triturated with hexanes and then dried under reduced pressure to afford 160 mg (47 % yield) of the desired product as a grey solid. ^1H NMR (CDCl_3): δ 6.94 (s, 8H), 6.68-6.66 (m, 2H), 6.27-6.24 (m, 4H), 5.18 (br, 2H), 4.99 (br, 2H), 2.36 (br, 6H), 2.31 (s, 6H), 2.17 (s, 12H), 2.13 (s, 12H). ^{13}C NMR (CDCl_3): δ 137.11, 137.06, 136.7, 135.7, 135.6, 134.0, 133.9, 133.54, 133.48, 133.3, 133.2, 133.1, 129.30, 129.26, 117.8, 114.7, 112.4, 20.9, 20.8, 18.1, 18.0. HRMS: $[\text{M}]^+$ calcd for $\text{C}_{48}\text{H}_{55}\text{N}_4$, 687.4427; Found: 687.4423.

Tetrakis(*tert*-butyl) benzobis(imidazolium) tetrafluoroborate (14). A 10 mL flask was charged with triethylorthoformate (5 mL), compound **4** (590 mg, 1.63 mmol), and HBF_4 (1 mL, 48% aq.). The reaction mixture was heated to 65 °C for 24 h. Upon completion, the product was collected by filtration, washed with hot acetonitrile (3 x 15 mL) to obtain 700 mg (77%) of the desired product as a light yellow powder. ^1H NMR ($\text{DMSO-}d_6$): δ 9.06 (s, 2H), 8.62 (s, 2H), 1.91 (s, 36H). ^{13}C NMR ($\text{DMSO-}d_6$): δ 142.9, 128.9, 102.7, 62.0, 28.0, 9.1.

Tetraadamantyl benzobis(imidazolium) tetrafluoroborate (15). In a manner analogous to **14** using tetraamine **6** (3.3 g, 4.89 mmol), the product was obtained in 70% yield as a light yellow powder. ^1H NMR (C_6D_6): δ 9.13 (s, 2H), 8.54 (s, 2H), 2.39 (s, 12H), 1.88-1.76 (br, 24H). ^{13}C NMR (C_6D_6): δ 142.9, 127.9, 103.3, 62.7, 40.4, 35.4, 29.1.

Tetraphenyl benzobis(imidazolium) tetrafluoroborate (16).

In a manner analogous to **14** using tetraamine **7** (0.3 g, 0.68 mmol), with a reaction temperature of 140 °C and time of 24 h 162 mg (51%) of the desired product was obtained as a light yellow powder (purification required rinsing with copious amounts of MeOH). ^1H NMR ($\text{DMSO-}d_6$) δ 10.8 (s, 2H), 8.15(s, 2H) 7.9-7.8 (br, 20H). ^{13}C NMR ($\text{DMSO-}d_6$) δ 147.3, 132.9, 131.0, 130.6, 125.6, 99.2. HRMS: $[\text{M}]^{2+}$ calcd for $\text{C}_{32}\text{H}_{24}\text{N}_4$, 232.1000; Found: 232.1002. Alternatively, a one-pot, two-step synthesis of **16** may be accomplished in 84% overall yield by eliminating the workup of the tetrakis(phenylamino)benzene. Aryl amination reaction of 1,2,4,5-tetrabromobenzene (6 g, 15.2 mmol) was carried out as described above. After cooling the reaction vessel, the reaction mixture was acidified with HBF_4 (5 mL, 48% aq.) and $\text{HC}(\text{OEt})_3$ (200 mL) was added. The vessel was then heated to 140 °C for 16 h, then cooled to 23 °C. Additional HBF_4 (3 mL) was added and the solution was re-heated to 140 °C for 6 h. After cooling to room temperature, the resulting precipitate was collected by filtration and then washed with water (3 x 50 mL), methanol (1 x 50 mL), and ether (2 x 30 mL) to obtain 8.2 g (84% yield) of analytically pure product as a brown solid.

Tetrakis(2-methoxyphenyl) benzobis(imidazolium) chloride (17). The tetrahydrochloride of tetraamine **10** (5.0 g, 7.06 mmol) was dissolved in $\text{HC}(\text{OEt})_3$ (60 mL) and conc. HCl (0.2 mL). The deep purple solution was stirred at 120 °C for 2 h during which time the homogenous reaction mixture became a light red slurry. The reaction mixture was allowed to cool and Et_2O (30 mL) was added to facilitate precipitation of the product. The

solids were collected, rinsed with Et₂O and recrystallized from hot MeOH/Et₂O to give 4.26 g (92%) of the bis(azolium) as a pink-brown solid. ¹H NMR (DMSO-*d*₆): δ 10.79 (s, 2H), 8.00 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.98 (s, 2H), 7.73 (t, *J* = 8.0 Hz, 4H), 7.48 (d, *J* = 6.8 Hz, 4H), 7.28 (t, *J* = 7.2 Hz, 4H), 3.87 (s, 12H). ¹³C NMR (DMSO-*d*₆): δ 153.7, 148.5, 133.0, 130.8, 128.4, 121.3, 120.6, 113.7, 100.4, 56.4. HRMS: [M]⁺ calcd for C₃₆H₃₂N₄O₄, 584.2462; Found: 584.2418.

X-ray Crystallographic Data for **4**:

Figure 1. View of **1** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The macrocycle lies on a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Atoms with labels appended by a ' are related by 1-x, 1-y, 1-z.

X-ray Experimental for **4** ($C_{22}H_{42}N_4$): Crystals grew as large, colorless needles by slow evaporation from toluene. The data crystal was cut from a larger crystal and had approximate dimensions; 0.34 x 0.28 x 0.24 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 417 frames of data were collected using ω -scans with a scan range of 1° and a counting time of 101 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The methyl group hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.5Ueq

of the attached atom. The hydrogen atoms on nitrogen and the ring carbon atoms were observed in a ΔF map and refined with isotropic displacement parameters. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0591*P)^2 + (0.1657*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.129, with $R(F)$ equal to 0.0462 and a goodness of fit, S , = 1.02. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (3.7(13) \times 10^{-5}) * F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

References

- 1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
- 2) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. J. Appl. Cryst. 32, 115-119.
- 3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for **4**.

Empirical formula	C ₂₂ H ₄₂ N ₄	
Formula weight	362.60	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.9656(2) Å	α = 71.1320(10)°.
	b = 8.8102(2) Å	β = 78.6270(10)°.
	c = 11.4701(4) Å	γ = 86.5320(10)°.
Volume	559.25(3) Å ³	
Z	1	
Density (calculated)	1.077 Mg/m ³	
Absorption coefficient	0.064 mm ⁻¹	
F(000)	202	
Crystal size	0.34 x 0.28 x 0.24 mm	
Theta range for data collection	3.48 to 27.50°.	
Index ranges	-6 ≤ h ≤ 7, -9 ≤ k ≤ 11, -10 ≤ l ≤ 14	
Reflections collected	3890	
Independent reflections	2558 [R(int) = 0.0175]	
Completeness to theta = 27.50°	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2558 / 0 / 131	
Goodness-of-fit on F ²	1.017	
Final R indices [I > 2σ(I)]	R ₁ = 0.0462, wR ₂ = 0.1135	
R indices (all data)	R ₁ = 0.0713, wR ₂ = 0.1291	
Extinction coefficient	3.7(13) × 10 ⁻⁵	
Largest diff. peak and hole	0.249 and -0.184 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
N1	1658(2)	4451(1)	7241(1)	21(1)
N2	6049(2)	5731(1)	7076(1)	20(1)
C1	3351(2)	4723(2)	6122(1)	19(1)
C2	5493(2)	5403(2)	6014(1)	18(1)
C3	7094(2)	5639(2)	4907(1)	19(1)
C4	1117(2)	2759(2)	8062(1)	23(1)
C5	-367(3)	2903(2)	9266(1)	31(1)
C6	-237(2)	1895(2)	7465(1)	29(1)
C7	3293(3)	1822(2)	8354(2)	33(1)
C8	5805(2)	7414(2)	7118(1)	23(1)
C9	6563(3)	7371(2)	8321(1)	31(1)
C10	3318(2)	7928(2)	7168(2)	31(1)
C11	7293(3)	8610(2)	5991(1)	31(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4**.

N1-C1	1.4294(17)	C6-H6B	0.96
N1-C4	1.4980(17)	C6-H6C	0.96
N1-H1N	0.908(18)	C7-H7A	0.96
N2-C2	1.4406(17)	C7-H7B	0.96
N2-C8	1.4967(18)	C7-H7C	0.96
N2-H2N	0.912(17)	C8-C10	1.5201(19)
C1-C3#1	1.3938(19)	C8-C9	1.524(2)
C1-C2	1.4107(18)	C8-C11	1.533(2)
C2-C3	1.3941(19)	C9-H9A	0.96
C3-C1#1	1.3938(19)	C9-H9B	0.96
C3-H3	0.982(16)	C9-H9C	0.96
C4-C5	1.525(2)	C10-H10A	0.96
C4-C6	1.5264(19)	C10-H10B	0.96
C4-C7	1.5299(19)	C10-H10C	0.96
C5-H5A	0.96	C11-H11A	0.96
C5-H5B	0.96	C11-H11B	0.96
C5-H5C	0.96	C11-H11C	0.96
C6-H6A	0.96		
C1-N1-C4	118.63(11)	N1-C4-C5	105.06(11)
C1-N1-H1N	107.7(11)	N1-C4-C6	111.31(11)
C4-N1-H1N	103.7(11)	C5-C4-C6	109.10(12)
C2-N2-C8	118.30(11)	N1-C4-C7	111.31(11)
C2-N2-H2N	106.0(10)	C5-C4-C7	109.97(12)
C8-N2-H2N	106.8(10)	C6-C4-C7	109.97(12)
C3#1-C1-C2	118.06(12)	C4-C5-H5A	109.5
C3#1-C1-N1	120.82(12)	C4-C5-H5B	109.5
C2-C1-N1	121.10(12)	H5A-C5-H5B	109.5
C3-C2-C1	119.06(12)	C4-C5-H5C	109.5
C3-C2-N2	121.18(11)	H5A-C5-H5C	109.5
C1-C2-N2	119.60(12)	H5B-C5-H5C	109.5
C1#1-C3-C2	122.85(12)	C4-C6-H6A	109.2
C1#1-C3-H3	119.2(9)	C4-C6-H6B	109.5
C2-C3-H3	118.0(9)	H6A-C6-H6B	109.5

C4-C6-H6C	109.8
H6A-C6-H6C	109.5
H6B-C6-H6C	109.5
C4-C7-H7A	109.7
C4-C7-H7B	109.6
H7A-C7-H7B	109.5
C4-C7-H7C	109.2
H7A-C7-H7C	109.5
H7B-C7-H7C	109.5
N2-C8-C10	109.84(11)
N2-C8-C9	105.53(11)
C10-C8-C9	109.94(12)
N2-C8-C11	112.64(12)
C10-C8-C11	109.20(12)
C9-C8-C11	109.63(12)
C8-C9-H9A	108.9
C8-C9-H9B	109.3
H9A-C9-H9B	109.5
C8-C9-H9C	110.2
H9A-C9-H9C	109.5
H9B-C9-H9C	109.5
C8-C10-H10A	109.9
C8-C10-H10B	110.2
H10A-C10-H10B	109.5
C8-C10-H10C	108.3
H10A-C10-H10C	109.5
H10B-C10-H10C	109.5
C8-C11-H11A	109.7
C8-C11-H11B	108.9
H11A-C11-H11B	109.5
C8-C11-H11C	109.8
H11A-C11-H11C	109.5
H11B-C11-H11C	109.5

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z+1$

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N1	22(1)	22(1)	19(1)	-7(1)	1(1)	-3(1)
N2	20(1)	23(1)	20(1)	-8(1)	-5(1)	1(1)
C1	18(1)	18(1)	19(1)	-5(1)	-2(1)	1(1)
C2	19(1)	18(1)	18(1)	-5(1)	-5(1)	2(1)
C3	17(1)	19(1)	21(1)	-6(1)	-3(1)	-2(1)
C4	22(1)	22(1)	22(1)	-5(1)	-1(1)	-3(1)
C5	33(1)	32(1)	23(1)	-5(1)	2(1)	-6(1)
C6	27(1)	27(1)	30(1)	-8(1)	-1(1)	-7(1)
C7	29(1)	29(1)	35(1)	-3(1)	-6(1)	0(1)
C8	22(1)	24(1)	23(1)	-10(1)	-4(1)	-2(1)
C9	34(1)	37(1)	29(1)	-17(1)	-7(1)	-3(1)
C10	27(1)	28(1)	42(1)	-18(1)	-7(1)	3(1)
C11	36(1)	26(1)	29(1)	-8(1)	-3(1)	-6(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**.

	x	y	z	U(eq)
H5A	480	3440	9649	47
H5B	-1714	3509	9073	47
H5C	-800	1852	9835	47
H6A	-1599	2491	7290	43
H6B	678	1819	6698	43
H6C	-645	837	8030	43
H7A	4137	2367	8731	49
H7B	2893	764	8921	49
H7C	4216	1745	7589	49
H9A	5619	6620	9020	47
H9B	8129	7036	8284	47
H9C	6414	8415	8422	47
H10A	2371	7192	7876	46
H10B	3139	8989	7235	46
H10C	2874	7923	6409	46
H11A	8871	8306	5962	46
H11B	6834	8602	5236	46
H11C	7099	9668	6062	46
H2N	7550(30)	5463(19)	7076(15)	28(4)
H1N	2170(30)	4900(20)	7747(16)	32(4)
H3	8600(30)	6080(19)	4858(14)	28(4)

Table 6. Torsion angles [°] for **4**.

C4-N1-C1-C3#1	71.81(16)
C4-N1-C1-C2	-109.84(14)
C3#1-C1-C2-C3	-1.9(2)
N1-C1-C2-C3	179.72(11)
C3#1-C1-C2-N2	-177.41(11)
N1-C1-C2-N2	4.20(19)
C8-N2-C2-C3	84.72(16)
C8-N2-C2-C1	-99.85(15)
C1-C2-C3-C1#1	2.0(2)
N2-C2-C3-C1#1	177.43(12)
C1-N1-C4-C5	169.45(12)
C1-N1-C4-C6	-72.60(15)
C1-N1-C4-C7	50.47(16)
C2-N2-C8-C10	62.78(15)
C2-N2-C8-C9	-178.76(11)
C2-N2-C8-C11	-59.18(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

X-ray Crystallographic Data for **5**:

Figure 2. View of **5** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The molecule lies around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Atoms with labels appended by a ' are related by 1-x, 1-y, 1-z.

X-ray Experimental for **5** ($C_{22}H_{40}N_4$): Crystals grew as large orange prisms by slow evaporation from chloroform. The data crystal was cut from a much larger crystal and had approximate dimensions; 0.28 x 0.25 x 0.18 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 259 frames of data were collected using ω -scans with a scan range of 2° and a counting time of 104 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atoms on carbon were observed in a ΔF map and refined with isotropic displacement parameters. The molecule resides around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0433 \cdot P)^2 + (0.2874 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.0957, with $R(F)$ equal to 0.0370 and a goodness of fit, S , = 1.01. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data were checked for secondary extinction effects but no correction was necessary. Neutral

atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

References

- 6) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
- 7) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. J. Appl. Cryst. 32, 115-119.
- 8) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 9) $R_w(F^2) = \{ \Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(|F_o|)^4 \}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 10) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for **5**.

Empirical formula	C22 H40 N4	
Formula weight	360.58	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 10.6527(2) Å	$\alpha = 90^\circ$.
	b = 10.3083(2) Å	$\beta = 114.116(1)^\circ$.
	c = 11.3530(2) Å	$\gamma = 90^\circ$.
Volume	1137.88(4) Å ³	
Z	2	
Density (calculated)	1.052 Mg/m ³	
Absorption coefficient	0.063 mm ⁻¹	
F(000)	400	
Crystal size	0.28 x 0.25 x 0.18 mm	
Theta range for data collection	2.88 to 27.48°.	
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 13, -14 ≤ l ≤ 14	
Reflections collected	4951	
Independent reflections	2600 [R(int) = 0.0132]	
Completeness to theta = 27.48°	99.7 %	
Max. and min. transmission	0.9888 and 0.9827	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2600 / 0 / 198	
Goodness-of-fit on F ²	1.013	
Final R indices [I > 2sigma(I)]	R1 = 0.0370, wR2 = 0.0906	
R indices (all data)	R1 = 0.0455, wR2 = 0.0957	
Largest diff. peak and hole	0.222 and -0.180 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
N1	4706(1)	2500(1)	5765(1)	25(1)
N2	6982(1)	3112(1)	5640(1)	23(1)
C1	4755(1)	3730(1)	5382(1)	20(1)
C2	6113(1)	4063(1)	5325(1)	20(1)
C3	3735(1)	4640(1)	5061(1)	21(1)
C4	3626(1)	1840(1)	6030(1)	24(1)
C5	4181(1)	473(1)	6484(1)	32(1)
C6	2294(1)	1726(1)	4806(1)	31(1)
C7	3372(1)	2528(1)	7107(1)	34(1)
C8	8380(1)	3180(1)	5679(1)	26(1)
C9	8992(1)	1826(1)	6115(1)	37(1)
C10	9272(1)	4163(1)	6686(1)	38(1)
C11	8359(1)	3437(1)	4341(1)	39(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **5**.

N1-C1	1.3487(12)	C6-H6B	0.985(15)
N1-C4	1.4696(12)	C6-H6C	1.005(14)
N1-H1N	0.860(13)	C7-H7A	0.977(14)
N2-C2	1.2941(12)	C7-H7B	0.979(16)
N2-C8	1.4739(12)	C7-H7C	0.988(15)
C1-C3	1.3670(13)	C8-C10	1.5320(15)
C1-C2	1.5128(12)	C8-C11	1.5332(16)
C2-C3#1	1.4372(13)	C8-C9	1.5344(14)
C3-C2#1	1.4372(13)	C9-H9A	0.985(14)
C3-H3	0.969(12)	C9-H9B	0.994(16)
C4-C7	1.5305(15)	C9-H9C	0.983(15)
C4-C6	1.5318(14)	C10-H10A	0.995(14)
C4-C5	1.5335(14)	C10-H10B	0.976(15)
C5-H5A	0.961(13)	C10-H10C	0.988(17)
C5-H5B	0.981(15)	C11-H11A	0.955(13)
C5-H5C	0.980(14)	C11-H11B	0.973(15)
C6-H6A	1.002(13)	C11-H11C	0.994(14)
C1-N1-C4	129.67(8)	N1-C4-C5	105.52(8)
C1-N1-H1N	111.6(8)	C7-C4-C5	109.09(9)
C4-N1-H1N	118.2(8)	C6-C4-C5	108.76(9)
C2-N2-C8	124.93(8)	C4-C5-H5A	112.7(8)
N1-C1-C3	126.82(9)	C4-C5-H5B	111.1(8)
N1-C1-C2	113.00(8)	H5A-C5-H5B	107.5(11)
C3-C1-C2	120.18(8)	C4-C5-H5C	108.7(8)
N2-C2-C3#1	129.20(8)	H5A-C5-H5C	108.0(11)
N2-C2-C1	113.89(8)	H5B-C5-H5C	108.6(11)
C3#1-C2-C1	116.91(8)	C4-C6-H6A	108.8(7)
C1-C3-C2#1	122.91(8)	C4-C6-H6B	113.4(8)
C1-C3-H3	120.3(7)	H6A-C6-H6B	107.9(11)
C2#1-C3-H3	116.8(7)	C4-C6-H6C	108.8(8)
N1-C4-C7	110.97(8)	H6A-C6-H6C	108.7(11)
N1-C4-C6	111.22(8)	H6B-C6-H6C	109.2(12)
C7-C4-C6	111.08(9)	C4-C7-H7A	109.6(8)

C4-C7-H7B	108.6(9)
H7A-C7-H7B	108.7(12)
C4-C7-H7C	111.2(8)
H7A-C7-H7C	108.0(11)
H7B-C7-H7C	110.8(12)
N2-C8-C10	111.40(9)
N2-C8-C11	111.88(9)
C10-C8-C11	112.26(10)
N2-C8-C9	104.92(8)
C10-C8-C9	107.97(9)
C11-C8-C9	108.01(9)
C8-C9-H9A	109.5(8)
C8-C9-H9B	109.0(9)
H9A-C9-H9B	109.3(12)
C8-C9-H9C	108.8(9)
H9A-C9-H9C	110.4(12)
H9B-C9-H9C	109.8(12)
C8-C10-H10A	109.2(8)
C8-C10-H10B	111.7(9)
H10A-C10-H10B	111.2(12)
C8-C10-H10C	108.9(9)
H10A-C10-H10C	108.5(12)
H10B-C10-H10C	107.2(13)
C8-C11-H11A	107.7(7)
C8-C11-H11B	112.4(9)
H11A-C11-H11B	110.0(11)
C8-C11-H11C	108.2(8)
H11A-C11-H11C	109.2(11)
H11B-C11-H11C	109.1(12)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z+1$

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N1	22(1)	20(1)	34(1)	6(1)	13(1)	1(1)
N2	21(1)	21(1)	27(1)	1(1)	9(1)	0(1)
C1	21(1)	20(1)	19(1)	0(1)	7(1)	-3(1)
C2	20(1)	21(1)	18(1)	-1(1)	6(1)	-2(1)
C3	19(1)	21(1)	23(1)	1(1)	9(1)	-2(1)
C4	25(1)	22(1)	26(1)	4(1)	11(1)	-3(1)
C5	34(1)	25(1)	36(1)	10(1)	13(1)	-1(1)
C6	27(1)	28(1)	33(1)	3(1)	7(1)	-5(1)
C7	45(1)	33(1)	31(1)	2(1)	21(1)	-3(1)
C8	21(1)	24(1)	35(1)	3(1)	11(1)	2(1)
C9	30(1)	28(1)	58(1)	10(1)	21(1)	8(1)
C10	24(1)	33(1)	47(1)	-1(1)	5(1)	-3(1)
C11	37(1)	43(1)	44(1)	8(1)	25(1)	9(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**.

	x	y	z	U(eq)
H1N	5480(13)	2109(12)	5969(12)	30(3)
H3	2869(12)	4431(11)	5105(11)	25(3)
H5A	4344(13)	-12(12)	5837(13)	35(3)
H5B	5050(15)	507(13)	7254(14)	47(4)
H5C	3505(14)	-3(13)	6696(13)	38(3)
H6A	1599(13)	1236(13)	5016(12)	38(3)
H6B	1890(14)	2572(14)	4444(14)	45(4)
H6C	2490(14)	1227(14)	4139(14)	45(4)
H7A	2728(15)	2021(13)	7334(14)	45(4)
H7B	4247(16)	2590(14)	7867(15)	50(4)
H7C	2970(14)	3397(14)	6830(14)	45(4)
H9A	9947(15)	1808(13)	6193(13)	45(4)
H9B	8438(16)	1178(16)	5460(15)	55(4)
H9C	8963(15)	1629(14)	6951(15)	51(4)
H10A	10244(15)	4076(14)	6794(14)	48(4)
H10B	8939(15)	5048(15)	6452(14)	51(4)
H10C	9228(16)	3969(15)	7520(16)	58(4)
H11A	7752(13)	2819(13)	3757(12)	31(3)
H11B	8059(15)	4313(15)	4037(15)	52(4)
H11C	9304(15)	3302(13)	4392(13)	49(4)

Table 6. Torsion angles [°] for **5**.

C4-N1-C1-C3	-4.98(16)
C4-N1-C1-C2	175.12(9)
C8-N2-C2-C3#1	0.57(16)
C8-N2-C2-C1	-179.29(8)
N1-C1-C2-N2	0.55(12)
C3-C1-C2-N2	-179.36(8)
N1-C1-C2-C3#1	-179.32(8)
C3-C1-C2-C3#1	0.77(14)
N1-C1-C3-C2#1	179.29(9)
C2-C1-C3-C2#1	-0.81(15)
C1-N1-C4-C7	-59.60(13)
C1-N1-C4-C6	64.59(13)
C1-N1-C4-C5	-177.63(10)
C2-N2-C8-C10	62.92(13)
C2-N2-C8-C11	-63.65(13)
C2-N2-C8-C9	179.49(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

X-ray Crystallographic Data for **8**:

Figure 3. View of **8** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The molecule lies on a crystallographic two-fold rotation axis at $\frac{1}{2}, y, \frac{1}{4}$. Atoms with labels appended by a ' are related by $1-x, y, \frac{1}{2}-z$.

X-ray Experimental for **8** ($\text{C}_{42}\text{H}_{30}\text{N}_4\text{O}_4 - \text{C}_7\text{H}_8$): Crystals grew as nicely formed yellow-brown prisms lathes by slow evaporation from toluene. The data crystal was a prism that had approximate dimensions; 0.34 x 0.33 x 0.23 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). A total of 269 frames of data were collected using ω -scans with a scan range of 1.5° and a counting time of 116 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The molecule of toluene was disordered about a crystallographic two-fold rotation axis at $\frac{1}{2}$, y, $\frac{1}{4}$. The toluene molecule was refined with half-weighted carbon atoms initially. The molecule was refined anisotropically as a rigid group with displacement parameters restrained to be approximately isotropic. The ammine also resided around the crystallographic two-fold rotation axis at $\frac{1}{2}$, y, $\frac{1}{4}$. The hydrogen atoms bound to nitrogen appeared to be disordered. For each nitrogen atom, two peaks in a reasonable position to be a H atom appeared in the ΔF map. In the final refinement model, two half-weighted hydrogen atoms were refined with isotropic displacement parameters.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0719 \cdot P)^2 + (1.3529 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.176, with $R(F)$ equal to 0.0624 and a goodness of fit, S , = 1.08. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

References

- 11) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
- 12) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. J. Appl. Cryst. 32, 115-119.
- 13) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 14) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.

$R(F) = \Sigma(|F_O| - |F_C|)/\Sigma|F_O|$ for reflections with $F_O > 4(\sigma(F_O))$.

$S = [\Sigma w(|F_O|^2 - |F_C|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

- 15) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for **8**.

Empirical formula	C ₄₉ H ₅₈ N ₄	
Formula weight	702.99	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/c	
Unit cell dimensions	a = 8.7265(1) Å	$\alpha = 90^\circ$.
	b = 11.1041(2) Å	$\beta = 96.666(1)^\circ$.
	c = 21.5922(3) Å	$\gamma = 90^\circ$.
Volume	2078.14(5) Å ³	
Z	2	
Density (calculated)	1.123 Mg/m ³	
Absorption coefficient	0.065 mm ⁻¹	
F(000)	760	
Crystal size	0.34 x 0.33 x 0.23 mm	
Theta range for data collection	2.64 to 27.48°.	
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -28 ≤ l ≤ 27	
Reflections collected	9143	
Independent reflections	4746 [R(int) = 0.0199]	
Completeness to theta = 27.48°	99.3 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4746 / 42 / 278	
Goodness-of-fit on F ²	1.015	
Final R indices [I > 2sigma(I)]	R1 = 0.0624, wR2 = 0.1565	
R indices (all data)	R1 = 0.0846, wR2 = 0.1761	
Largest diff. peak and hole	0.530 and -0.389 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N1	7390(2)	7174(2)	3497(1)	34(1)
N2	1865(2)	7157(2)	2714(1)	34(1)
C1	6181(2)	7165(2)	3002(1)	28(1)
C2	4639(2)	7159(2)	3107(1)	29(1)
C3	3450(2)	7158(2)	2614(1)	28(1)
C4	7004(2)	7303(2)	4122(1)	28(1)
C5	6811(2)	8451(2)	4363(1)	33(1)
C6	6424(2)	8552(2)	4972(1)	37(1)
C7	6235(2)	7548(2)	5337(1)	36(1)
C8	6428(2)	6416(2)	5082(1)	33(1)
C9	6804(2)	6275(2)	4475(1)	29(1)
C10	6992(3)	9550(2)	3973(1)	50(1)
C11	5832(3)	7676(2)	5995(1)	55(1)
C12	6959(2)	5038(2)	4206(1)	40(1)
C13	1516(2)	7291(2)	3344(1)	29(1)
C14	1471(2)	8436(2)	3605(1)	38(1)
C15	1159(2)	8544(2)	4224(1)	41(1)
C16	898(2)	7549(2)	4584(1)	34(1)
C17	947(2)	6424(2)	4310(1)	33(1)
C18	1251(2)	6267(2)	3693(1)	31(1)
C19	1792(3)	9537(2)	3234(1)	65(1)
C20	561(3)	7684(2)	5250(1)	46(1)
C21	1296(3)	5026(2)	3422(1)	50(1)
C1A	6093(5)	2548(3)	2644(2)	83(2)
C2A	5273(6)	1543(3)	2513(3)	49(2)
C3A	3555(5)	1792(4)	2292(2)	75(2)
C4A	3003(6)	2965(5)	2229(3)	105(3)
C5A	3995(8)	3929(4)	2373(4)	126(4)
C6A	5541(7)	3721(3)	2580(4)	84(3)
C7A	7766(5)	2395(6)	2881(3)	131(4)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **8**.

N1-C1	1.413(2)	C13-C18	1.399(3)
N1-C4	1.435(2)	C14-C15	1.400(3)
N1-H1NB	0.92(5)	C14-C19	1.506(3)
N1-H1NA	0.82(4)	C15-C16	1.384(3)
N2-C3	1.424(2)	C15-H15	0.95
N2-C13	1.435(2)	C16-C17	1.385(3)
N2-H2NB	0.93(4)	C16-C20	1.509(3)
N2-H2NA	0.88(6)	C17-C18	1.397(2)
C1-C2	1.391(2)	C17-H17	0.95
C1-C3#1	1.404(2)	C18-C21	1.499(3)
C2-C3	1.398(2)	C19-H19A	0.98
C2-H2	0.95	C19-H19B	0.98
C3-C1#1	1.404(2)	C19-H19C	0.98
C4-C5	1.395(3)	C20-H20A	0.98
C4-C9	1.396(3)	C20-H20B	0.98
C5-C6	1.400(3)	C20-H20C	0.98
C5-C10	1.503(3)	C21-H21A	0.98
C6-C7	1.386(3)	C21-H21B	0.98
C6-H6	0.95	C21-H21C	0.98
C7-C8	1.390(3)	C1A-C2A	1.338
C7-C11	1.511(3)	C1A-C6A	1.390
C8-C9	1.396(2)	C1A-C7A	1.500
C8-H8	0.95	C2A-C3A	1.545
C9-C12	1.503(3)	C2A-H2AA	0.960
C10-H10A	0.98	C3A-C4A	1.390
C10-H10B	0.98	C3A-H3AA	0.96
C10-H10C	0.98	C4A-C5A	1.390
C11-H11A	0.98	C4A-H4AA	0.96
C11-H11B	0.98	C5A-C6A	1.390
C11-H11C	0.98	C5A-H5AA	0.96
C12-H12A	0.98	C6A-H6AA	0.96
C12-H12B	0.98	C7A-H7AA	0.96
C12-H12C	0.98	C7A-H7AB	0.96
C13-C14	1.393(3)	C7A-H7AC	0.96

C1-N1-C4	118.42(14)	C4-C9-C12	120.91(15)
C1-N1-H1NB	110(3)	C8-C9-C12	120.44(17)
C4-N1-H1NB	111(3)	C5-C10-H10A	109.5
C1-N1-H1NA	120(3)	C5-C10-H10B	109.5
C4-N1-H1NA	118(3)	H10A-C10-H10B	109.5
C3-N2-C13	117.36(14)	C5-C10-H10C	109.5
C3-N2-H2NB	107(2)	H10A-C10-H10C	109.5
C13-N2-H2NB	95(2)	H10B-C10-H10C	109.5
C3-N2-H2NA	114(3)	C7-C11-H11A	109.5
C13-N2-H2NA	115(3)	C7-C11-H11B	109.5
C2-C1-C3#1	119.26(15)	H11A-C11-H11B	109.5
C2-C1-N1	121.83(15)	C7-C11-H11C	109.5
C3#1-C1-N1	118.91(14)	H11A-C11-H11C	109.5
C1-C2-C3	121.43(15)	H11B-C11-H11C	109.5
C1-C2-H2	119.3	C9-C12-H12A	109.5
C3-C2-H2	119.3	C9-C12-H12B	109.5
C2-C3-C1#1	119.31(15)	H12A-C12-H12B	109.5
C2-C3-N2	122.21(15)	C9-C12-H12C	109.5
C1#1-C3-N2	118.48(14)	H12A-C12-H12C	109.5
C5-C4-C9	120.96(15)	H12B-C12-H12C	109.5
C5-C4-N1	119.68(17)	C14-C13-C18	120.59(16)
C9-C4-N1	119.35(17)	C14-C13-N2	119.82(17)
C4-C5-C6	118.56(17)	C18-C13-N2	119.58(17)
C4-C5-C10	120.46(17)	C13-C14-C15	118.85(18)
C6-C5-C10	120.98(19)	C13-C14-C19	120.68(19)
C7-C6-C5	121.73(18)	C15-C14-C19	120.5(2)
C7-C6-H6	119.1	C16-C15-C14	122.02(19)
C5-C6-H6	119.1	C16-C15-H15	119.0
C6-C7-C8	118.40(17)	C14-C15-H15	119.0
C6-C7-C11	120.94(19)	C15-C16-C17	117.66(17)
C8-C7-C11	120.66(18)	C15-C16-C20	121.24(18)
C7-C8-C9	121.70(18)	C17-C16-C20	121.10(18)
C7-C8-H8	119.2	C16-C17-C18	122.60(18)
C9-C8-H8	119.2	C16-C17-H17	118.7
C4-C9-C8	118.64(17)	C18-C17-H17	118.7

C17-C18-C13	118.28(17)	C1A-C6A-C5A	120.0
C17-C18-C21	120.27(18)	C1A-C6A-H6AA	120.0
C13-C18-C21	121.45(16)	C5A-C6A-H6AA	120.0
C14-C19-H19A	109.5	C1A-C7A-H7AA	109.5
C14-C19-H19B	109.5	C1A-C7A-H7AB	109.5
H19A-C19-H19B	109.5	H7AA-C7A-H7AB	109.5
C14-C19-H19C	109.5	C1A-C7A-H7AC	109.5
H19A-C19-H19C	109.5	H7AA-C7A-H7AC	109.5
H19B-C19-H19C	109.5	H7AB-C7A-H7AC	109.5
C16-C20-H20A	109.5		
C16-C20-H20B	109.5		
H20A-C20-H20B	109.5		
C16-C20-H20C	109.5		
H20A-C20-H20C	109.5		
H20B-C20-H20C	109.5		
C18-C21-H21A	109.5		
C18-C21-H21B	109.5		
H21A-C21-H21B	109.5		
C18-C21-H21C	109.5		
H21A-C21-H21C	109.5		
H21B-C21-H21C	109.5		
C2A-C1A-C6A	126.2		
C2A-C1A-C7A	116.9		
C6A-C1A-C7A	116.9		
C1A-C2A-C3A	113.1		
C1A-C2A-H2AA	123.5		
C3A-C2A-H2AA	123.4		
C4A-C3A-C2A	120.7		
C4A-C3A-H3AA	119.6		
C2A-C3A-H3AA	119.6		
C5A-C4A-C3A	120.0		
C5A-C4A-H4AA	120.0		
C3A-C4A-H4AA	120.0		
C4A-C5A-C6A	120.0		
C4A-C5A-H5AA	120.0		
C6A-C5A-H5AA	120.0		

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, y, -z+1/2$

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³ U ¹²	
N1	19(1)	66(1)	18(1)	2(1)	1(1)	3(1)
N2	19(1)	62(1)	20(1)	2(1)	3(1)	-2(1)
C1	20(1)	43(1)	21(1)	0(1)	0(1)	2(1)
C2	22(1)	48(1)	18(1)	0(1)	4(1)	1(1)
C3	18(1)	43(1)	23(1)	1(1)	3(1)	-2(1)
C4	19(1)	47(1)	18(1)	0(1)	-1(1)	2(1)
C5	27(1)	42(1)	29(1)	5(1)	-2(1)	3(1)
C6	35(1)	42(1)	33(1)	-7(1)	2(1)	6(1)
C7	34(1)	51(1)	23(1)	-5(1)	4(1)	2(1)
C8	32(1)	43(1)	25(1)	1(1)	4(1)	-1(1)
C9	23(1)	42(1)	22(1)	-4(1)	0(1)	0(1)
C10	51(1)	49(1)	51(1)	14(1)	4(1)	4(1)
C11	72(2)	65(2)	29(1)	-10(1)	18(1)	2(1)
C12	41(1)	45(1)	36(1)	-8(1)	5(1)	-1(1)
C13	16(1)	49(1)	23(1)	0(1)	2(1)	0(1)
C14	31(1)	45(1)	38(1)	3(1)	5(1)	-4(1)
C15	37(1)	46(1)	39(1)	-9(1)	6(1)	1(1)
C16	21(1)	53(1)	27(1)	-5(1)	3(1)	2(1)
C17	29(1)	46(1)	24(1)	4(1)	3(1)	1(1)
C18	24(1)	44(1)	24(1)	-1(1)	1(1)	2(1)
C19	84(2)	52(2)	60(2)	10(1)	16(1)	-14(1)
C20	41(1)	69(2)	29(1)	-10(1)	7(1)	5(1)
C21	70(2)	48(1)	32(1)	-3(1)	6(1)	5(1)
C1A	131(6)	98(5)	26(3)	2(3)	40(3)	-12(4)
C2A	79(6)	43(2)	33(2)	-2(3)	33(3)	-9(3)
C3A	133(6)	65(4)	36(3)	-2(3)	42(3)	0(4)
C4A	134(7)	148(8)	41(3)	12(5)	41(4)	38(6)
C5A	235(9)	86(5)	74(6)	7(5)	90(6)	22(6)
C6A	181(9)	43(3)	40(4)	-11(3)	64(5)	-35(4)
C7A	162(8)	170(8)	65(5)	1(5)	29(5)	-39(7)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **8**.

	x	y	z	U(eq)
H2	4388	7155	3524	35
H6	6289	9331	5141	44
H8	6300	5721	5327	40
H10A	8026	9556	3837	76
H10B	6853	10274	4219	76
H10C	6217	9537	3606	76
H11A	5724	8532	6093	82
H11B	6654	7321	6286	82
H11C	4858	7259	6034	82
H12A	6799	4431	4522	61
H12B	7993	4944	4078	61
H12C	6185	4932	3843	61
H15	1126	9324	4403	49
H17	768	5733	4550	40
H19A	2895	9573	3188	97
H19B	1495	10259	3452	97
H19C	1195	9495	2821	97
H20A	1480	7468	5533	69
H20B	-294	7152	5325	69
H20C	277	8521	5325	69
H21A	1090	4431	3736	75
H21B	2318	4878	3290	75
H21C	510	4960	3060	75
H2AA	5708	749	2553	59
H3AA	2860	1129	2198	90
H4AA	1935	3109	2086	126
H5AA	3614	4740	2328	151
H6AA	6227	4387	2679	101
H7AA	8013	1552	2906	197
H7AB	8388	2784	2602	197

H7AC	7966	2749	3288	197
H2NB	1470(50)	7900(40)	2582(18)	27(10)
H1NB	8120(50)	7730(40)	3420(20)	33(11)
H2NA	1310(60)	6610(50)	2490(20)	59(15)
H1NA	8220(50)	6860(40)	3449(18)	24(10)

Table 6. Torsion angles [°] for **8**.

C4-N1-C1-C2	-6.5(3)
C4-N1-C1-C3#1	173.86(18)
C3#1-C1-C2-C3	-0.7(3)
N1-C1-C2-C3	179.63(19)
C1-C2-C3-C1#1	-0.1(3)
C1-C2-C3-N2	-179.69(19)
C13-N2-C3-C2	6.7(3)
C13-N2-C3-C1#1	-172.89(18)
C1-N1-C4-C5	-85.6(2)
C1-N1-C4-C9	93.4(2)
C9-C4-C5-C6	0.6(3)
N1-C4-C5-C6	179.61(15)
C9-C4-C5-C10	-178.54(17)
N1-C4-C5-C10	0.5(3)
C4-C5-C6-C7	0.1(3)
C10-C5-C6-C7	179.23(18)
C5-C6-C7-C8	-0.4(3)
C5-C6-C7-C11	179.41(19)
C6-C7-C8-C9	0.0(3)
C11-C7-C8-C9	-179.79(18)
C5-C4-C9-C8	-1.0(2)
N1-C4-C9-C8	-179.97(15)
C5-C4-C9-C12	177.85(16)
N1-C4-C9-C12	-1.2(2)
C7-C8-C9-C4	0.7(3)
C7-C8-C9-C12	-178.17(17)
C3-N2-C13-C14	83.0(2)
C3-N2-C13-C18	-95.9(2)
C18-C13-C14-C15	0.2(3)
N2-C13-C14-C15	-178.71(16)
C18-C13-C14-C19	178.58(19)
N2-C13-C14-C19	-0.3(3)
C13-C14-C15-C16	0.1(3)
C19-C14-C15-C16	-178.3(2)

C14-C15-C16-C17	-0.3(3)
C14-C15-C16-C20	-179.88(18)
C15-C16-C17-C18	0.2(3)
C20-C16-C17-C18	179.79(17)
C16-C17-C18-C13	0.1(3)
C16-C17-C18-C21	179.78(18)
C14-C13-C18-C17	-0.2(3)
N2-C13-C18-C17	178.62(15)
C14-C13-C18-C21	-179.94(18)
N2-C13-C18-C21	-1.1(3)
C6A-C1A-C2A-C3A	-1.8
C7A-C1A-C2A-C3A	178.1
C1A-C2A-C3A-C4A	1.7
C3A-C4A-C5A-C6A	0.0
C2A-C1A-C6A-C5A	1.1
C7A-C1A-C6A-C5A	-178.9
C4A-C5A-C6A-C1A	0.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

X-ray Crystallographic Data for **9**:

Figure 4. View of **9** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The methyl group hydrogen atoms have been removed for clarity. The molecule lies around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Atoms with labels appended by a ' are related by $1-x, 1-y, 1-z$.

X-ray Experimental for **9** ($C_{42}H_{48}N_4$): Crystals grew as brown-orange prisms by slow evaporation from toluene. The data crystal was a prism that had approximate dimensions; 0.20 x 0.14 x 0.14 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 372 frames of data were collected using ω -scans with a scan range of 1.5° and a counting time of 176 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atoms on the methyl carbon atoms were calculated in ideal positions with isotropic displacement parameters set to $1.5 \times U_{eq}$ of the attached atom. The remaining hydrogen atoms were observed in a ΔF map and refined

with isotropic displacement parameters. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0465 \cdot P)^2 + (0.126 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.136, with $R(F)$ equal to 0.0522 and a goodness of fit, S , = 1.12. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (3.9(6) \times 10^{-5}) \cdot F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶ Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

References

- 16) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.
- 17) SIR97. (1999). A program for crystal structure solution. Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. J. Appl. Cryst. 32, 115-119.
- 18) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
- 19) $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \sum (|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 20) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
- 6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for **9**.

Empirical formula	C42 H48 N4	
Formula weight	608.84	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.2910(2) Å	$\alpha = 99.955(2)^\circ$.
	b = 10.8604(3) Å	$\beta = 99.543(2)^\circ$.
	c = 12.4091(4) Å	$\gamma = 108.311(2)^\circ$.
Volume	892.98(5) Å ³	
Z	1	
Density (calculated)	1.132 Mg/m ³	
Absorption coefficient	0.066 mm ⁻¹	
F(000)	328	
Crystal size	0.20 x 0.14 x 0.14 mm ³	
Theta range for data collection	2.03 to 27.50°.	
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 14, -16 ≤ l ≤ 15	
Reflections collected	6810	
Independent reflections	4085 [R(int) = 0.0264]	
Completeness to theta = 27.50°	99.4 %	
Absorption correction	None	
Max. and min. transmission	1 and 3891	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4085 / 0 / 239	
Goodness-of-fit on F ²	1.118	
Final R indices [I > 2σ(I)]	R1 = 0.0522, wR2 = 0.1185	
R indices (all data)	R1 = 0.0960, wR2 = 0.1358	
Extinction coefficient	3.9(6) × 10 ⁻⁵	
Largest diff. peak and hole	0.180 and -0.155 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N1	3196(2)	3027(1)	3083(1)	43(1)
N2	8046(2)	7357(1)	5106(1)	41(1)
C1	4102(2)	4008(2)	3959(1)	35(1)
C2	5676(2)	5229(1)	4008(1)	35(1)
C3	6556(2)	6181(1)	4984(1)	35(1)
C4	3770(2)	3070(2)	2044(1)	40(1)
C5	5210(3)	2551(2)	1806(2)	53(1)
C6	5639(3)	2504(2)	750(2)	57(1)
C7	4703(3)	2963(2)	-58(1)	53(1)
C8	3260(3)	3454(2)	190(2)	57(1)
C9	2744(2)	3501(2)	1227(1)	48(1)
C10	6270(4)	2049(3)	2681(2)	100(1)
C11	5263(3)	2927(2)	-1181(2)	76(1)
C12	1130(3)	4007(3)	1476(2)	86(1)
C13	8754(2)	7852(1)	4200(1)	36(1)
C14	10024(2)	7350(2)	3694(1)	42(1)
C15	10703(3)	7877(2)	2826(1)	46(1)
C16	10196(3)	8899(2)	2481(1)	48(1)
C17	8966(3)	9391(2)	3020(1)	47(1)
C18	8193(2)	8876(2)	3873(1)	41(1)
C19	10668(3)	6277(2)	4070(2)	60(1)
C20	10924(3)	9448(2)	1524(2)	70(1)
C21	6768(3)	9377(2)	4401(2)	55(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **9**.

N1-C1	1.2931(19)	C11-H11B	0.98
N1-C4	1.4241(18)	C11-H11C	0.98
N2-C3	1.3569(19)	C12-H12A	0.98
N2-C13	1.4302(18)	C12-H12B	0.98
N2-H2N	0.906(19)	C12-H12C	0.98
C1-C2	1.440(2)	C13-C14	1.393(2)
C1-C3#1	1.4941(19)	C13-C18	1.399(2)
C2-C3	1.356(2)	C14-C15	1.395(2)
C2-H2	0.978(15)	C14-C19	1.502(2)
C3-C1#1	1.4941(19)	C15-C16	1.386(2)
C4-C5	1.387(2)	C15-H15	0.994(18)
C4-C9	1.392(2)	C16-C17	1.383(2)
C5-C6	1.393(2)	C16-C20	1.518(2)
C5-C10	1.505(3)	C17-C18	1.398(2)
C6-C7	1.370(3)	C17-H17	1.009(17)
C6-H6	0.97(2)	C18-C21	1.504(2)
C7-C8	1.375(3)	C19-H19A	0.98
C7-C11	1.514(2)	C19-H19B	0.98
C8-C9	1.397(2)	C19-H19C	0.98
C8-H8	1.03(2)	C20-H20A	0.98
C9-C12	1.500(3)	C20-H20B	0.98
C10-H10A	0.98	C20-H20C	0.98
C10-H10B	0.98	C21-H21A	0.98
C10-H10C	0.98	C21-H21B	0.98
C11-H11A	0.98	C21-H21C	0.98
C1-N1-C4	120.34(12)	C3-C2-H2	120.7(9)
C3-N2-C13	124.90(13)	C1-C2-H2	117.9(9)
C3-N2-H2N	113.6(12)	C2-C3-N2	125.25(13)
C13-N2-H2N	119.5(12)	C2-C3-C1#1	120.59(13)
N1-C1-C2	126.38(13)	N2-C3-C1#1	114.16(13)
N1-C1-C3#1	115.56(12)	C5-C4-C9	120.18(14)
C2-C1-C3#1	118.06(13)	C5-C4-N1	119.58(14)
C3-C2-C1	121.35(13)	C9-C4-N1	119.90(14)

C4-C5-C6	118.77(17)	C13-C14-C15	118.21(15)
C4-C5-C10	119.92(16)	C13-C14-C19	121.49(14)
C6-C5-C10	121.31(18)	C15-C14-C19	120.30(15)
C7-C6-C5	122.38(18)	C16-C15-C14	122.01(16)
C7-C6-H6	120.7(11)	C16-C15-H15	119.5(10)
C5-C6-H6	116.9(11)	C14-C15-H15	118.4(10)
C6-C7-C8	117.90(16)	C17-C16-C15	118.06(14)
C6-C7-C11	120.39(18)	C17-C16-C20	120.54(16)
C8-C7-C11	121.71(18)	C15-C16-C20	121.38(17)
C7-C8-C9	122.08(18)	C16-C17-C18	122.48(16)
C7-C8-H8	121.7(12)	C16-C17-H17	121.9(10)
C9-C8-H8	116.2(12)	C18-C17-H17	115.6(10)
C4-C9-C8	118.63(16)	C17-C18-C13	117.56(15)
C4-C9-C12	119.83(15)	C17-C18-C21	121.44(15)
C8-C9-C12	121.54(17)	C13-C18-C21	120.98(14)
C5-C10-H10A	109.5	C14-C19-H19A	109.5
C5-C10-H10B	109.5	C14-C19-H19B	109.5
H10A-C10-H10B	109.5	H19A-C19-H19B	109.5
C5-C10-H10C	109.5	C14-C19-H19C	109.5
H10A-C10-H10C	109.5	H19A-C19-H19C	109.5
H10B-C10-H10C	109.5	H19B-C19-H19C	109.5
C7-C11-H11A	109.5	C16-C20-H20A	109.5
C7-C11-H11B	109.5	C16-C20-H20B	109.5
H11A-C11-H11B	109.5	H20A-C20-H20B	109.5
C7-C11-H11C	109.5	C16-C20-H20C	109.5
H11A-C11-H11C	109.5	H20A-C20-H20C	109.5
H11B-C11-H11C	109.5	H20B-C20-H20C	109.5
C9-C12-H12A	109.5	C18-C21-H21A	109.5
C9-C12-H12B	109.5	C18-C21-H21B	109.5
H12A-C12-H12B	109.5	H21A-C21-H21B	109.5
C9-C12-H12C	109.5	C18-C21-H21C	109.5
H12A-C12-H12C	109.5	H21A-C21-H21C	109.5
H12B-C12-H12C	109.5	H21B-C21-H21C	109.5
C14-C13-C18	121.63(13)		
C14-C13-N2	120.16(13)		
C18-C13-N2	118.18(14)		

Symmetry transformations used to generate equivalent atoms:

#1 $-x+1, -y+1, -z+1$

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
N1	50(1)	40(1)	30(1)	7(1)	17(1)	3(1)
N2	50(1)	35(1)	28(1)	6(1)	15(1)	-1(1)
C1	40(1)	35(1)	29(1)	10(1)	11(1)	8(1)
C2	42(1)	35(1)	28(1)	11(1)	14(1)	9(1)
C3	37(1)	35(1)	32(1)	12(1)	13(1)	8(1)
C4	45(1)	35(1)	30(1)	5(1)	15(1)	-1(1)
C5	62(1)	56(1)	49(1)	20(1)	25(1)	20(1)
C6	64(1)	56(1)	56(1)	11(1)	33(1)	20(1)
C7	52(1)	58(1)	34(1)	0(1)	18(1)	0(1)
C8	49(1)	82(1)	36(1)	18(1)	14(1)	12(1)
C9	44(1)	61(1)	36(1)	12(1)	15(1)	9(1)
C10	118(2)	146(3)	99(2)	77(2)	58(2)	90(2)
C11	71(1)	98(2)	41(1)	1(1)	28(1)	5(1)
C12	76(2)	143(2)	75(2)	57(2)	43(1)	58(2)
C13	42(1)	33(1)	27(1)	7(1)	12(1)	2(1)
C14	49(1)	36(1)	36(1)	8(1)	15(1)	7(1)
C15	54(1)	40(1)	40(1)	6(1)	23(1)	6(1)
C16	64(1)	39(1)	34(1)	9(1)	21(1)	2(1)
C17	60(1)	39(1)	41(1)	16(1)	14(1)	11(1)
C18	43(1)	39(1)	37(1)	8(1)	13(1)	7(1)
C19	77(1)	57(1)	58(1)	22(1)	31(1)	30(1)
C20	102(2)	52(1)	48(1)	17(1)	37(1)	3(1)
C21	55(1)	56(1)	56(1)	16(1)	19(1)	20(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **9**.

	x	y	z	U(eq)
H10A	7141	2805	3300	150
H10B	7068	1586	2341	150
H10C	5291	1428	2971	150
H11A	6669	3471	-1061	114
H11B	4444	3283	-1655	114
H11C	5040	2002	-1555	114
H12A	210	3364	1780	129
H12B	407	4117	781	129
H12C	1719	4870	2029	129
H19A	10683	6345	4869	89
H19B	12004	6387	3957	89
H19C	9737	5398	3627	89
H20A	12142	9276	1445	105
H20B	11199	10413	1686	105
H20C	9900	9010	822	105
H21A	5516	8633	4289	82
H21B	6513	10066	4048	82
H21C	7346	9756	5208	82
H2	6080(20)	5362(14)	3310(13)	38(4)
H17	8530(20)	10126(18)	2801(14)	58(5)
H15	11640(30)	7537(17)	2478(15)	58(5)
H2N	8340(30)	7925(19)	5790(16)	60(5)
H8	2500(30)	3810(20)	-382(18)	85(7)
H6	6630(30)	2117(19)	602(16)	71(6)

Table 6. Torsion angles [°] for **9**.

C4-N1-C1-C2	2.1(2)
C4-N1-C1-C3#1	-176.88(13)
N1-C1-C2-C3	-178.36(15)
C3#1-C1-C2-C3	0.6(2)
C1-C2-C3-N2	179.97(14)
C1-C2-C3-C1#1	-0.6(2)
C13-N2-C3-C2	8.2(2)
C13-N2-C3-C1#1	-171.26(14)
C1-N1-C4-C5	90.49(19)
C1-N1-C4-C9	-96.23(19)
C9-C4-C5-C6	1.7(3)
N1-C4-C5-C6	174.91(15)
C9-C4-C5-C10	-178.16(19)
N1-C4-C5-C10	-4.9(3)
C4-C5-C6-C7	0.6(3)
C10-C5-C6-C7	-179.6(2)
C5-C6-C7-C8	-1.6(3)
C5-C6-C7-C11	178.24(18)
C6-C7-C8-C9	0.3(3)
C11-C7-C8-C9	-179.47(17)
C5-C4-C9-C8	-2.8(2)
N1-C4-C9-C8	-176.04(15)
C5-C4-C9-C12	177.41(18)
N1-C4-C9-C12	4.2(2)
C7-C8-C9-C4	1.8(3)
C7-C8-C9-C12	-178.39(19)
C3-N2-C13-C14	-78.3(2)
C3-N2-C13-C18	103.98(18)
C18-C13-C14-C15	-1.3(2)
N2-C13-C14-C15	-178.98(14)
C18-C13-C14-C19	178.28(15)
N2-C13-C14-C19	0.6(2)
C13-C14-C15-C16	1.8(2)
C19-C14-C15-C16	-177.81(16)

C14-C15-C16-C17	-0.4(3)
C14-C15-C16-C20	-179.12(16)
C15-C16-C17-C18	-1.4(3)
C20-C16-C17-C18	177.25(16)
C16-C17-C18-C13	1.9(2)
C16-C17-C18-C21	-176.54(16)
C14-C13-C18-C17	-0.5(2)
N2-C13-C18-C17	177.27(14)
C14-C13-C18-C21	177.96(15)
N2-C13-C18-C21	-4.3(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1