CHIRAL CHELATING SYSTEMS: UNUSUAL FORMATION AND X-RAY-STRUCTURE OF *RAC*-3A(R),4(S),5,9B(S)-TETRAHYDRO-4-(PYRID-2-YL)-3*H*-CYCLOPENTA[C]QUINOLINE

Klaus Wurst1), Michael R. Buchmeiser*2)
1) Institute of General, Inorganic and Theoretical Chemistry, 2) Institute of Analytical Chemistry and Radiochemistry. University of Innsbruck, Innrain 52a, A-6020 Innsbruck. AUSTRIA.
e-mail: michael.r.buchmeiser@uibk.ac.at.

Abstract

N-Phenyl-2-(pyrid-2-yl)imine reacts with zinc iodide to give the corresponding diiodo zinc imine complex **1**. **1** reacts with cyclopentadiene (CPD) at 0°C under ultrasound-assisted conditions to yield *rac*-3a(R),4(S),5,9b(S)-tetrahydro-4-(pyrid-2-yl)-3*H*-cyclopenta[c]quino-line **2** instead of N-phenyl-5-aza-6-pyrid-2-ylnorborn-2-ene. The starting imine reacts with CPD in the same way yet more smoothly using BF_3Et_2O. With both Lewis-acids, the reaction proceeds regio- and distereoselectively. **1** crystallizes in the centrosymmetric space group $P\bar{1}$, a = 8.127(1), b = 9.133(1), c = 10.467(1) Å, α = 104.36(1)°, β = 100.35(1)°, γ = 95.93(1)°V = 731.4(1) $Å^3$, Z = 2. **2** crystallizes in the centrosymmetric space group $P2_1/c$. a = 10.559(3)), b = 15.061(2), c = 8.252(1) Å, β = 95.90(2)°, V = 13054(4) $Å^3$, Z = 4.

Introduction

Cycloaddition reactions address the issues of stereo- and enantiocontrol and are compatible with a large variety of functional groups. Diels-Alder reactions are of particular interest as they offer a unique access to bicyclic alkenes, which represent highly active monomers for metathesis-type polymerizations(1, 2). [4+2] Cycloadditions may be mediated by high pressure(3), heat, light, sonication(4-7) or Lewis acids(8-16). Chiral Lewis acid systems such as certain boron catalysts(17) or organoaluminum compounds(18) are even known to promote enantioselective cycloadditions. Despite the broad applicability of various transition metals as catalysts for cycloadditions, they sometimes give raise to unexpected, yet versatile reactions as they often change the electronic situation of the entire system. Many transition metal promoted cycloreactions do not proceed any longer in a strictly concerted way and show ionic or at least dipolar intermediates(19-21). In this contribution, we describe the Lewis-acid catalyzed cyclo-reaction of N-phenyl-2-(pyrid-2-yl)imine with cyclopentadiene. The unusual reaction leads to the formation of cyclopentene-substituted pyrid-2-ylquinolines which represent valuable precursor for polymeric chiral chelating systems.

Results and Discussion

Diels-Alder reactions of cyclopentadiene (CPD) with imines bearing electron-withdrawing substituents are well known and represent a straight forward route to azanorbornenes (4-aza-[2.2.1]bicyclohept-2-enes)(22-29). Usually a 4Πs + 2Πs reaction occurs, in which CPD represents the diene-component and the imine reacts as a dienophile. Nevertheless, ketoimines(30-32) are known to act either as a dienophile or as a diene, depending on the Lewis-acid employed. Here we report the reaction of a Lewis acid catalyzed system in which CPD represents the dienophile and the aryl imine works as a diene. Both $BF \cdot Et_2O$ as well as zinc iodide have been used for that purpose. While the reaction proceeds smoothly under boron trifluoride catalysis, the reaction needs to be performed under ultrasound-assisted conditions when zinc iodide is used. Nevertheless, despite rather low yields, the use of zinc iodide allows to elucidate the reaction mechanism. The rather unfavorable reaction pathway involves the aromatic system which undergoes rearomatization via a [1,3]-sigmatropic H-shift. In the case of zinc iodide, irridiation by ultrasound is required in order to promote the reaction. While boron trifluoride is believed to coordinate with the imino nitrogen, the use of zinc iodide leads to the formation of the corresponding N-phenyl-2-(pyrid-2-yl)imine zinc iodide complex 1. As can be seen from Figure 1, the square planar complex forces the phenyl ring as well as the imine-group almost into one plane forming a s-cis double bond.

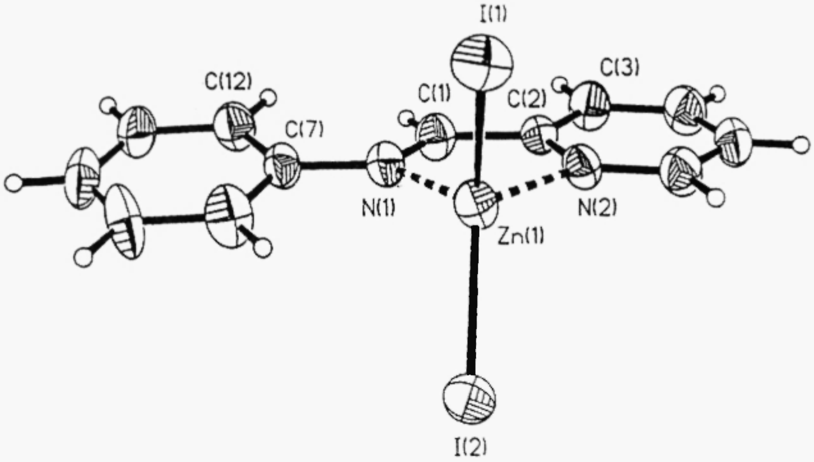
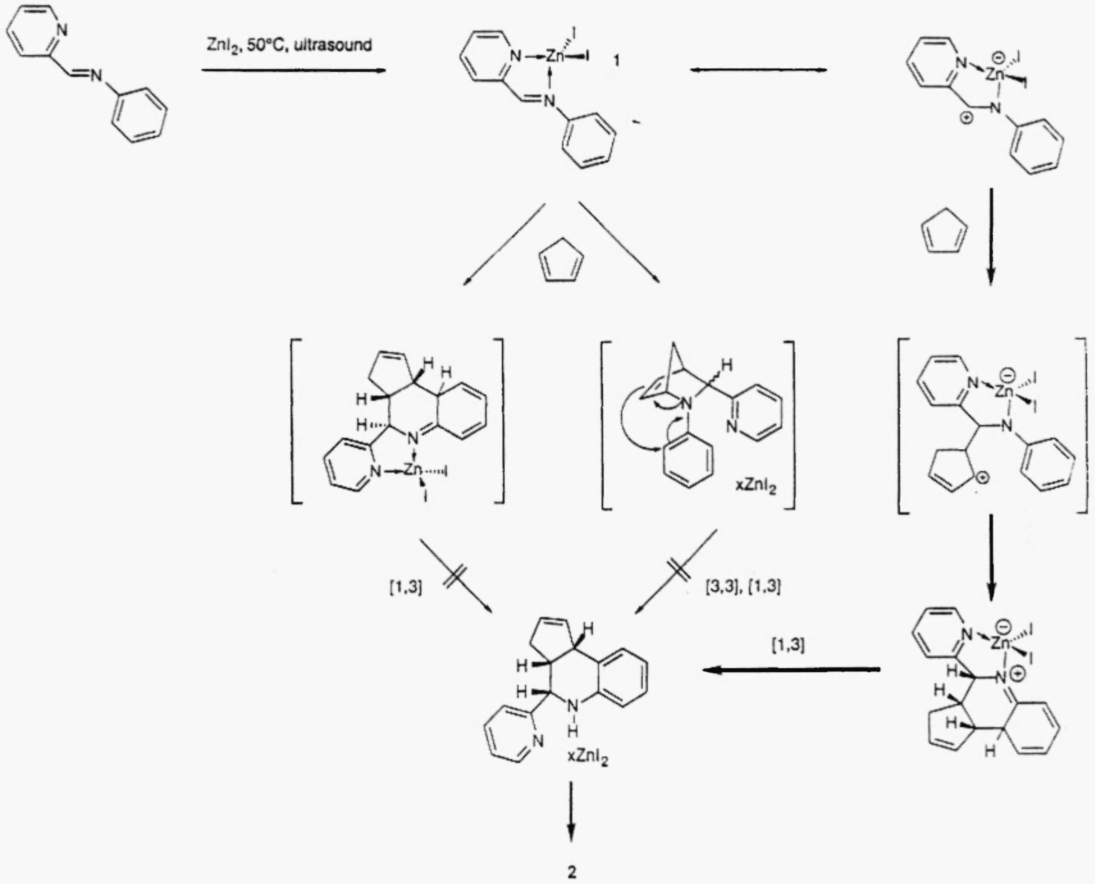


Figure 1: X-ray-structure of 1. Selected bond lengths (Å) and angles (°): Zn(1)-N(1) 2.092(4), Zn(1)-N(2) 2.074(4), N(1)-C(7) 1.426(6) N(1)-C(1) 1.274(7), C(1)-C(2) 1.465(7), N(2)-C(2) 1.336(6) N(1)-C(1)-C(2) 120.1(5), C(1)-N(1)-C(7) 121.5(4)

Consequently, the resulting torsion angle C_{12}-C_7-N_1-C_1 in 1 is only 9.8(8)°. This coplanar conformation is favored in order to generate a conjugated Π-donor-Π-acceptor system involving both the phenyl as well as the pyridyl ring. It is worth mentioning, that the high stabilities of the imine-zinc-complex 1 as well as of the final compound 2 with zinc iodide require a stoichiometric amount of zinc iodide. Starting from the „activated" imine, different reaction mechanisms for the reaction of the planar, c_s-symmetric starting complex **1** with CPD may be discussed, yet only one accounts for the high distereoselectivity in the formation of **2**.

Scheme 1 shows three reasonable reaction pathways. The first one involves the formation of a (zinc-iodide complexed) azanorbornene which instantanously rearranges into **2** via [3,3] cycloreversion(33, 34). According to the x-ray structure of **2**, the relative configurations of the hydrogens in the 3,4 and 9-position in **2** are all-cis. A preliminarily formed azanorbornene would exist in two enantiomeric forms with the nitrogen at either side of the molecule. Additionally, one might expect to observe exo-endo isomers. A [3,3] and subsequent [1,3] rearrangement would result in the formation of at least two diastereomeric forms of **2** with H-3a, H-4 being either cis or trans and must therefore be ruled out.



Scheme 1: Reaction pathway for the formation of **1** and **2**.

Alternatively, the mechanism may be described by a Diels-Alder reaction of the phenylimine with CPD followed by a [1,3] sigmatropic H-shift. Despite the fact, that this reaction sequence accounts for the relative configuration of the protons in the H-3a, H-4 and H-9b positions, it does not explain the regioselectivity in the approach of CPD, with the methylene group in compound **2** pointing selectively towards the pyridyl moiety . Finally, **1** may be regarded as a dipolar system with a positive charge or at least a positive polarization at the imine carbon. This is in accordance with a shift of the $\delta_{CH=N}$ from 1660 cm^{-1} for the free imine(35) to 1600 cm^{-1} in **1** in the IR. A subsequent nucleophilic addition of CPD results in a resonance stabilized allylium cation which itself undergoes an electrophilic attack at the phenyl ring.

Rearomatization via a [1,3] sigmatropic H-shift results in the formation of 2 still complexed by zinc iodide. Only this mechanism explains both the relative configuration at chiral positions in 2 as well as the regioselective addition of CPD (Figure 2). Dipolar species have already been proposed earlier for similar systems(30-32). The present investigation provides further significant evidence for this assumption. We therefore suggest this mechanism for the formation of **2**.

In conclusion, we have found that the Lewis-acid mediated cycloreaction of N-aryl-pyrid-2-ylimines with cyclopentadiene offers a highly distereaselective route to tetrahydroquinolines. We are presently seeking to further extend this reaction onto other imines bearing various substituents at the pyridyl ring in order to obtain tuneable chelating systems for the selective extraction of metal ions.

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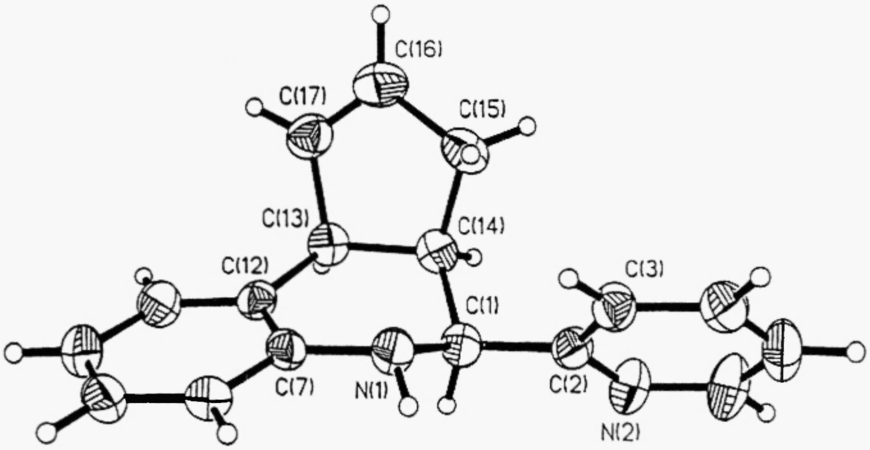

Figure 2: Crystal structure of **2**. Selected bond lengths (Å) and angles (°): N(1)-C(7) 1.406(3), N(1)-C(1) 1.468(3), C(1)-C(2) 1.510(3), C(1)-C(14) 1.529(3), N(2)-C(2) 1.344(3), C(16)-C(17) 1.312(3), C(7)-N(1)-C(1) 115.4(2), N(1)-C(1)-C(2) 111.1(2)

Experimental

Reaction solvents were purified by standard methods. Toluene was distilled from sodium benzophenone ketyl, methylene chloride from calcium hydride. Purchased starting materials were used without any further purification. Cyclopentadiene was prepared from dicyclopentadiene by cracking of the dimer at 180°C and was stored at -18°C. NMR data were obtained in the indicated solvent at 25°C and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in

Hertz. IR-spectra were recorded on a FT-IR. Elemental analysis was performed at the Microanalytical Laboratory, Institute of Physical Chemistry, University of Vienna, Vienna, Austria.

N-Phenyl-2-(pyrid-2-yl)imine: The compound was prepared according to the procedure described in the literature(35, 36), followed by a modified work-up. 2-Formylpyridine (16.2 g, 151 mmol) and aniline (14.1 g, 152 mmol) were dissolved in 15 ml of ethanol. The solution was refluxed for 3 hours, after which it was evaporated to dryness. The oily residue was dissolved in diethyl ether and filtered through a bed of silica (G 60, 220-440 mesh). Distillation of the crude product yielded 20.8 g (75.2 %) of the imine. b.p. 115-118 °C (2 Torr). Spectroscopical data were identical with those reported in the literature (35, 36).

Preparation of the zinc(II)iodide complex 1: Zinc iodide (3.50 g, 11.0 mmol) was added to a solution of N-phenyl-2-(pyrid-2-yl)imine (2.0 g, 11.0 mmol) in 10 ml of THF and the mixture was heated to 50°C. After 20 hours, it was cooled to room temperature. Diethylether was added, and the resulting precipitate was recrystallized from THF:diethylether to yield 5.2 g (95.0 %) of the complex. IR (KBr): 3058 w, 3020 w, 2920 w, 2850w, 1600 s, 1560 s, 1415 m 1495 s, 1476 s, 1460 m, 1443 s, 1368 s, 1302 s, 1277 m, 1104 m, 1023 vs, 918 m, 783 vs, 680 s, 532 s, 415 s. ^{1}H-NMR (DMSO-d_6): 8.84 (dxd, 1 H, J_1 = 4.9, J_2 = 0.6, H_6), 8.83 (s, 1 H, N=C*H*), 8.27 (d, 1 H, J = 7.9, H_4), 8.13 (d, 1 H, J = 7.8), 7.86 (txd, 1 H, J_1 = 7.3, J_2 = 1.2, H_3), 7.43 (d, 2 H, J = 6.8), 7.36-7.31 (m, 3 H); ^{13}C-NMR (DMSO-d_6): 160.7, 150.2 149.5, 147.5, 140.8, 129.3, 128.8, 128.4, 127.9, 122.0. Elemental analysis calcd. for $C_{12}H_{10}N_2ZnI_2$ (M_w = 501.414 gmol^{-1}): C 28.75, H 2.01, N 5.59, found C 28.60, H 1.98, N 5.57. Crystals suitable for x-ray were obtained from THF : diethyl ether.

Synthesis of 2, Procedure A: The imine (11.1 g, 61 mmol) was added to a suspension of zinc (II) iodide (6.7 g, 21 mmol) in cyclopentadiene (8.0 g, 121 mmol). The reaction mixture was sonicated at 0° C for 6 hours. Sonification was continued until the temperature had reached 40°C. A solution of sodium hydroxide in water (2 N) as well as sodium chloride were added and all organic compounds were extracted with acetone. The combined organic extracts were passed through a bed of silica and finally evaporated to dryness. Recrystallization from THF : diethyl ether yielded 1.5 g (10 %) of analytically pure **2**. IR (KBr): 3366bm, 3060m, 1616vs, 1595 vs, 1482 s, 1282 m, 1054 b,vs, 748 vs, 685 m. ^{1}H-NMR ($CDCl_3$): 8.52 (d, 1 H, J =4), 7.63 (dxt, 1 H, J_1 =7.9, J_2 =1.8), 7.35 (d, 1 H, J =7.9), 7.13 (dxd, 1 H, J_1=J_2=7.6), 6.96 (m, 2 H), 6.66 (m, 2 H). 5.75 (d, 1 H, J = 4), 5.51 (d, 1H, J =4), 4.64 (d, 1 H, J =3), 4.11 (d, 1 H. J =14.8), 4.0 (bs, 1 H, N*H*), 3.34 (m, 1 H), 2.40 (dxdxd, J_1 =16.1, J_2 = 9.2, J_3=2.1, 1H, CH_2), 1.80 (dxdxd, J_1 =16.1, J_2= 8.4, J_3=2.1, 1H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 149.1, 145.3, 136.8, 134.4, 130.2, 129.0, 126.5, 122.3, 120.7, 119.2, 116.2, 89.0, 58.5, 46.6, 44.0, 31.9. Elemental analysis calcd. for $C_{17}H_{16}N_2$ (M_w = 248.33 gmol^{-1}): C 82.21, H 6.50, N 11.29, found C 81.94, H 6.33, N 11.08.

Procedure B: The imine (1.0 g, 5.5 mmol) was dissolved in dry methylene chloride (30 mL) and the solution was cooled to -50°C. Cyclopentadiene (0.4 g, 6.1 mmol) and borontrifluoride diethyletherate (60 µL, 0.4 mmol) were added and the reaction mixture was warmed to room temperature within 2 hours. The organic layer was extracted with saturated sodium bicarbonate solution (50 mL), dried over sodium sulphate and evaporated to dryness. Recrystallization from methylene chloride:diethyl ether yielded 0.585 g (42.8 %) of analytically pure **2**.

X-ray Analysis and Structure Determination of 1 and 2: A diffractometer with graphite-monochromatized Mo-Kα radiation (λ=71.073 pm) was used for data collection (Table 1). The unit cell parameters were determined and refined from 35 (for 1) and 25 (for 2) randomly selected reflections.

obtained by P4 automatic routines. Data were measured via ω scan and corrected for Lorentz and polarization effects. For **1** an empirical absorption correction(37) was applied. The structures were solved by direct methods (SHELXS-86) (38) and refined by full matrix least-squares against F^2 (SHELXL-93) (39). The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by difference Fourier methods, but in the refinement they were included in calculated positions and refined with isotropic displacement parameters 1.2 times higher than U(eq) of the attached C atoms, except for the hydrogen atom at N1 in **2**, which was refined isotropically. The coordinates of **1** and **2** are shown in Table 2.

Table 1: Selected Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
mol formula	$C_{12}H_{10}I_2N_2Zn$	$C_{17}H_{16}N_2$
fw	501.39	248.32
cryst system	triclinic	monoclinic
space group	P1 (No.2)	P2$_1$/c (No.14)
unit cell dimens	a = 8.127(1) Å b = 9.133(1) Å c = 10.467(1) Å α = 104.36(1)° β = 100.35(1)° γ = 95.93(1)°	a = 10.559(3) Å b = 15.061(2) Å c = 8.252(1) Å β = 95.90(2)°
vol	731.4(1) Å^3	1305.4(4) Å^3
Z	2	4
temp	218 K	213 K
density (calcd)	2.277 g/cm^3	1.264 g/cm^3
abs coeff	5.880 mm^{-1}	0.075 mm^{-1}
F(000)	464	528
color, habit	colorless platelet	colorless prism
cryst size	0.6 x 0.35 x 0.1 mm	0.52 x 0.32 x 0.25 mm
θ range for data collection	3.2 - 23.5°	2.7 - 20.5°
index range	$0 \leq h \leq 9$, $-9 \leq k \leq 9$, $-11 < l < 11$	$-10 \leq h \leq 10$, $-1 \leq k \leq 14$, $0 < l < 8$
no. of rflns collected	2171	1562
no. of indep rflns	2098	1307
no. of rflns with I > 2σ(I)	1938	1029
absorption correction	ψ-scan	none
max. and min. transmission		1.000, 0.230
refinement method	fullmatrix least-squares on F^2	
parameters	155	177
goodness of fit on F^2	1.072	1.068
final R indices (I > 2σ(I))	R1 = 0.0289, *w*R2 = 0.0771	R1 = 0.0353 *w*R2 = 0.0822
largest diff. peak and hole	0.810, -0.536 e Å^{-3}	0.123, -0.124 e Å^{-3}

Table 2: Atomic coordinates and equivalent isotropic displacement parameters (Å^2 x 10^3) for 1 and 2.

	x	y	z	U(eq)
Zn(1)	0.2110(1)	0.8568(1)	0.2182(1)	37(1)
I(1)	-0.0724(1)	0.6853(1)	0.1678(1)	49(1)
I(2)	0.4554(1)	0.7634(1)	0.3424(1)	47(1)
N(1)	0.2539(5)	0.9442(5)	0.0583(4)	35(1)
N(2)	0.1787(5)	1.0816(5)	0.2949(4)	34(1)
C(1)	0.2342(7)	1.0842(6)	0.0802(5)	39(1)
C(2)	0.1911(6)	1.1636(6)	0.2067(5)	34(1)
C(3)	0.1652(8)	1.3141(6)	0.2332(6)	44(1)
C(4)	0.1321(8)	1.3833(6)	0.3568(6)	49(1)
C(5)	0.1211(8)	1.2993(7)	0.4481(6)	49(1)
C(6)	0.1465(7)	1.1488(6)	0.4140(5)	43(1)
C(7)	0.2961(6)	0.8635(6)	-0.0637(5)	34(1)
C(8)	0.3437(8)	0.7207(7)	-0.0662(6)	51(2)
C(9)	0.3884(9)	0.6360(6)	-0.1820(7)	61(2)
C(10)	0.3859(8)	0.6931(7)	-0.2906(6)	52(2)
C(11)	0.3394(8)	0.8328(7)	-0.2888(6)	49(1)
C(12)	0.2952(7)	0.9197(7)	-0.1740(6)	46(1)

	x	y	z	U(eq)
N(1)	0.5665(2)	0.1310(1)	0.0522(2)	32(1)
N(2)	0.3646(2)	0.2431(1)	-0.2657(2)	43(1)
C(1)	0.5439(2)	0.1780(1)	-0.1040(3)	31(1)
C(2)	0.4048(2)	0.1750(2)	-0.1687(3)	31(1)
C(3)	0.3259(2)	0.1050(2)	-0.1365(3)	36(1)
C(4)	0.2016(2)	0.1042(2)	-0.2066(3)	43(1)
C(5)	0.1590(2)	0.1737(2)	-0.3047(3)	49(1)
C(6)	0.2429(2)	0.2409(2)	-0.3304(3)	53(1)
C(7)	0.6933(2)	0.1308(1)	0.1235(3)	28(1)
C(8)	0.7204(2)	0.1222(1)	0.2912(3)	33(1)
C(9)	0.8440(2)	0.1234(2)	0.3631(3)	41(1)
C(10)	0.9437(2)	0.1335(2)	0.2685(3)	42(1)
C(11)	0.9171(2)	0.1395(2)	0.1014(3)	39(1)
C(12)	0.7935(2)	0.1371(1)	0.0250(3)	30(1)
C(13)	0.7701(2)	0.1344(2)	-0.1589(3)	33(1)
C(14)	0.6272(2)	0.1378(2)	-0.2261(3)	33(1)
C(15)	0.5912(2)	0.0420(2)	-0.2790(3)	41(1)
C(16)	0.7169(2)	-0.0021(2)	-0.2869(3)	47(1)
C(17)	0.8122(2)	0.0466(2)	-0.2230(3)	42(1)
H(1N)	0.5157(21)	0.1494(15)	0.1188(28)	38(7)

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