

SUPPORTING INFORMATION

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**Complexation-Induced Unfolding of Heterocyclic Ureas.
A Hydrogen-Bonded, Sheet-like Heterodimer**

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CHARACTERIZATION DATA

Bis-2,7-(3-(butyl))uryl-1,8-naphthyridine (1): Crystals suitable for X-ray analysis were obtained from methanol by slow evaporation; mp >260 °C (dec.); ¹H NMR (DMSO-*d*₆) δ 9.79 (s, 2H, NH), 9.38 (s, 2H, NH), 8.07 (d, 2H, J = 8.5, 2H, H-4, H-5), 7.13 (d, J = 8.5, 2H, H-3, H-6), 3.30 (alkyl peaks hidden by H₂O signal), 1.50 (m, 4H, CH₂CH₂CH₂CH₃), 1.35 (m, 4H, CH₂CH₂CH₂CH₃), 0.90 (t, J = 7.5, 6H, CH₃); ¹³C NMR (Sample was insufficiently soluble to obtain a ¹³C NMR spectrum); Anal Calcd for C₁₈H₂₆N₆O₂: C, 60.32; H, 7.31; N, 23.45. Found: C, 59.94; H, 7.41; N, 23.05.

Bis-2,7-(3-(3,4,5-tridodecyloxyphenyl))uryl-1,8-naphthyridine (2): mp 223 °C (dec); TLC (R_f = 0.20, 10% methanol, 90% methylene chloride); ¹H NMR (CDCl₃, 15 mM) δ 12.50 (s, 2H, NH-1), 9.81 (s, 2H, NH-2), 7.95 (d, J = 7.9, 2H, H-4, H-5), 7.08 (d, J = 7.9, 2H, H-3, H-6), 6.89 (s, 4H, H-2', H-6'), 3.92 (t, J = 6.3, 4H, OCH₂-4'), 3.66 (t, J = 5.5, 9H, OCH₂-3', 5'), 1.70 (m, 12H, OCH₂CH₂-3', 4', 5'), 1.49 (m, 4H, OCH₂CH₂CH₂-4'), 1.30 (m, 105H, CH₂), 0.82 (m, 18H, CH₃); ¹³C NMR δ 155.06, 153.55, 153.32, 152.12, 138.54, 134.47, 133.28, 114.52, 119.92, 98.38, 73.44, 68.45, 31.97, 31.92, 30.58, 29.91, 19.88, 29.87, 29.86, 29.78, 29.72, 29.65, 29.50, 29.45, 29.40, 26.30, 26.19, 22.70, 22.68, 14.08; IR (KBr, cm⁻¹) 3220 (NH), 3142 (NH), 1690 (C=O); Anal Calcd for C₉₉H₁₆₂N₆O₈: C, 75.07; H, 10.85; N, 5.59. Found: C, 75.07; H, 10.82; N, 5.77.

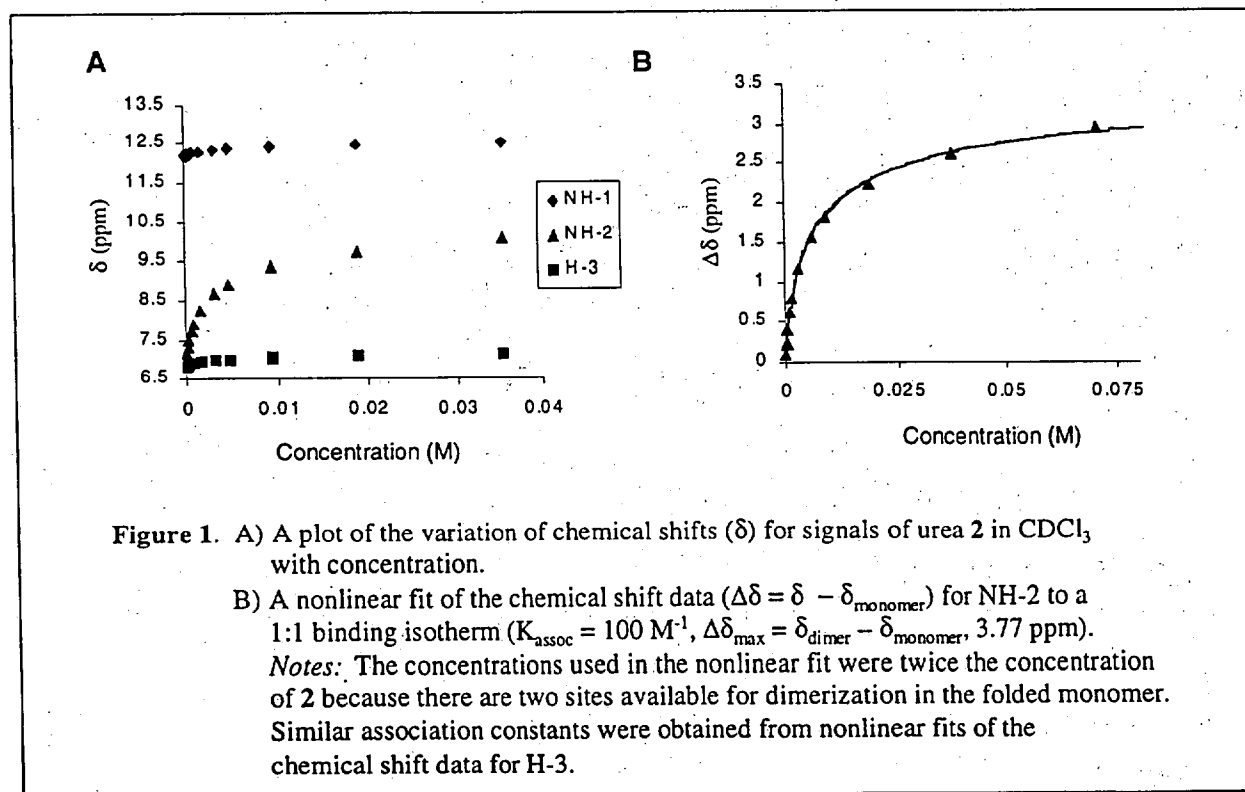
N,N'-Di-((5,7-dipropyl(1,8-naphthyridin))2-yl) urea (3): mp 239-241 °C; ¹H NMR (DMSO-*d*₆) δ 11.32 (s, 2H, NH), 8.56 (d, J = 9.1, 2H, H-4), 7.92 (broad s, 2H, H-3), 7.25 (s, 2H, H-6), 3.00 (t, J = 7.6, 4H, CH₂), 2.88 (t, J = 7.3, 4H, CH₂), 1.81 (m, 4H, CH₂), 1.67 (m, 4H, CH₂), 0.95 (m, 12H, CH₃); ¹³C NMR (DMSO-*d*₆) δ 165.63, 154.34, 153.68, 152.23, 149.70,

136.01, 120.39, 116.88, 113.32, 40.24, 32.68, 23.22, 22.34, 13.82, 13.78; Anal Calcd for $C_{29}H_{26}N_6O$: C, 71.86; H, 7.49; N, 17.35. Found: C, 71.61; H, 7.36; N, 17.20.

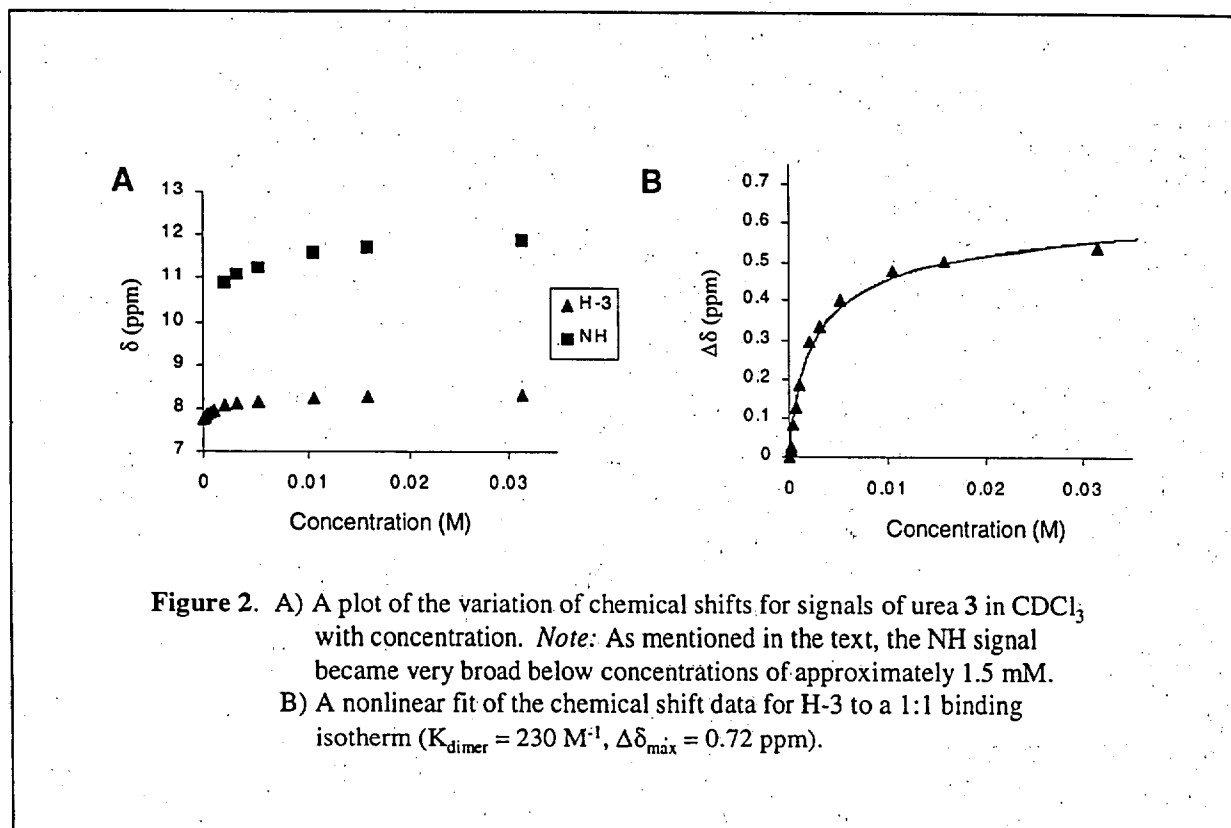
***N,N'*-Di-2-pyridylurea**: Crystals suitable for X-ray analysis were obtained from methanol by slow evaporation; mp 175-176 °C; 1H NMR (DMSO- d_6) δ 10.58 (s, 2H, NH), 8.27 (d, J = 5.2, 2H, H-6), 7.68-7.78 (m, 4H, H-3, H-4), 7.03 (m, 2H, H-5); 1H NMR ($CDCl_3$, 23 mM, 50 °C) δ 10.14 (broad s, 2H, NH), 8.38 (d, J = 4.9, 2H, H-6), 7.68 (m, 2H, H-4), 7.55 (broad s, 2H, H-3), 7.00 (m, 2H, H-5); ^{13}C NMR δ 153.63, 152.47, 147.15, 138.31, 118.18, 113.12; IR (KBr, cm^{-1}) 3323 (NH), 3119 (NH), 1698 (C=O); UV λ_{max} (chloroform, nm) 280, 250; Anal Calcd for $C_{11}H_{10}N_4O$: C, 61.67, H, 4.70, N, 26.15. Found: C, 61.61, H, 4.71, N, 26.18.

QUANTITATIVE BINDING STUDIES

General: All 1H NMR studies reported were carried out at 500 MHz on a Varian Inova 500NB spectrometer in the Varian Oxford Instruments Center for Excellence in NMR Spectroscopy (VOICE) laboratory at the University of Illinois. Chloroform- d ($CDCl_3$) used in studies was passed through a short plug of vacuum dried, activated (Brockmann I), basic alumina prior to use.



Association constants reported for $(2^*)_n$ and $3 \cdot 3$ are the average of two or more replicate experiments and were obtained by fitting chemical shift data to 1:1 binding isotherms using standard, non-linear curve-fitting procedures (see text for reference). Representative chemical shift plots and curve fits for studies of $(2^*)_n$ and $3 \cdot 3$ are shown in Figures 1 and 2 (see this and previous page). The association constant for $2 \cdot 3$ was estimated by integrating signals for the complexed and uncomplexed components in 1:1 mixtures of **2** and **3** at concentrations at which the self-association of **2** and **3** was negligible. Delay times used in acquiring spectra were at least five times the maximum T_1 relaxation time for the signals of **2**, **3**, and $2 \cdot 3$ to insure accurate integration. Representative spectra of 1:1 mixtures of **2** and **3** are shown in the text and in Figure 3.



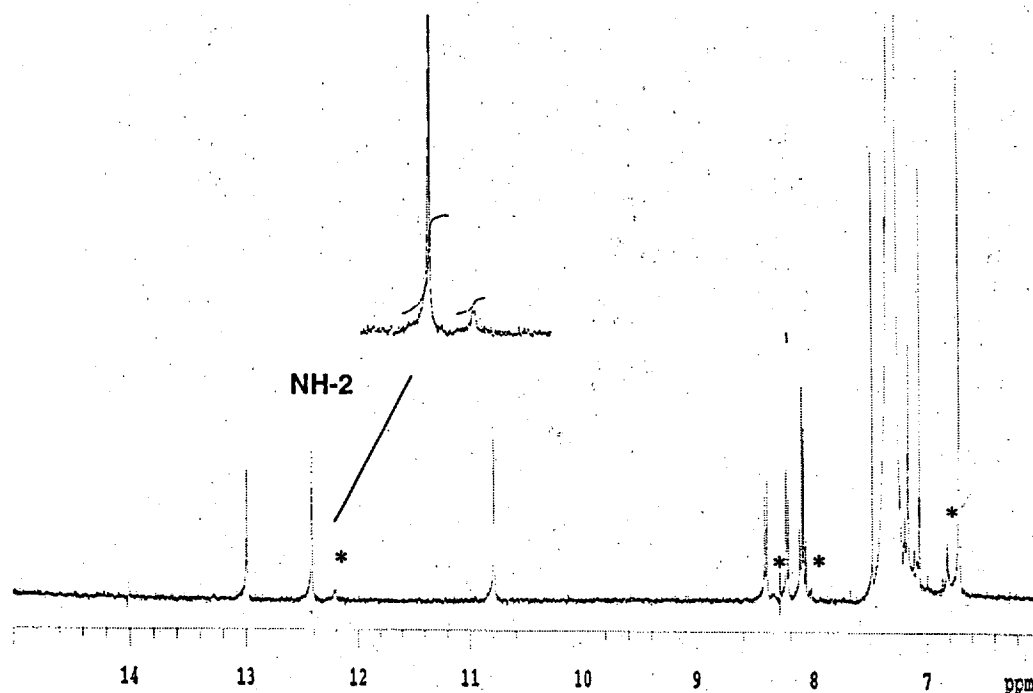


Figure 3. A representative spectrum of a 1:1 mixture of **2** and **3** at a concentration of 72 μM . The percentage of **2**:**3** in this mixture was determined to be ~85% from the relative integration of signals for the complexed and uncomplexed components and corresponds to a K_{assoc} of approximately $5 \times 10^5 \text{ M}^{-1}$. The inset shows the integration of the NH-2 signal of **2** in **2**:**3** and the NH-1 signal in monomer **2**. Similar results were obtained from the integration of the phenyl/H-3 signal of monomer **2** at approximately 6.8 ppm and the phenyl signal of **2**:**3** at approximately 6.7 ppm. *Note: The asterisks denote uncomplexed **2** and **3**.*

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X-RAY CRYSTALLOGRAPHIC DATA FOR COMPOUND 1

Table 1. Crystal data and structure refinement for 1.

Empirical formula	C18 H26 N6 O2
Formula weight	358.45
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 4.5545(12) Å alpha = 88.142(6) deg b = 11.807(3) Å beta = 85.245(6) deg c = 17.539(5) Å gamma = 86.652(6) deg V = 938.0(4) Å ³ Z = 2
from 656 reflns with 4<=theta<=23	
Density (calculated)	1.269 mg/m ³
Absorption coefficient	0.087 mm ⁻¹
Crystal size, color	0.34 x 0.06 x 0.05 mm colorless
Theta range for data collection	1.17 to 23.00 deg
Index ranges	-5<=h<=5, -12<=k<=14, -20<=l<=20
Collection method	0.15 deg \w scans for 0.1667 min/scan
Reflections collected	6036 [primary R(int) = 0.124]
Independent reflections	6036 [1961 obs, I >2sigma(I)]
Absorption correction	None
Refinement (shift/err=-0.001)	Full-matrix least-squares on F ²
Data / restraints / parameters	6036 / 0 / 238
Goodness-of-fit on F ²	1.172
Final R indices (obs data)	R1 = 0.0976, wR2 = 0.2060
R indices (all data)	R1 = 0.2523, wR2 = 0.2393
calc w=1/[δ ² (F _o ²)+(0.0500P) ² +0.0000P] where P=(F _o ² +2F _c ²)/3	
Largest diff. peak and hole	0.354 and -0.367 e.Å ⁻³

Crystal preparation and structure refinement summary for 1.

The data crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber with the (1 0 -1) scattering planes roughly normal to the spindle axis. Crystals were small and severely twinned. The largest available sample was selected for data collection. Two distinct non-merohedral orientations were identified and integrated. Each integrated set was filtered before the sets were combined to removed statistical outliers and limit resolution to 0.91 Å. Reflection with no overlap or complete overlap were combined for refinement.

Systematic conditions suggested the ambiguous space group. Structure was solved by direct methods (Sheldrick, 1998) using non-overlapping data from the primary orientation. H atoms were included as idealized riding contributors. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2 (Sheldrick, 1998). The relative volume of the primary component converged at 0.634(2). The highest peak in the final difference Fourier map was in the vicinity of atom C7; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed slight dependence on amplitude and resolution.

Sheldrick, G.M. (1998). SHELX-97-2. Program for crystal structure solution and refinement. Institute fur anorg chemie, Göttingen, Germany.

Bruker AXS, Inc. (1998). Madison, Wisconsin, USA.

Table 2. Atomic coordinates ($\text{\AA} \times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
N(1)	4086(10)	5001(4)	6946(3)	27(1)
C(2)	5069(13)	4532(5)	6300(4)	29(2)
C(3)	4200(13)	3495(5)	6036(3)	33(2)
C(4)	2124(13)	2949(5)	6488(3)	36(2)
C(5)	-1180(13)	2920(5)	7690(4)	37(2)
C(6)	-2252(14)	3414(5)	8334(4)	40(2)
C(7)	-1125(14)	4495(5)	8488(3)	32(2)
N(8)	920(10)	4977(4)	8044(3)	31(2)
C(9)	1953(13)	4444(5)	7397(4)	30(2)
C(10)	947(13)	3389(5)	7176(4)	33(2)
N(11)	7220(10)	5063(4)	5818(3)	34(2)
C(12)	8790(14)	6045(5)	5929(4)	34(2)
O(13)	10720(9)	6300(3)	5429(2)	40(1)
N(14)	7992(10)	6594(4)	6564(3)	34(1)
C(15)	9859(13)	7477(5)	6803(4)	47(2)
C(16)	8215(14)	8668(5)	6783(3)	48(2)
C(17)	7655(15)	9109(5)	5992(4)	57(2)
C(18)	6074(15)	10296(5)	6013(4)	81(3)
N(19)	-2388(11)	5003(4)	9146(3)	38(2)
C(20)	-1877(15)	6031(6)	9466(4)	42(2)
O(21)	-3329(9)	6334(3)	10055(2)	47(1)
N(22)	122(11)	6659(4)	9086(3)	45(2)
C(23)	837(14)	7741(5)	9399(3)	48(2)
C(24)	2262(14)	8510(5)	8772(3)	51(2)
C(25)	2812(16)	9660(5)	9090(3)	63(2)
C(26)	4250(17)	10444(5)	8503(4)	91(3)

Table 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.
The anisotropic displacement factor exponent takes the form:
 $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

	U11	U22	U33	U23	U13	U12
N(1)	29(4)	20(3)	30(4)	5(3)	14(3)	-3(3)
C(2)	26(4)	33(5)	27(4)	5(4)	2(3)	-2(4)
C(3)	39(5)	27(4)	33(5)	-8(3)	0(4)	-3(4)
C(4)	48(5)	24(4)	37(5)	-1(4)	3(4)	-14(4)
C(5)	44(5)	19(4)	47(5)	1(4)	2(4)	-8(4)
C(6)	46(5)	20(4)	52(6)	6(4)	8(4)	-11(4)
C(7)	39(5)	31(4)	25(5)	-2(3)	4(4)	0(4)
N(8)	35(4)	20(3)	36(4)	6(3)	8(3)	-6(3)
C(9)	36(5)	28(4)	24(4)	-1(4)	7(4)	-4(4)
C(10)	35(5)	28(4)	34(5)	-3(4)	7(4)	-7(4)
N(11)	48(4)	24(3)	31(4)	-1(3)	6(3)	-10(3)
C(12)	45(5)	19(4)	41(5)	-3(4)	-6(4)	-4(4)
O(13)	39(3)	36(3)	43(3)	0(2)	11(2)	-14(2)
N(14)	38(4)	24(3)	38(4)	-5(3)	4(3)	-10(3)
C(15)	53(5)	23(4)	64(5)	-9(4)	5(4)	-13(4)
C(16)	59(5)	34(5)	54(6)	-7(4)	-11(4)	-11(4)
C(17)	89(6)	25(4)	61(6)	6(4)	-20(4)	-9(4)
C(18)	116(7)	29(5)	99(7)	0(4)	-23(5)	0(5)
N(19)	52(4)	25(4)	35(4)	1(3)	8(3)	-12(3)
C(20)	45(5)	30(5)	50(6)	3(4)	5(4)	-5(4)
O(21)	54(3)	35(3)	49(3)	-4(2)	22(3)	-18(2)
N(22)	65(4)	33(4)	36(4)	-6(3)	10(3)	-25(3)
C(23)	77(6)	32(4)	38(5)	-2(4)	-1(4)	-20(4)
C(24)	76(6)	38(5)	42(5)	5(4)	6(4)	-30(4)
C(25)	105(7)	46(5)	41(5)	3(4)	2(4)	-45(5)
C(26)	127(8)	43(5)	101(7)	-7(5)	17(6)	-30(5)

Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. Treatment of hydrogen atoms not specifically described in the refinement summary was "noref."

	x	y	z	U(eq)
H(3)	5025(13)	3193(5)	5565(3)	39
H(4)	1470(13)	2252(5)	6328(3)	43
H(5)	-1900(13)	2211(5)	7575(4)	44
H(6)	-3692(14)	3072(5)	8675(4)	48
H(11)	7670(10)	4738(4)	5376(3)	41
H(14)	6362(10)	6434(4)	6842(3)	40
H(15A)	11692(13)	7487(5)	6458(4)	56
H(15B)	10417(13)	7295(5)	7329(4)	56
H(16A)	6300(14)	8629(5)	7091(3)	58
H(16B)	9393(14)	9213(5)	7026(3)	58
H(17A)	6430(15)	8580(5)	5749(4)	69
H(17B)	9557(15)	9145(5)	5677(4)	69
H(18A)	4038(28)	10237(6)	6233(21)	97
H(18B)	6065(76)	10620(14)	5491(4)	97
H(18C)	7111(49)	10788(10)	6327(18)	97
H(19)	-3741(11)	4611(4)	9405(3)	45
H(22)	1012(11)	6429(4)	8649(3)	54
H(23A)	2206(14)	7591(5)	9805(3)	58
H(23B)	-989(14)	8130(5)	9631(3)	58
H(24A)	4157(14)	8144(5)	8563(3)	62
H(24B)	951(14)	8620(5)	8350(3)	62
H(25A)	907(16)	10022(5)	9295(3)	76
H(25B)	4085(16)	9540(5)	9520(3)	76
H(26A)	4311(88)	11197(12)	8717(9)	109
H(26B)	3114(52)	10501(28)	8051(10)	109
H(26C)	6264(34)	10147(20)	8355(18)	109

Table 5. Bond lengths [Å] and angles [deg] for 1.

N(1)-C(2)	1.311(6)
N(1)-C(9)	1.384(6)
C(2)-N(11)	1.403(6)
C(2)-C(3)	1.412(8)
C(3)-C(4)	1.361(7)
C(4)-C(10)	1.384(7)
C(5)-C(6)	1.330(7)
C(5)-C(10)	1.394(7)
C(6)-C(7)	1.445(7)
C(7)-N(8)	1.308(6)
C(7)-N(19)	1.384(6)
N(8)-C(9)	1.352(6)
C(9)-C(10)	1.427(7)
N(11)-C(12)	1.424(7)
C(12)-O(13)	1.232(6)
C(12)-N(14)	1.322(6)
N(14)-C(15)	1.476(7)
C(15)-C(16)	1.554(7)
C(16)-C(17)	1.503(7)
C(17)-C(18)	1.538(7)
N(19)-C(20)	1.394(7)
C(20)-O(21)	1.230(6)
C(20)-N(22)	1.331(7)
N(22)-C(23)	1.470(7)
C(23)-C(24)	1.529(6)
C(24)-C(25)	1.525(7)
C(25)-C(26)	1.498(7)
C(2)-N(1)-C(9)	117.0(5)
N(1)-C(2)-N(11)	119.4(6)
N(1)-C(2)-C(3)	125.7(6)
N(11)-C(2)-C(3)	114.9(6)
C(4)-C(3)-C(2)	116.8(6)
C(3)-C(4)-C(10)	121.3(6)
C(6)-C(5)-C(10)	123.3(6)
C(5)-C(6)-C(7)	116.9(6)
N(8)-C(7)-N(19)	121.5(6)
N(8)-C(7)-C(6)	123.4(6)
N(19)-C(7)-C(6)	115.1(6)
C(7)-N(8)-C(9)	117.7(6)
N(8)-C(9)-N(1)	115.1(6)
N(8)-C(9)-C(10)	123.7(6)
N(1)-C(9)-C(10)	121.2(6)
C(4)-C(10)-C(5)	127.1(6)
C(4)-C(10)-C(9)	118.0(6)
C(5)-C(10)-C(9)	114.9(6)
C(2)-N(11)-C(12)	130.3(6)
O(13)-C(12)-N(14)	126.8(6)
O(13)-C(12)-N(11)	117.5(6)
N(14)-C(12)-N(11)	115.7(6)
C(12)-N(14)-C(15)	119.4(5)
N(14)-C(15)-C(16)	111.1(5)
C(17)-C(16)-C(15)	114.1(5)
C(16)-C(17)-C(18)	111.3(6)
C(7)-N(19)-C(20)	130.9(6)

O(21)-C(20)-N(22)	123.5(6)
O(21)-C(20)-N(19)	119.9(6)
N(22)-C(20)-N(19)	116.5(6)
C(20)-N(22)-C(23)	119.7(5)
N(22)-C(23)-C(24)	111.0(5)
C(25)-C(24)-C(23)	110.7(5)
C(26)-C(25)-C(24)	113.0(6)

Table 6. Torsion angles [deg] for 1.

C(9)-N(1)-C(2)-N(11)	179.6(5)
C(9)-N(1)-C(2)-C(3)	-1.8(9)
N(1)-C(2)-C(3)-C(4)	1.2(9)
N(11)-C(2)-C(3)-C(4)	179.8(5)
C(2)-C(3)-C(4)-C(10)	-0.5(9)
C(10)-C(5)-C(6)-C(7)	0.4(10)
C(5)-C(6)-C(7)-N(8)	-2.1(9)
C(5)-C(6)-C(7)-N(19)	177.3(6)
N(19)-C(7)-N(8)-C(9)	-177.4(6)
C(6)-C(7)-N(8)-C(9)	2.0(8)
C(7)-N(8)-C(9)-N(1)	179.2(5)
C(7)-N(8)-C(9)-C(10)	-0.2(9)
C(2)-N(1)-C(9)-N(8)	-177.6(5)
C(2)-N(1)-C(9)-C(10)	1.8(8)
C(3)-C(4)-C(10)-C(5)	179.9(6)
C(3)-C(4)-C(10)-C(9)	0.6(9)
C(6)-C(5)-C(10)-C(4)	-178.2(7)
C(6)-C(5)-C(10)-C(9)	1.1(9)
N(8)-C(9)-C(10)-C(4)	178.2(6)
N(1)-C(9)-C(10)-C(4)	-1.3(9)
N(8)-C(9)-C(10)-C(5)	-1.3(9)
N(1)-C(9)-C(10)-C(5)	179.3(6)
N(1)-C(2)-N(11)-C(12)	5.1(9)
C(3)-C(2)-N(11)-C(12)	-173.6(6)
C(2)-N(11)-C(12)-O(13)	175.6(5)
C(2)-N(11)-C(12)-N(14)	-4.8(9)
O(13)-C(12)-N(14)-C(15)	-12.5(10)
N(11)-C(12)-N(14)-C(15)	168.0(5)
C(12)-N(14)-C(15)-C(16)	114.9(6)
N(14)-C(15)-C(16)-C(17)	-67.6(7)
C(15)-C(16)-C(17)-C(18)	-179.0(6)
N(8)-C(7)-N(19)-C(20)	0.0(10)
C(6)-C(7)-N(19)-C(20)	-179.5(6)
C(7)-N(19)-C(20)-O(21)	178.2(6)
C(7)-N(19)-C(20)-N(22)	1.0(9)
O(21)-C(20)-N(22)-C(23)	4.5(10)
N(19)-C(20)-N(22)-C(23)	-178.4(5)
C(20)-N(22)-C(23)-C(24)	-159.7(6)
N(22)-C(23)-C(24)-C(25)	176.3(5)
C(23)-C(24)-C(25)-C(26)	179.2(6)

Table 7. Special geometric details for 1.

Distance D-A

2.822 (0.006) N11 - O13_\$1
2.695 (0.007) N14 - N1
2.833 (0.006) N19 - O21_\$2
2.731 (0.007) N22 - N8

Distance DH

0.880 N11 - H11
0.880 N14 - H14
0.880 N19 - H19
0.880 N22 - H22

Distance H-A

1.966 (0.006) H11 - O13_\$1
2.031 (0.007) H14 - N1
1.954 (0.006) H19 - O21_\$2
2.050 (0.007) H22 - N8

Angle DH-A

163.79 (0.17) N11 - H11 - O13_\$1
131.36 (0.18) N14 - H14 - N1
176.72 (0.20) N19 - H19 - O21_\$2
133.53 (0.18) N22 - H22 - N8

equivalent positions: \$1 -x+2, -y+1, -z+1
\$2 -x-1, -y+1, -z+2

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

3.344 (0.004) x - 5.109 (0.018) y + 9.286 (0.017) z = 5.239 (0.018)

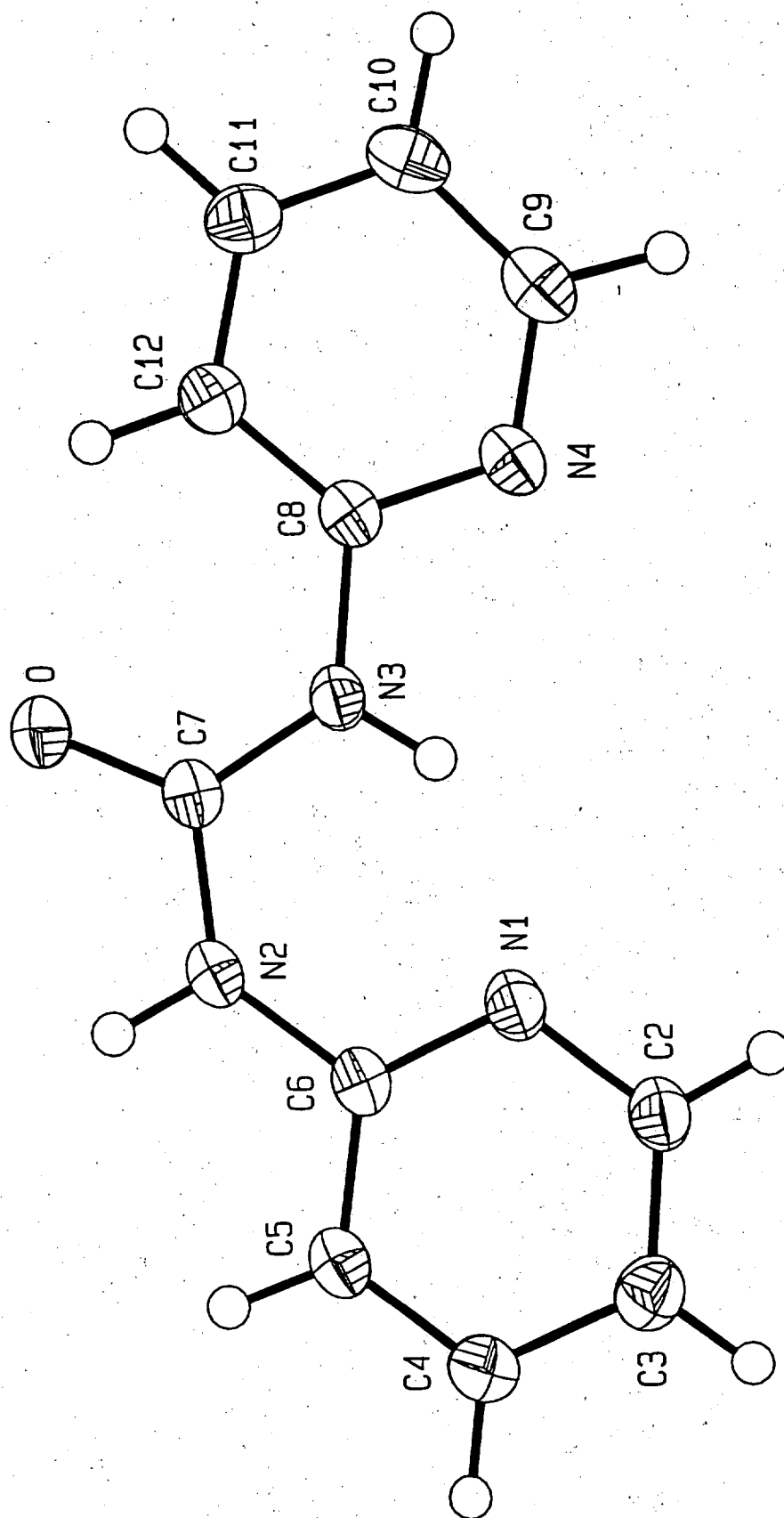
* 0.023 (0.004) N1
* -0.009 (0.005) C2
* -0.015 (0.005) C3
* -0.010 (0.005) C4
* 0.016 (0.005) C5
* 0.003 (0.005) C6
* -0.029 (0.005) C7
* -0.004 (0.004) N8
* 0.013 (0.006) C9
* 0.010 (0.006) C10
-0.009 (0.006) N11
0.118 (0.008) C12

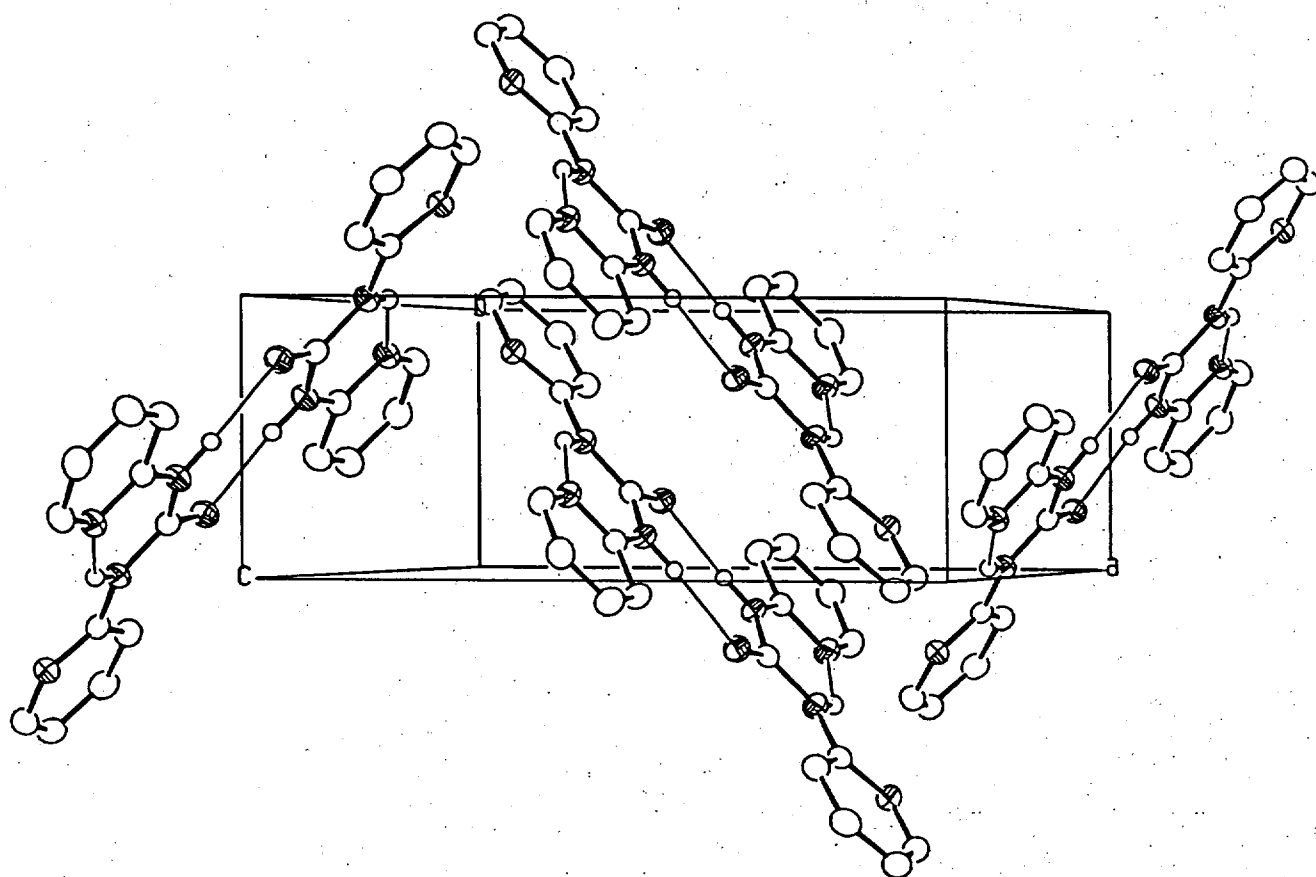
0.169	(0.008)	O13
0.161	(0.008)	N14
0.556	(0.011)	C15
-0.621	(0.012)	C16
-1.768	(0.012)	C17
-2.884	(0.014)	C18
-0.100	(0.007)	N19
-0.157	(0.009)	C20
-0.251	(0.009)	O21
-0.163	(0.009)	N22
-0.186	(0.011)	C23
-0.684	(0.012)	C24
-0.792	(0.014)	C25
-1.257	(0.015)	C26

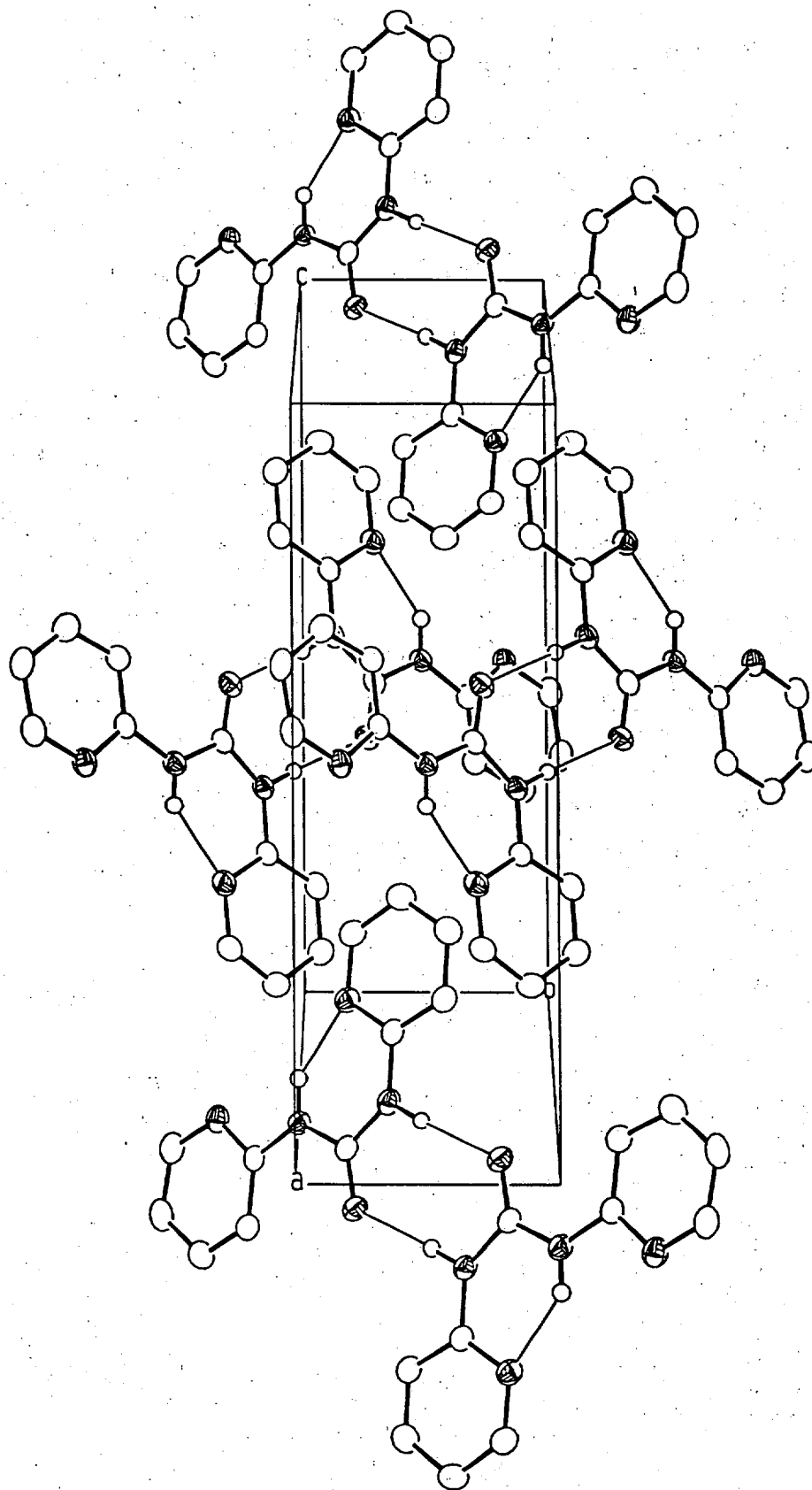
Rms deviation of fitted atoms = 0.015

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

X-RAY CRYSTALLOGRAPHIC DATA FOR *N,N'*-DI-2-PYRIDYL UREA







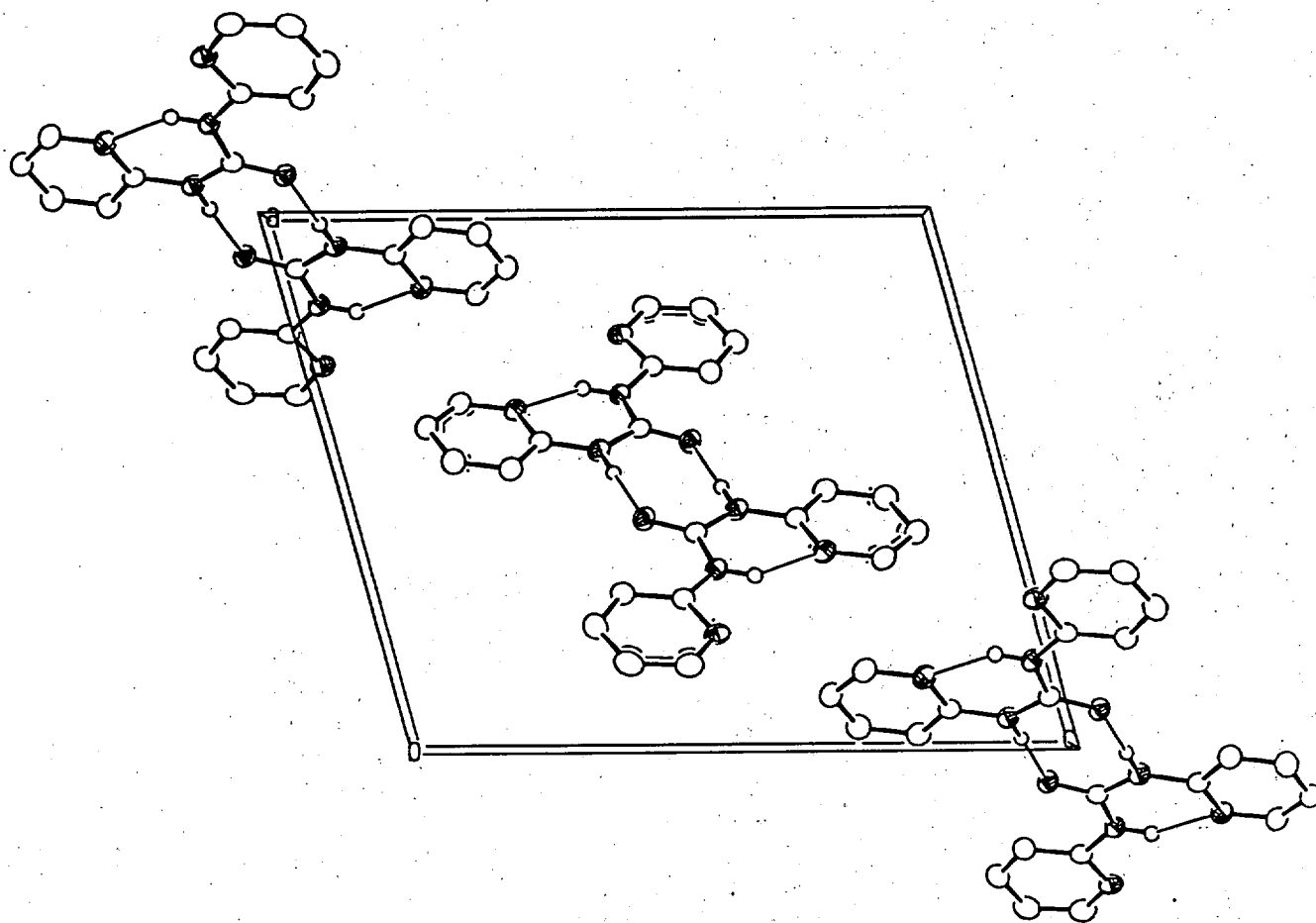


Table 1. Crystal data and structure refinement for 1 (w92p)

Empirical formula	C11 H10 N4 O
Formula weight	214.23
Temperature	198(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ -/n
Unit cell	a = 12.983(2) Å alpha = 90 deg b = 5.2520(10) Å beta = 104.6(2) deg c = 15.472(2) Å gamma = 90 deg V = 1021.0(3) Å ³ Z = 4
Density (calculated)	1.394 Mg/m ³
Absorption coefficient	0.095 mm ⁻¹
F(000)	448
Crystal size	0.70 x 0.30 x 0.16 mm
Theta range for data collection	2.72 to 26.47 deg
Index ranges	0 ≤ h ≤ 16, -6 ≤ k ≤ 0, -19 ≤ l ≤ 18
Reflections collected	2206
Independent reflections	2113 [R(int) = 0.0263]
Absorption correction	Not applied
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2113 / 0 / 186
Goodness-of-fit on F ²	1.062
R indices [1597 I > 2σ(I)]	R1 = 0.0377, wR2 = 0.0990
R indices (all data)	R1 = 0.0625, wR2 = 0.1140
Extinction coefficient	0.014(4)
Largest diff. peak and hole	0.172 and -0.169 e/Å ³

Crystal data and structure refinement summary for 1

The columnar, colorless translucent data crystal was mounted using epoxy to a thin glass fiber with the (6 -1 1) scattering planes roughly normal to the spindle axis. The data crystal was bound by the (1 0 -1), (-1 0 1), (1 0 1), (-1 0 -1), (0 1 0) and (0 -1 0) faces. Distances from the crystal center to these facial boundaries were 0.08, 0.08, 0.15, 0.15, 0.32 and 0.35 mm, respectively. Data were measured at 198 K on an Enraf-Nonius CAD4 diffractometer. Crystal and refinement details are given in Table 1. Systematic conditions suggested the unambiguous space group P 2₁/n. Periodically monitored standard intensities showed no decay. Step-scanned intensity data were reduced by profile analysis (Coppens, 1972) and corrected for Lorentz-polarization effects. Scattering factors and anomalous dispersion terms were taken from standard tables (Wilson, 1992).

The structure was solved by direct methods (Sheldrick, 1990); correct positions for all non-H atoms were deduced from an E-map. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for H atoms. All H atoms were refined with isotropic thermal parameters. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 (Sheldrick, 1993) was indicated by the maximum shift/error for the last cycle. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

Coppens, P., Blessing, R.H. and Becker, P. (1972). J. Appl. Cryst. 7, 488.

Johnson, C.K. (1971). ORTEP-II. Fortran thermal ellipsoid plot program, ORNL-3794, Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G.M. (1990). SHELXS-86. Acta Cryst. A46, 467-473.

Sheldrick, G.M. (1993). SHELXL-93. In preparation for J. Appl. Cryst.

Wilson, A.J.C., Ed. (1992). "International Tables for X-ray Crystallography" Vol. C. Kluwer Academic Publishers, Dordrecht: (a) scattering factors, pp. 500-502; (b) anomalous dispersion corrections, pp. 219-222.

Figure captions

Figure 1. ORTEP plot showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms (Johnson, 1971).

Figure 2. ORTEP packing diagram showing the contents of the unit cell with respect to the three edges. H-bonds shown as thin lines (Johnson, 1971)

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1 (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor)

	x	y	z	U(eq)
N(1)	8673(1)	2009(2)	2018(1)	36(1)
C(2)	8544(1)	2226(3)	2851(1)	40(1)
C(3)	9008(1)	4095(3)	3439(1)	43(1)
C(4)	9633(1)	5886(3)	3153(1)	44(1)
C(5)	9778(1)	5725(3)	2307(1)	39(1)
C(6)	9282(1)	3745(3)	1757(1)	31(1)
N(2)	9447(1)	3581(2)	903(1)	33(1)
O	9289(1)	2271(2)	-507(1)	35(1)
C(7)	9041(1)	1960(3)	201(1)	30(1)
N(3)	8377(1)	100(2)	353(1)	32(1)
C(8)	7852(1)	-1747(3)	-249(1)	31(1)
N(4)	7230(1)	-3252(2)	97(1)	37(1)
C(9)	6695(1)	-5092(3)	-426(1)	43(1)
C(10)	6743(1)	-5514(3)	-1295(1)	44(1)
C(11)	7392(1)	-3929(3)	-1637(1)	44(1)
C(12)	7958(1)	-2016(3)	-1118(1)	37(1)

Table 3. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1

	x	y	z	U(eq)
H(2)	8079(14)	943(35)	3003(12)	47(5)
H(3)	8871(14)	4214(35)	4018(13)	50(5)
H(4)	9977(15)	7255(38)	3549(13)	52(5)
H(5)	10190(14)	6942(34)	2081(12)	46(5)
H(2N)	9864(13)	4838(36)	766(11)	42(4)
H(3N)	8260(13)	108(34)	891(13)	48(5)
H(9)	6245(14)	-6178(36)	-137(12)	50(5)
H(10)	6346(16)	-6860(40)	-1649(13)	60(5)
H(11)	7471(14)	-4209(34)	-2249(13)	51(5)
H(12)	8443(14)	-922(33)	-1344(11)	41(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1
(anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$)

	U11	U22	U33	U23	U13	U12
N(1)	37(1)	35(1)	40(1)	2(1)	15(1)	-5(1)
C(2)	40(1)	40(1)	42(1)	4(1)	17(1)	-4(1)
C(3)	43(1)	49(1)	39(1)	0(1)	16(1)	0(1)
C(4)	47(1)	42(1)	44(1)	-7(1)	12(1)	-7(1)
C(5)	41(1)	34(1)	43(1)	3(1)	13(1)	-6(1)
C(6)	29(1)	29(1)	36(1)	5(1)	9(1)	3(1)
N(2)	33(1)	30(1)	37(1)	4(1)	12(1)	-4(1)
O	38(1)	33(1)	36(1)	6(1)	13(1)	-2(1)
C(7)	29(1)	28(1)	36(1)	7(1)	9(1)	4(1)
N(3)	34(1)	30(1)	34(1)	2(1)	12(1)	-3(1)
C(8)	28(1)	26(1)	38(1)	4(1)	7(1)	5(1)
N(4)	33(1)	33(1)	47(1)	2(1)	13(1)	-2(1)
C(9)	36(1)	33(1)	59(1)	3(1)	12(1)	-3(1)
C(10)	39(1)	32(1)	57(1)	-6(1)	3(1)	0(1)
C(11)	46(1)	41(1)	42(1)	-4(1)	7(1)	4(1)
C(12)	38(1)	34(1)	38(1)	3(1)	10(1)	2(1)

Table 5. Bond lengths [Å] and angles [deg] for 1

N(1)-C(6)	1.334(2)
N(1)-C(2)	1.346(2)
C(2)-C(3)	1.370(3)
C(2)-H(2)	0.97(2)
C(3)-C(4)	1.385(2)
C(3)-H(3)	0.96(2)
C(4)-C(5)	1.372(2)
C(4)-H(4)	0.98(2)
C(5)-C(6)	1.394(3)
C(5)-H(5)	0.96(2)
C(6)-N(2)	1.394(2)
N(2)-C(7)	1.376(2)
N(2)-H(2N)	0.91(2)
O-C(7)	1.228(2)
C(7)-N(3)	1.361(2)
N(3)-C(8)	1.397(2)
N(3)-H(3N)	0.88(2)
C(8)-N(4)	1.334(2)
C(8)-C(12)	1.392(2)
N(4)-C(9)	1.337(3)
C(9)-C(10)	1.379(2)
C(9)-H(9)	1.00(2)
C(10)-C(11)	1.381(3)
C(10)-H(10)	0.96(2)
C(11)-C(12)	1.377(3)
C(11)-H(11)	0.99(2)
C(12)-H(12)	0.98(2)
C(6)-N(1)-C(2)	117.3(2)
N(1)-C(2)-C(3)	123.8(2)
N(1)-C(2)-H(2)	114.0(11)
C(3)-C(2)-H(2)	122.2(11)
C(2)-C(3)-C(4)	118.0(2)
C(2)-C(3)-H(3)	120.9(11)
C(4)-C(3)-H(3)	121.0(11)
C(5)-C(4)-C(3)	119.7(2)
C(5)-C(4)-H(4)	119.5(11)
C(3)-C(4)-H(4)	120.8(11)
C(4)-C(5)-C(6)	118.4(2)
C(4)-C(5)-H(5)	122.2(11)
C(6)-C(5)-H(5)	119.4(11)
N(1)-C(6)-C(5)	122.87(14)
N(1)-C(6)-N(2)	119.3(2)
C(5)-C(6)-N(2)	117.85(14)
C(7)-N(2)-C(6)	131.78(12)
C(7)-N(2)-H(2N)	113.4(11)
C(6)-N(2)-H(2N)	114.7(11)

O-C(7)-N(3)	124.6(2)
O-C(7)-N(2)	119.12(12)
N(3)-C(7)-N(2)	116.24(14)
C(7)-N(3)-C(8)	127.39(13)
C(7)-N(3)-H(3N)	115.2(12)
C(8)-N(3)-H(3N)	117.4(12)
N(4)-C(8)-C(12)	123.0(2)
N(4)-C(8)-N(3)	112.74(13)
C(12)-C(8)-N(3)	124.30(14)
C(8)-N(4)-C(9)	117.39(14)
N(4)-C(9)-C(10)	124.2(2)
N(4)-C(9)-H(9)	114.5(11)
C(10)-C(9)-H(9)	121.3(10)
C(9)-C(10)-C(11)	117.3(2)
C(9)-C(10)-H(10)	121.7(12)
C(11)-C(10)-H(10)	121.1(12)
C(12)-C(11)-C(10)	120.2(2)
C(12)-C(11)-H(11)	119.9(11)
C(10)-C(11)-H(11)	119.8(11)
C(11)-C(12)-C(8)	118.0(2)
C(11)-C(12)-H(12)	121.1(10)
C(8)-C(12)-H(12)	120.9(10)

Table 6. Torsion angles [deg] for 1

C(6)-N(1)-C(2)-C(3)	-0.6(2)
N(1)-C(2)-C(3)-C(4)	0.9(3)
C(2)-C(3)-C(4)-C(5)	-0.7(2)
C(3)-C(4)-C(5)-C(6)	0.2(2)
C(2)-N(1)-C(6)-C(5)	0.0(2)
C(2)-N(1)-C(6)-N(2)	179.34(12)
C(4)-C(5)-C(6)-N(1)	0.2(2)
C(4)-C(5)-C(6)-N(2)	-179.16(13)
N(1)-C(6)-N(2)-C(7)	4.1(2)
C(5)-C(6)-N(2)-C(7)	-176.54(14)
C(6)-N(2)-C(7)-O	177.51(13)
C(6)-N(2)-C(7)-N(3)	-2.3(2)
O-C(7)-N(3)-C(8)	-0.9(2)
N(2)-C(7)-N(3)-C(8)	178.96(12)
C(7)-N(3)-C(8)-N(4)	-177.99(12)
C(7)-N(3)-C(8)-C(12)	2.1(2)
C(12)-C(8)-N(4)-C(9)	0.2(2)
N(3)-C(8)-N(4)-C(9)	-179.74(13)
C(8)-N(4)-C(9)-C(10)	-0.4(2)
N(4)-C(9)-C(10)-C(11)	0.3(3)
C(9)-C(10)-C(11)-C(12)	-0.1(2)
C(10)-C(11)-C(12)-C(8)	0.0(2)
N(4)-C(8)-C(12)-C(11)	0.0(2)
N(3)-C(8)-C(12)-C(11)	179.92(13)

Table 7. H-bonding distances [Å] and angles [deg] for 1

Distance NH

0.884 (0.018) N3 - H3N
0.912 (0.018) N2 - H2N

Distance H-N

1.963 (0.019) H3N - N1

Distance N--N

2.701 (0.002) N3 - N1

Angle NH-N

140.02 (1.56) N3 - H3N - N1

Distance H-O

1.974 (0.019) H2N - O_\$2

Distance N--O

2.885 (0.002) N2 - O_\$2

Angle NH-O

176.01 (1.57) N2 - H2N - O_\$2

equivalent position: \$2 -x+2, -y+1, -z

Table 8. Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$$9.620 (0.034) x - 3.038 (0.011) y + 2.219 (0.012) z = 8.180 (0.029)$$

*	0.001 (0.001)	N1
*	-0.004 (0.001)	C2
*	0.004 (0.001)	C3
*	-0.002 (0.001)	C4
*	-0.001 (0.001)	C5
*	0.002 (0.001)	C6
	-0.028 (0.017)	H2
	-0.035 (0.018)	H3
	0.001 (0.019)	H4
	-0.025 (0.017)	H5
	0.020 (0.002)	N2
	-0.034 (0.003)	C7
	-0.073 (0.003)	N3
	-0.047 (0.003)	O
	-0.151 (0.003)	C8
	-0.215 (0.004)	N4
	-0.287 (0.004)	C9
	-0.306 (0.005)	C10
	-0.239 (0.005)	C11
	-0.160 (0.004)	C12

Rms deviation of fitted atoms = 0.003

$$9.182 (0.033) x - 3.293 (0.012) y + 2.133 (0.012) z = 7.732 (0.027)$$

Angle to previous plane (with approximate esd) = 3.49 (0.22)

*	0.000 (0.001)	C8
*	-0.001 (0.001)	N4
*	0.002 (0.001)	C9
*	-0.001 (0.001)	C10
*	0.000 (0.001)	C11
*	0.001 (0.001)	C12
	0.008 (0.018)	H9
	0.003 (0.020)	H10
	0.034 (0.018)	H11
	0.037 (0.017)	H12
	0.002 (0.002)	N3
	-0.034 (0.003)	C7
	-0.060 (0.003)	O
	-0.045 (0.003)	N2
	-0.067 (0.004)	C6

-0.147 (0.004) C5
-0.153 (0.005) C4
-0.076 (0.005) C3
-0.011 (0.004) C2
0.000 (0.003) N1

Rms deviation of fitted atoms = 0.001

9.305 (0.033) x - 3.225 (0.011) y + 2.155 (0.008) z = 7.805 (0.027)

Angle to previous plane (with approximate esd) = 0.95 (0.21)

* 0.052 (0.001) N1
* 0.042 (0.001) C2
* -0.003 (0.001) C3
* -0.060 (0.001) C4
* -0.056 (0.001) C5
* 0.003 (0.001) C6
* 0.025 (0.001) N2
* 0.019 (0.001) C7
* -0.004 (0.001) O
* 0.034 (0.001) N3
* 0.012 (0.001) C8
* 0.009 (0.001) C12
* -0.013 (0.001) C11
* -0.031 (0.001) C10
* -0.024 (0.001) C9
* -0.007 (0.001) N4
-0.021 (0.017) H2N
0.038 (0.017) H3N

Rms deviation of fitted atoms = 0.031