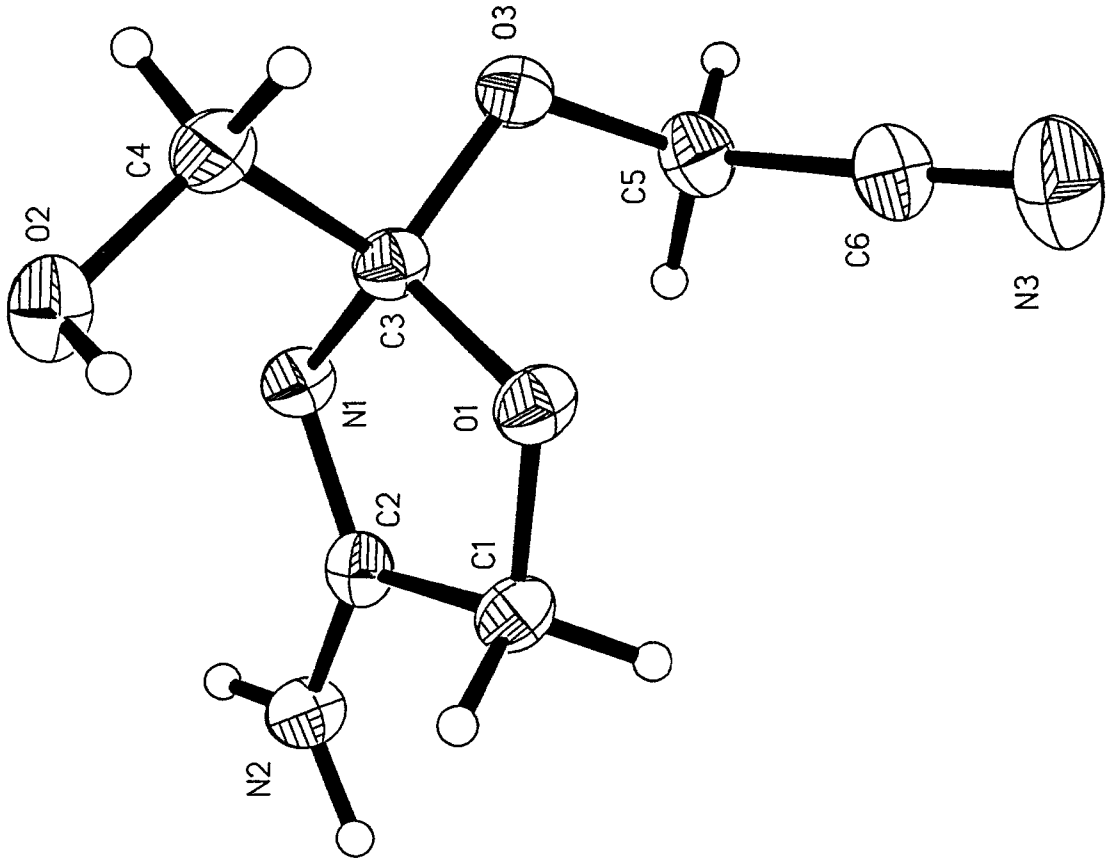
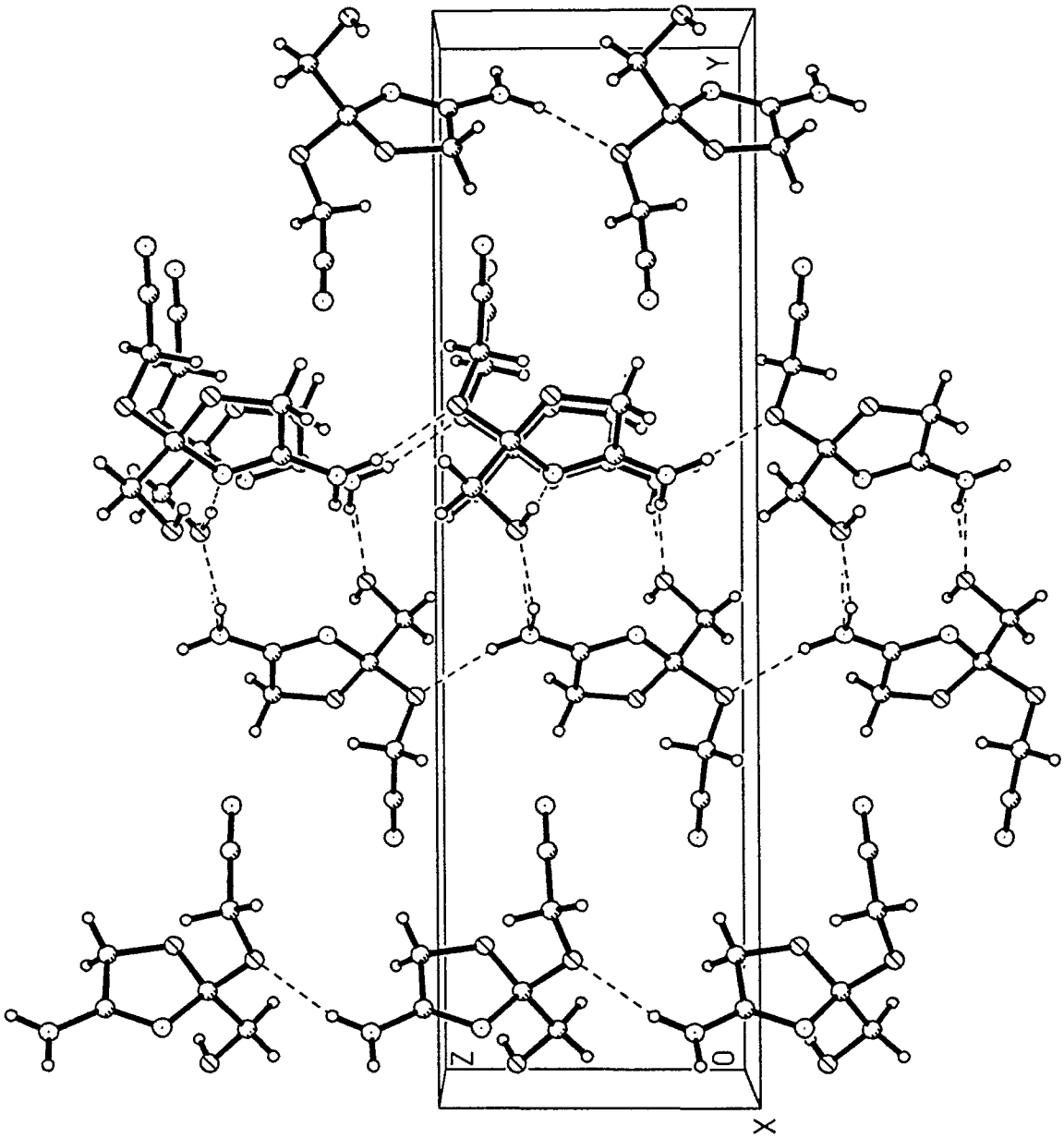
JOC The Journal of Organic Chemistry

J. Org. Chem., 1997, 62(16), 5522-5525, DOI:10.1021/jo962185r




Y
Z
O
X

STRUCTURE DETERMINATION SUMMARY

Crystal Data

Empirical Formula	$C_6 H_9 N_3 O_3$
Color; Habit	colorless block
Crystal size (mm)	0.2 x 0.45 x 0.45
Crystal System	Monoclinic
Space Group	$P2_1/n$
Unit Cell Dimensions	$\underline{a}$ = 4.906(2) Å
	$\underline{b}$ = 23.694(10) Å
	$\underline{c}$ = 6.677(3) Å
	β = 91.33(4)°
Volume	775.9(6) $Å^3$
Z	4
Formula weight	171.2
Density(calc.)	1.465 Mg/m^3
Absorption Coefficient	0.111 mm^{-1}
F(000)	360

Data Collection

Diffractometer Used	Siemens R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature (K)	169
Monochromator	Highly oriented graphite crystal
2θ Range	3.0 to 60.0°
Scan Type	Wyckoff
Scan Speed	Constant; 4.99°/min. in ω
Scan Range (ω)	0.60°
Background Measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 0.5% of total scan time
Standard Reflections	3 measured every 197 reflections
Index Ranges	$0 \leq h \leq 6$, $0 \leq k \leq 33$ $-9 \leq l \leq 9$
Reflections Collected	2488
Independent Reflections	2257 (R_{int} = 1.24%)
Observed Reflections	1634 ($F > 4.0\sigma(F)$)
Absorption Correction	N/A

Solution and Refinement

System Used	Siemens SHELXTL PLUS (PC Version)
Solution	Direct Methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\sum w(F_o-F_c)^2$
Absolute Structure	N/A
Extinction Correction	N/A
Hydrogen Atoms	Riding model, fixed isotropic U
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of Parameters Refined	117
Final R Indices (obs. data)	R = 4.52 %, wR = 6.21 %
R Indices (all data)	R = 6.76 %, wR = 7.09 %
Goodness-of-Fit	1.34
Largest and Mean Δ/σ	0.016, 0.003
Data-to-Parameter Ratio	14.0:1
Largest Difference Peak	0.32 $e\text{Å}^{-3}$
Largest Difference Hole	-0.21 $e\text{Å}^{-3}$

Table 1. Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2 x10^4$)

	x	y	z	U(eq)
O(1)	6797(3)	1380(1)	8589(2)	237(3)
O(3)	9593(3)	1327(1)	5812(2)	254(4)
O(2)	5172(3)	234(1)	7590(2)	281(4)
N(1)	10362(3)	739(1)	8654(2)	209(4)
N(2)	11389(3)	729(1)	12080(2)	250(4)
N(3)	7865(4)	2694(1)	6623(4)	526(7)
C(3)	8350(3)	1010(1)	7387(3)	207(4)
C(2)	9976(3)	900(1)	10471(3)	203(4)
C(4)	6484(4)	600(1)	6274(3)	256(5)
C(1)	7715(3)	1322(1)	10625(3)	227(5)
C(5)	11047(4)	1813(1)	6463(3)	280(5)
C(6)	9234(4)	2307(1)	6577(3)	326(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2. Bond lengths (Å)

O(1)-C(3)	1.423 (2)	O(1)-C(1)	1.428 (2)
O(3)-C(3)	1.439 (2)	O(3)-C(5)	1.418 (2)
O(2)-H(2)	0.898 (26)	O(2)-C(4)	1.401 (2)
N(1)-C(3)	1.436 (2)	N(1)-C(2)	1.290 (2)
N(2)-C(2)	1.328 (2)	N(3)-C(6)	1.137 (3)
C(3)-C(4)	1.518 (3)	C(2)-C(1)	1.499 (2)
C(5)-C(6)	1.473 (3)		

Table 3. Bond angles (°)

C(3)-O(1)-C(1)	108.5(1)	C(3)-O(3)-C(5)	114.8(1)
H(2)-O(2)-C(4)	108.4(17)	C(3)-N(1)-C(2)	107.9(1)
O(1)-C(3)-O(3)	109.4(1)	O(1)-C(3)-N(1)	108.2(1)
O(3)-C(3)-N(1)	111.5(1)	O(1)-C(3)-C(4)	110.3(1)
O(3)-C(3)-C(4)	103.8(1)	N(1)-C(3)-C(4)	113.6(1)
N(1)-C(2)-N(2)	125.8(2)	N(1)-C(2)-C(1)	112.8(1)
N(2)-C(2)-C(1)	121.4(2)	O(2)-C(4)-C(3)	111.7(2)
O(1)-C(1)-C(2)	102.5(1)	O(3)-C(5)-C(6)	111.2(2)
N(3)-C(6)-C(5)	178.2(2)		

Table 4. Anisotropic displacement coefficients ($Å^2 x 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	208(6)	252(6)	250(6)	73(5)	6(5)	-34(5)
O(3)	293(7)	244(6)	228(6)	-13(5)	47(5)	0(5)
O(2)	192(6)	235(7)	419(8)	26(5)	54(6)	-18(5)
N(1)	170(6)	231(7)	225(7)	30(5)	9(5)	-14(5)
N(2)	238(7)	283(8)	228(7)	51(6)	-12(6)	-13(6)
N(3)	529(13)	326(10)	724(15)	101(9)	57(11)	61(10)
C(3)	188(7)	223(8)	212(8)	33(6)	19(6)	-16(6)
C(2)	158(7)	194(8)	259(9)	-13(6)	17(6)	-1(6)
C(4)	243(8)	260(9)	265(9)	-1(7)	-10(7)	-32(7)
C(1)	195(8)	247(8)	239(8)	29(6)	14(6)	-43(7)
C(5)	241(8)	260(9)	339(10)	4(7)	23(7)	43(7)
C(6)	333(10)	253(9)	392(11)	-18(8)	6(8)	32(8)

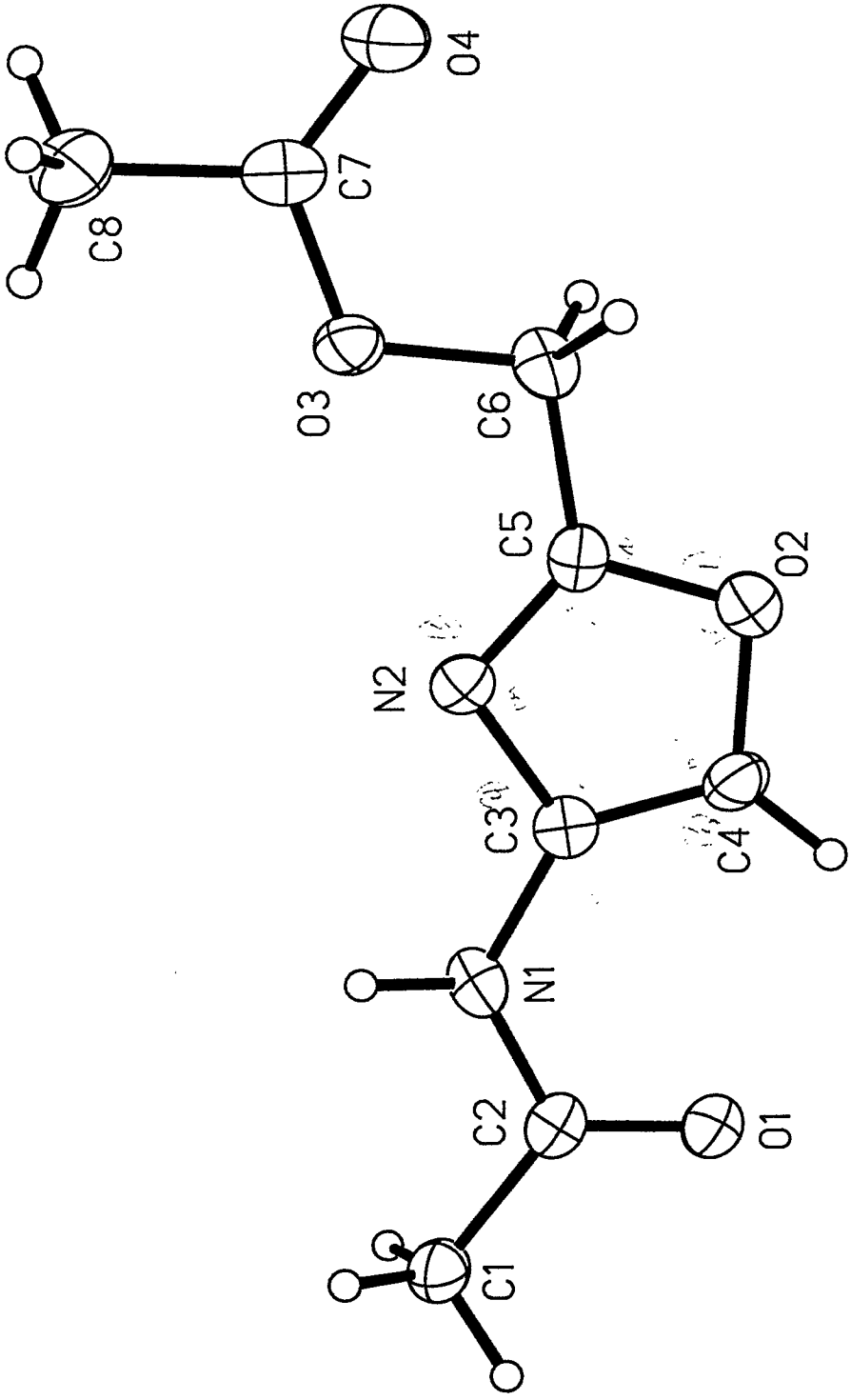
The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 5. H-Atom coordinates ($x10^4$) and isotropic displacement coefficients ($Å^2 x 10^3$)

	x	y	z	U
H(2)	3684(54)	409(11)	8045(40)	44(7)
H(2A)	10986	865	13297	40(5)
H(2B)	12745	477	11953	40(5)
H(4A)	5138	808	5512	33(4)
H(4B)	7533	382	5355	33(4)
H(1B)	6288	1182	11448	36(4)
H(1A)	8363	1675	11161	36(4)
H(5A)	12481	1891	5548	40(5)
H(5B)	11865	1743	7759	40(5)

15 peaks from centering film measurements, 6-25 degrees two-theta, gave unit cell and orientation. All hydrogens were located in difference maps, but all except H(2) were placed at idealized positions. 2602 intensity measurements at 5 degrees/minute took 14 hours, with liquid nitrogen cooling. $100 + $70 + $25 = $195



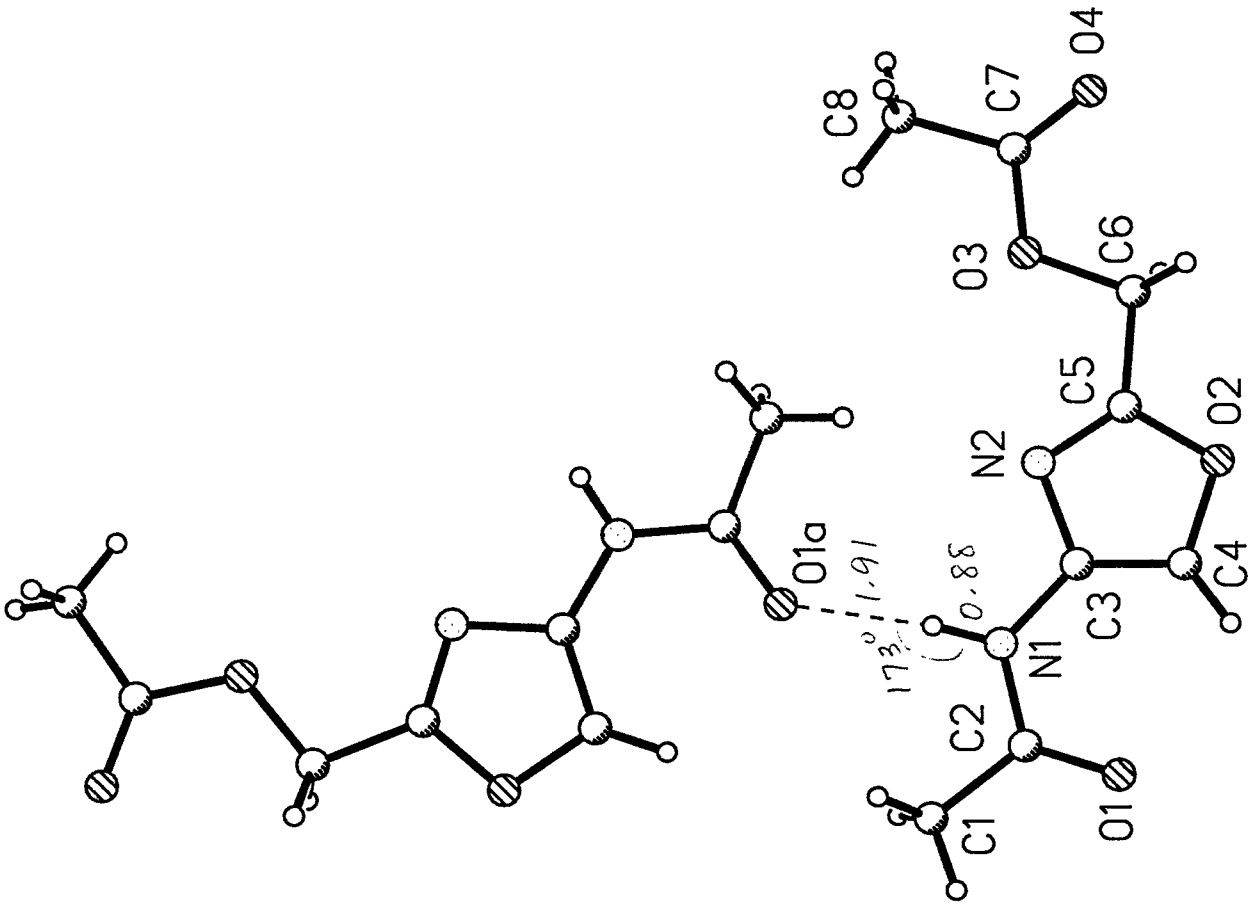


Table 1. Crystal data for .

Identification code	mn507
Empirical formula	$C_8H_{10}N_2O_4$
Formula weight	198.18
Crystal size	0.55 x 0.45 x 0.30 mm
Crystal habit	parallelepiped
Crystal color	colorless
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	a = 9.389(2) Å α = 90° b = 14.786(2) Å β = 90° c = 6.5170(10) Å γ = 90°
Volume	904.7(3) $Å^3$
Z	4
Density (calculated)	1.455 $Mg \cdot m^3$
Absorption coefficient	1.011 mm^{-1}
F(000)	416
Absorption correction[1]	XABS2
Max. and min. transmission	0.78 and 0.63

1) XABS2 (Sean Parkin Dec. 1992) calculates 24 coefficients from a least-squares fit of (1/A vs $\sin^2(\theta)$) to a cubic equation in $\sin^2(\theta)$ by minimization of Fo^2 and Fc^2 differences.

Table 2. Data collection for .

Diffractometer	Syntex $P2_1$
Temperature	130(2) K
Radiation source	normal-focus sealed tube
Wavelength	1.54178 Å (CuKα)
Monochromator	graphite
θ range for data collection	5.58 to 56.99°
Scan type	2θ–ω
Index ranges	$-1 \le h \le 10$, $-1 \le k \le 16$, $-1 \le \ell \le 7$
Reflections collected	1058
Independent reflections	801 (R_{int} = 0.013)
Standard reflections	2
Stability of standards	<0.1 % decay

Table 3. Solution and refinement of .

System for solution	SHELTL PLUS (Sheldrick, 1990)
Structure solution	direct
System for refinement	SHELXL-93 (Sheldrick, 1993)
Refinement method	Full-matrix least-squares on F^2
Hydrogen atoms	riding
Data / restraints / parameters	801 / 1 / 129
Goodness-of-fit on F^2	0.658
Final R indices [$I>2\sigma(I)$]	R1 = 0.0292, wR2 = 0.0687
Weighting scheme	$w^{-1} = \sigma^2(Fo^2) + (0.0500P)^2 + 1.50P$, where $P = (Fo^2 + 2Fc^2)/3$
R indices (all data)	R1 = 0.0310, wR2 = 0.0702
Absolute structure parameter	0.6(8)
Largest diff. peak and hole	0.171 and -0.163 $eÅ^{-3}$

1) $R1 = \sum||Fo-Fc||/\sum|Fo|$

$wR2 = [\sum[w(Fo^2-Fc^2)^2]/\sum[w(Fo^2)^2]]^{½}$

2) $Goodness\text{-}of\text{-}Fit = [\sum[w(Fo^2-Fc^2)^2]/(M-N)]^{½}$

where M is the number of reflections

and N is the number of parameters refined.

Table 4. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3]

for .

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	3801(2)	2746(1)	2719(13)	31(1)
O(2)	2305(2)	5434(1)	2752(12)	28(1)
O(3)	-1434(1)	5944(1)	2787(12)	25(1)
O(4)	-2049(2)	7406(1)	2751(12)	36(1)
N(1)	1475(2)	3074(1)	2802(13)	21(1)
N(2)	414(2)	4533(1)	2787(12)	21(1)
C(1)	2141(2)	1505(1)	2733(17)	29(1)
C(2)	2554(2)	2482(1)	2803(12)	22(1)
C(3)	1645(2)	4014(1)	2788(15)	19(1)
C(4)	2788(2)	4545(1)	2780(17)	26(1)
C(5)	874(2)	5354(1)	2790(12)	21(1)
C(6)	40(2)	6207(1)	2767(13)	24(1)
C(7)	-2388(2)	6621(1)	2775(16)	24(1)
C(8)	-3876(2)	6273(2)	2782(16)	32(1)

Table 5. Bond lengths [Å] for .

O(1)-C(2)	1.236(3)	O(2)-C(5)	1.349(2)
O(2)-C(4)	1.391(2)	O(3)-C(7)	1.344(2)
O(3)-C(6)	1.437(2)	O(4)-C(7)	1.203(3)
N(1)-C(2)	1.339(3)	N(1)-C(3)	1.398(3)
N(2)-C(5)	1.288(3)	N(2)-C(3)	1.388(2)
C(1)-C(2)	1.496(3)	C(3)-C(4)	1.330(3)
C(5)-C(6)	1.484(3)	C(7)-C(8)	1.489(3)

Table 6. Bond angles [°] for .

C(5)-O(2)-C(4)	104.0(2)	C(7)-O(3)-C(6)	116.1(2)
C(2)-N(1)-C(3)	124.3(2)	C(5)-N(2)-C(3)	104.0(2)
O(1)-C(2)-N(1)	120.7(2)	O(1)-C(2)-C(1)	123.3(2)
N(1)-C(2)-C(1)	115.8(2)	C(4)-C(3)-N(2)	110.2(2)
C(4)-C(3)-N(1)	132.8(2)	N(2)-C(3)-N(1)	117.0(2)
C(3)-C(4)-O(2)	107.2(2)	N(2)-C(5)-O(2)	114.6(2)
N(2)-C(5)-C(6)	128.6(2)	O(2)-C(5)-C(6)	116.8(2)
O(3)-C(6)-C(5)	106.1(2)	O(4)-C(7)-O(3)	122.9(2)
O(4)-C(7)-C(8)	125.6(2)	O(3)-C(7)-C(8)	111.6(2)

Table 7. Anisotropic displacement parameters [$Å^2$ x 10^3] for .

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	21(1)	30(1)	41(1)	6(3)	-2(3)	0(1)
O(2)	26(1)	24(1)	34(1)	-2(3)	-1(3)	-2(1)
O(3)	26(1)	22(1)	25(1)	4(3)	-5(3)	2(1)
O(4)	39(1)	26(1)	44(1)	-3(4)	-2(4)	5(1)
N(1)	20(1)	22(1)	22(1)	-8(3)	13(3)	-2(1)
N(2)	23(1)	24(1)	16(1)	2(3)	0(3)	1(1)
C(1)	26(1)	25(1)	36(2)	-3(4)	-6(4)	1(1)
C(2)	22(1)	28(1)	16(1)	-2(4)	0(5)	2(1)
C(3)	24(1)	23(1)	10(1)	-2(4)	3(4)	1(1)
C(4)	25(1)	25(1)	27(1)	1(4)	-7(4)	4(1)
C(5)	22(1)	29(1)	12(1)	9(4)	-2(4)	-4(1)
C(6)	26(1)	24(1)	21(1)	-13(4)	8(4)	-2(1)
C(7)	35(1)	26(1)	11(1)	-1(4)	0(5)	5(1)
C(8)	31(1)	36(1)	30(2)	-5(5)	6(5)	5(1)

Table 8. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for .

	x	y	z	U(eq)
H(1)	601(2)	2858(1)	2812(13)	26
H(1A)	1900(16)	1337(3)	1321(17)	35
H(1B)	1314(11)	1405(3)	3621(25)	35
H(1C)	2940(7)	1134(2)	3211(29)	35
H(4)	3754(2)	4353(1)	2791(17)	31
H(6A)	267(2)	6579(1)	3986(13)	28
H(6B)	258(2)	6562(1)	1518(13)	28
H(8A)	-3885(3)	5649(4)	2273(29)	39
H(8B)	-4469(4)	6652(7)	1893(23)	39
H(8C)	-4252(6)	6288(10)	4184(16)	39