The Preparation of 3,3a,4,5-Tetrahydronaphth[1,2-*c*]isoxazoles from Dilithiated 1-Tetralone Oxime and Select Aromatic Aldehydes

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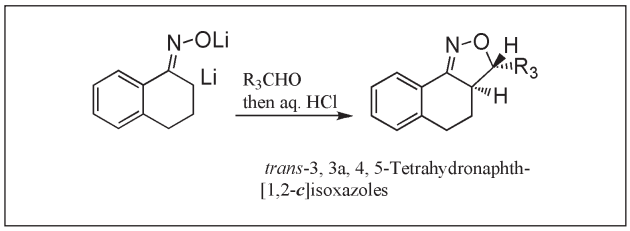

Dilithiated 1-tetralone oxime was condensed with several electron enriched aromatic aldehydes, such as 4-methoxybenzaldehyde or lithiated 4-hydroxybenzaldehyde, followed by acid cyclization to new tetrahydronaphthisoxazoles, 3,3a,4,5-tetrahydronaphth[1,2-*c*]isoxazoles, with a *trans* geometry of the C_3-H and C_{3a}-H protons that was confirmed by X-ray single crystal analysis.

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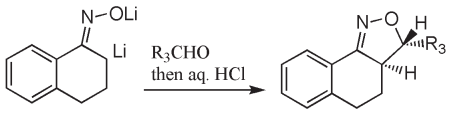
Dihydroisoxazoles (4,5-), 2-isoxazolines, are well known [1] for their biological potential in agriculture and medicine, for their spectral studies, and for their use in other syntheses. Dihydronaphthisoxazoles have received less investigative attention [2].

The preparation of several 3-aryltetrahydronaphthisoxazoles, 3,3a,4,5-tetrahydronaphth[1,2-*c*]isoxazoles, was cited in a single study [3] where 1-tetralone was condensed with aromatic aldehydes to give the α,β-unsaturated ketones. These materials underwent dibromination, followed by base promoted elimination back to the α,β-unsaturated ketones, and then a condensation-cyclodehydration with hydroxylamine to afford the fused-ring products. This three-stage process was shortened to two by making the α,β-unsaturated tetralones and directly condensing-cyclizing them with hydroxylamine. The yields for the last step in each process ranged from 25-40%. Also, based on coupling constants, J = 11.5 Hz, H-1 NMR and other information available, a *cis*-arrangement of C_3-H and C_{3a}-H protons was reported.

Another well-established method for the preparation of the dihydroisoxazole ring system is the 1,3-dipolar addition of nitrile oxides with alkenes [4]. Our developing syntheses of these compounds involves the dilithiation of C(α),*O*-oximes, such as acetophenone oxime, followed by an aldol-type condensation of the dianion-type intermediates with aldehydes or ketones, and an acid cyclization of resulting β-hydroxyoximes. In an initial report, oximes were dilithiated with *n*-butyllithium, and the resulting 1,4-dianion-type intermediates were condensed with carbonyl compounds to afford β-hydroxyoximes that were isolated and separately cyclized with cold concentrated sulfuric acid [5]. Recently, we dilithiated similar oximes with lithium diisopropylamide (LDA), followed by condensation with electron-enriched carbonyl compounds, such as lithiated 4-hydroxybenzaldehyde or 4'-methoxyacetophenone, to give β-hydroxyoxime intermediates that were not isolated, but cyclized directly with aqueous hydrochloric acid to the targeted dihydroisoxazoles [6-8].



1.-7.

1. R_3 = 4-$CH_3OC_6H_4$
2. R_3 = 3, 4-$(CH_3O)_2C_6H_3$
3. R_3 = 3, 4, 5-$(CH_3O)_3C_6H_2$
4. R_3 = 2, 4, 6-$(CH_3O)_3C_6H_2$
5. R_3 = 2, 4, 5-$(CH_3O)_3C_6H_2$
6. R_3 = 4-HOC_6H_4
7. R_3 = 4-HO-3-$CH_3OC_6H_3$

Figure 1. *trans*-3, 3a, 4, 5-Tetrahydronaphth[1,2-*c*]isoxazoles **1-7**.

During the current investigation, several multiple anion type synthesis procedures were explored involving dilithiated 1-tetralone oxime condensation with select aromatic

aldehydes, followed by direct acid cyclization of β-hydroxyoxime intermediates to tetrahydronaphthisoxazles **1-7** (Figure 1). The first and second procedures were single pot methods where the only difference was the use of tetramethylethylenediamine (TMEDA) in combination with LDA in the second procedure. TMEDA did not enhance the yield of products. When *n*-butyllithium was the only base employed, the yields of products **1-5** were comparable to LDA alone. When a hydroxylaryl aldehyde was used for **6** and **7**, LDA appeared to offer a slightly better yield advantage [6]. The oxime was dilithiated at 0° with two equivalents of *n*-butyllithium or three equivalents of LDA (for hydroxybenzalehydes), followed by condensation with an electron-enriched aldehyde, such as *p*-anisaldehyde or a hydroxybenzaldehyde, such as vanillin. An extended condensation time, overnight at room temperature, usually improved the yield of products. The cyclization process involving rapid addition of dilute hydrochloric acid, and the isolation and separate cyclization of a β-hydroxyoxime was not necessary. The yields of **1-7** for the three-step, one pot process ranged from 32-67 %.

Absorption spectra for **1-7** with support from combustion analyses are presented in the experimental section. The three carbon atoms making up the dihydroisoxazole ring were noted in the C-13 NMR spectra as follows: δ (ppm), imine carbon, 157.9-160.0; C-3a (C-2, ORTEP diagram), 53.9-55.1; and C-3 (C-1 ORTEP diagram), 83.7-89.3. The H-1 NMR absorptions for the C_{3a}-H absorptions were displayed as a complex multiplet, and the most characteristic absorption in the spectrum was for the C_3-H, always displayed as a well-defined doublet, δ 4.79-5.77 ppm, with coupling constants, *J*, ranging from 12.2-12.9 Hz. This is compared to the coupling constant, *J* = 11.5 Hz, in the earlier report for the synthesis of these compounds [3]. The earlier report with information available [9] led to assignment of a *cis*-arrangement of the C_3-H (C_1-H, ORTEP) and C_{3a}-H (C_2-H, ORTEP) protons (Figure 2). The X-ray single crystal analysis of tetrahydronaphthisoxazole **7** demonstrated *trans*-geometry between the C_3-H (C_2-H, ORTEP) and C_{3a}-H (C_1-H, ORTEP) protons. When the experimentally obtained dihedral angle, θ = –159.6° (Table 3, last entry), is used in the Karplus equation [10], it can be predicted that the *trans* isomer would have a coupling of *J* = 11.7 Hz. Also, theoretical calculations [11] indicated that the *trans* isomer is the more stable by 1.003 kcal mol^{-1}. A theoretical estimation of the dihedral angle, θ = -154.3°, would also give a coupling constant, *J* = 11.9 Hz. Similar calculations with the *cis* isomer for the C_3-H proton gave a predicted dihedral angle, θ = 18.664°. When this angle was used in the Karplus equation [10], *J* = 10.0 Hz, and when it was used in the Gaussian '03 program [11], *J* = 11.1 Hz. The coupling constants recently reported for 4,5-dihydroisoxazoles and related compounds with a single proton bonded to either C_4-H (C_3-H, ORTEP) and C_5-H, (C_4-H, ORTEP) reported larger coupling constants (*J* >7 Hz) [4a-c] or smaller coupling constants (*J* = 2-5 Hz) [4 d-g] for the *trans* isomer.

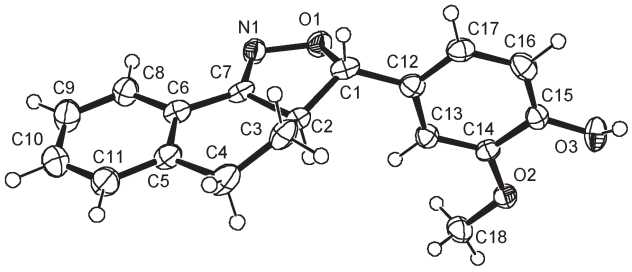


Figure 2. ORTEP diagram (50% ellipsoids for non-Hydrogen atoms) for **7**, $C_{18}H_{17}NO_3$.

The X-ray crystal analysis of **7** indicated a *trans*-geometry (Figure 2) of the hydrogen atoms bonded to C_3-H (C_1-H, ORTEP) and C_{3a}-H (C_2-H, ORTEP). The molecular structure is shown in Figure 2, crystallographic data in Table 1, atomic positional parameters are listed in Table 2, and selected bond distances and angles are listed in Table 3. The molecules, a pair of enantiomers, are connected in the unit cell by hydrogen bonding between the H atom on the O(3) atom and the electrons on the N(1) atom (see ORTEP diagram, Figure 2).

EXPERIMENTAL

Melting points were obtained with a Mel-Temp II melting point apparatus in open capillary tubes and are uncorrected. Fourier Transform infrared spectra were obtained with a Mattson Genesis II FT-IR with Specac Golden Gate Accessory. Proton and ^{13}C magnetic resonance spectra were obtained with a Varian Associates Mercury Oxford 300 MHz, NMR spectrometer, and chemical shifts are recorded in δ ppm downfield from an internal tetramethylsilane (TMS) standard. Combustion analyses were performed by Quantitative Technologies, Inc., P.O. Box 470, Whitehouse, NJ 08888. Chemicals were purchased from Aldrich and Lancaster chemical companies.

General Procedure for Preparation of 3-Aryl-3,3a,4,5-tetrahydronaphth[1,2-*c*]isoxazoles, **1-7**.

[Ratio of reagents - oxime: *n*-butyllithium or LDA: aldehyde - 1:2:1 or 1:3:1 for hydroxybenzaldehydes]

In a typical reaction sequence, 20 ml (0.032 mol) of 1.6 *M n*-butyllithium for condensations with methoxybenzaldehydes (for **1-5**) and 30 ml of 1.6 *M n*-butyllithium (0.047 mol) for condensations with hydroxybenzaldehydes (for **6, 7**). They were added to a three-neck round-bottomed flask (*e.g.*, 500 ml), equipped with a nitrogen inlet tube, a side-arm addition funnel (*e.g.*, 125 ml), and a magnetic stir bar. LDA (0.047 mol) (for **6** and **7**) was prepared by adding 4.80 g (0.047 mol) of diisopropylamine (Aldrich Chem. Co., 99.5%), dissolved in 25-30

ml of dry tetrahydrofuran (THF) (sodium/benzophenone - ketyl), from the addition funnel at a fast dropwise rate during a 5 min period (0 °, N_2) to the *n*-butyllithium. This was followed by addition *via* the addition funnel with 2.42 g of 1-tetralone oxime (0.015 mol) dissolved in 35-45 ml of THF. The addition time was 5 minutes. After 45-60 min at 0°, 0.016 mol of aldehyde, dissolved in 25-35 ml of THF, was added to the dilithiated intermediate, and the solution was stirred at room temperature overnight (N_2). Finally, 100 ml of 3 *M* hydrochloric acid (rapid addition) and 75-100 ml of solvent grade THF were added, and the two-phase mixture was well stirred and heated under reflux for 45-60 min. At the end of this period, the mixture was poured into a large flask containing ice (*ca*., 100 g) followed by 100 ml of solvent grade ether. The layers were separated, and the aqueous layer was extracted with ether (2 x 75 ml), and the organic fractions were extracted with 100 ml of 5 % sodium bicarbonate solution, washed with 50-75 ml water, combined, evaporated, and recrystallized.

3-(4-Methoxyphenyl)-3,3a,4,5-tetrahydronaphth[1,2-*c*]isoxazole (**1**).

This compound was prepared in 60 % yield (2.51 g), mp 122-124° (ethanol) (lit. mp, 123° [3]) using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime (from *n*-butyllithium) and 4-methoxybenzaldehyde; IR 1609 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 1.88-1.94 (m, 1H), 2.22-2.28 (m, 1H), 2.92-2.97 (m, 2H), 3.39-3.47 (m, 1H), 3.83 (s, 3H), 5.12 (d, 1H, *J* = 12.9 Hz), 6.95 (d, 2H, *J* = 8.7 Hz), 7.21-7.27 (m, 3H), 7.43 (d, 2H, *J* = 8.6 Hz), and 8.02 (d, 1H, *J* = 7.8 Hz); ^{13}C NMR (deuteriochloroform): δ (ppm) 26.8, 29.5, 54.8, 55.5, 89.1, 114.3, 125.5, 125.6, 127.0, 128.3, 129.2, 130.2, 130.6, 138.9, 158.5, and 160.0.

Anal. Calcd for $C_{18}H_{17}NO_2$ (279): C, 77.49; H, 6.13; N, 5.01. Found: C, 77.12; H, 5.92; N, 4.92.

3-(3,4-Dimethoxyphenyl)-3,3a,4,5-tetrahydronaphth[1,2-*c*]isoxazole (**2**).

This compound was prepared in 67 % yield, (3.11 g), mp 160-163° (ethanol), using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime and 3,4-dimethoxybenzaldehyde: IR 1593 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 1.82-2.00 (m, 1H), 2.24-2.28 (m, 1H), 2.97 (m broad, 2H), 3.40-3.47 (m, 1H), 3.91 (s broad, 6H), 5.11 (d, 1H, *J* = 12.9 Hz), 6.87-7.05, 7.21-7.34 (m, 6H), and 8.00 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR (deuteriochloroform): δ (ppm) 27.0, 29.6, 55.1, 56.2 (2), 89.3, 109.4, 111.1, 119.5, 125.4, 127.0, 129.1, 130.6, 138.8, 149.3, 149.4, and 158.5.

Anal. Calcd for $C_{19}H_{19}NO_3$ (309): C, 73.77; H, 6.19; N, 4.53. Found: C, 73.85; H, 6.23; N, 4.25.

3-(3,4,5-Trimethoxyphenyl)-3,3a,4,5-tetrahydronaphth[1,2-*c*]-isoxazole (**3**).

This compound was prepared in 32 % yield (1.63 g), mp 99-101° (ethanol), using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime and 3,4,5-trimethoxybenzaldehyde: IR 1600 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 1.87-1.99 (m, 1H), 2.28-2.35 (m, 1H), 2.91-2.94 (m, 1H), 3.48-3.58 (m, 2H), 3.87 (s, 3H), 3.90 (s, 3H), 3.93 (s, 3H), 5.40 (d, 1H, *J* = 12.3 Hz), 6.70 (s, 1H), 6.72 (s, 1H), 7.19-7.33 (m, 3H), and 7.98 (d, 1H, *J* = 7.2 Hz); ^{13}C NMR (deuteriochloroform): δ (ppm) 27.2, 29.6, 55.0, 56.2 (2), 84.7, 107.6, 122.4, 124.3, 125.6, 126.9, 129.1, 130.4, 139.0, 142.4, 152.6, 154.0, and 158.5.

Anal. Calcd for $C_{20}H_{21}NO_4$ (339): C, 70.78; H, 6.24; N, 4.13. Found: C, 70.61; H, 6.17; N, 4.01.

3-(2,4,6-Trimethoxyphenyl)-3,3a,4,5-tetrahydronaphth[1,2-*c*]-isoxazole (**4**).

This compound was prepared in 44 % yield (2.29 g), mp 160-163° (ethanol), using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime and 2, 4, 6-trimethoxybenzaldehyde: IR 3200 broad (w), 1600 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 1.80-1.90 (m, 1H), 2.16-2.21 (m, 1H), 2.58 (s broad), 2.92-2.95 (m, 2H), 3.79 (s, 6H), 3.82 (s, 3H), 3.93-3.99 (m, 2H), 5.77 (d, 1H, *J* = 12.2 Hz), 6.16 (s, 2H), 7.20-7.37 (m, 3H), and 7.94-7.97 (m, 1H); ^{13}C NMR (deuteriochloroform): δ (ppm) 27.7, 29.4, 49.8, 55.2, 55.9, 80.4, 91.0, 105.3, 124.9, 126.3, 128.9, 129.7, 138.7, 158.9, 159.8, 160.3, and 161.5.

Anal. Calcd for $C_{20}H_{21}NO_4 \cdot 1/4\ H_2O$ (350): C, 69.85; H, 6.30; N, 4.07. Found: C, 69.70; H, 6.22; N, 4.37.

3-(2,4,5-Trimethoxyphenyl)-3,3a,4,5-tetrahydronaphth[1,2-*c*]-isoxazole (**5**).

This compound was prepared in 33 % yield (1.68 g), mp 144-146° (ethanol), using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime and 2,4,5-trimethoxybenzaldehyde: IR 1613 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 1.66-1.74 (m, 1H), 2.09-2.14 (m, 1H), 2.70 (s broad, 2H), 3.09-3.19 (m, 1H), 3.55-3.66 (m, 9H), 5.31 (d, 1H, *J* = 12.3 Hz), 6.30 (s, 1H), 6.61-7.00 (m, 4H), and 7.74 (d, 1H, *J* = 7.5 Hz). ^{13}C NMR (deuteriochloroform): δ (ppm) 27.2, 29.6, 54.6, 56.3, 56.7, 83.7, 97.6, 110.6, 118.5, 125.4, 125.8, 126.9, 129.1, 130.5, 139.1, 143.5, 149.5, 151.8, and 158.6.

Anal. Calcd for $C_{20}H_{21}NO_4$ (339): C, 70.78; H, 6.24; N, 4.13. Found: C, 70.48; H, 6.13; N, 4.09.

3-(4-Hydroxyphenyl)-3,3a,4,5-tetrahydronaphth[1,2-*c*]isoxazole (**6**).

This compound was prepared in 41 % yield (1.63 g), mp 199-201° (ethanol), using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime (from LDA) and 4-hydroxybenzaldehyde, IR 3180 b, 1614, 1594 cm^{-1}; ^1H NMR (deuterio-chloroform): δ (ppm) 1.81-1.96 (m, 1H), 2.20-2.28 (m, 1H), 2.59-2.63 (m, 1H), 2.92-2.97 (m, 1H), 3.38-3.49 (m, 1H), 5.07 (d, 2H, *J* = 12.9 Hz), 6.87-6.91 (m, 2H), 7.21-7.37 (m, 5H), 7.96-7.98 (m, 1H), and 8.90 (s, 1H); ^{13}C NMR (deuteriochloroform): δ (ppm) 26.5, 29.2, 54.3, 89.1, 115.7, 125.1, 125.3, 126.7, 128.2 (2), 129.0, 130.4, 138.8, 157.7, and 158.4.

Anal. Calcd for $C_{17}H_{15}NO_2$ (265): C, 76.96; H, 5.70; N, 5.28. Found: C, 76.69; H, 5.61; N, 5.14.

3-(4-Hydroxy-3-methoxyphenyl)-3,3a,4,5-tetrahydronaphth-[1,2-*c*]isoxazole (**7**).

This compound was prepared in 40 % yield (1.77 g), mp 189-191° (ethanol), using the general procedure for the condensation-cyclization of dilithiated 1-tetralone oxime (from LDA) and vanillin; IR 1591 cm^{-1}; ^1H NMR (deuteriochloroform): δ (ppm) 1.58-1.64 (m, 1H), 1.94-2.00 (m, 1H), 2.70 (m, 2H), 3.12-3.22 (m, 1H), 3.61 (s, 3H), 4.78 (d, 1H, *J* = 12.9 Hz), 6.61-7.09 (m, 6H), 7.66 (d, 1H, *J* = 6.9 Hz), and 7.98 (s, 1H); ^{13}C NMR (deuteriochloroform): δ (ppm) 26.0, 28.7, 53.9, 55.4, 88.8, 109.3,

114.8, 119.4, 124.5, 124.8, 126.2, 128.4, 128.6, 130.0, 138.4, 146.4, 147.3, and 157.9.

Anal. Calcd for $C_{18}H_{17}NO_3$ (295): C, 73.29; H, 5.80; N, 4.74. Found: C, 73.01; H, 5.59; N, 4.75.

Single crystal X-ray measurements for crystals of **7**, $C_{18}H_{17}NO_3$, recrystallized from benzene, were collected on a Mercury CCD area detector coupled with a Rigaku AFC8 diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. The data were collected at a temperature of -100° to a maximum θ value of 25.15°. Data were collected in 0.50° oscillations in ω with 15 s exposures (two identical scans were performed at each position to identify detector anomalies). A sweep of data was done using ω oscillations from -90.0 to 90.0° at χ = 45.0° and ϕ = 0.0°; a second sweep was performed using ω oscil-

Table 1

Crystallographic Data for **7**, $C_{18}H_{17}NO_3$

Crystal Dimensions (mm)	0.72 x 0.12 x 0.05
Space Group	P2(1)/c
a (Å)	11.792(2)
b (Å)	14.362(3)
c (Å)	8.465(2)
β	92.27(3)°
V (Å^3)	1432.5(5)
fw	295.33
Z	4
d_{calc} (g/cm^3)	1.369
μ (mm^{-1})	0.093
R_1 [a]	0.0827
wR_2 [b]	0.2140
Goodness of Fit	1.114

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2]/ \Sigma [w(F_o^2)^2]\}^{1/2}$.

Table 2

Atomic Positional Parameters for **7**, $C_{18}H_{17}NO_3$

Atom	*x*	*y*	*z*	*U*(eq)*
O(1)	0.3496(2)	0.2013(2)	-0.2318(3)	0.034(1)
O(2)	0.6595(2)	0.4114(2)	0.0859(3)	0.031(1)
O(3)	0.7515(2)	0.4908(2)	-0.1558(4)	0.037(1)
N(1)	0.2418(2)	0.1629(2)	-0.1955(4)	0.030(1)
C(1)	0.3321(3)	0.3028(2)	-0.2538(4)	0.029(1)
C(2)	0.2367(3)	0.3227(2)	-0.1452(4)	0.026(1)
C(3)	0.1522(3)	0.3991(3)	-0.1896(5)	0.034(1)
C(4)	0.0530(3)	0.3950(3)	-0.0821(6)	0.040(1)
C(5)	0.0016(3)	0.2990(3)	-0.0645(5)	0.032(1)
C(6)	0.0616(3)	0.2183(3)	-0.1038(4)	0.029(1)
C(7)	0.1787(3)	0.2295(2)	-0.1494(4)	0.025(1)
C(8)	0.0090(3)	0.1310(3)	-0.0923(5)	0.034(1)
C(9)	-0.0975(4)	0.1238(3)	-0.0367(5)	0.044(1)
C(10)	-0.1562(4)	0.2035(3)	0.0075(6)	0.048(1)
C(11)	-0.1072(3)	0.2897(3)	-0.0085(6)	0.042(1)
C(12)	0.4440(3)	0.3518(2)	-0.2278(4)	0.029(1)
C(13)	0.4979(3)	0.3565(3)	-0.0759(4)	0.027(1)
C(14)	0.6007(3)	0.4022(2)	-0.0554(4)	0.025(1)
C(15)	0.6518(3)	0.4454(2)	-0.1842(4)	0.026(1)
C(16)	0.5988(3)	0.4389(3)	-0.3317(5)	0.033(1)
C(17)	0.4952(3)	0.3920(3)	-0.3546(4)	0.030(1)
C(18)	0.6125(3)	0.3693(3)	0.2209(5)	0.039(1)

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

Table 3

Selected Bond Distances (Å) and Angles (°) for **7**, $C_{18}H_{17}NO_3$

C(1)-O(1)	1.482(4)
O(1)-N(1)	1.431(4)
N(1)-C(7)	1.282(5)
C(7)-C(2)	1.503(5)
C(1)-C(2)	1.508(5)
C(2)-C(3)	1.519(5)
C(3)-C(4)	1.512(6)
C(4)-C(5)	1.515(6)
C(5)-C(6)	1.405(5)
C(6)-C(7)	1.458(5)
C(6)-C(8)	1.404(5)
C(8)-C(9)	1.362(6)
C(9)-C(10)	1.397(6)
C(10)-C(11)	1.376(7)
C(5)-C(11)	1.391(6)
C(1)-C(12)	1.504(5)
C(12)-C(13)	1.413(5)
C(13)-C(14)	1.383(5)
C(14)-C(15)	1.411(5)
C(15)-C(16)	1.377(6)
C(16)-C(17)	1.402(5)
C(17)-C(12)	1.379(5)
C(14)-O(2)	1.365(4)
O(2)-C(18)	1.424(5)
C(15)-O(3)	1.358(4)
N(1)-O(1)-C(1)	106.6(2)
C(7)-N(1)-O(1)	108.0(3)
N(1)-C(7)-C(2)	113.7(3)
C(7)-C(2)-C(1)	99.6(3)
O(1)-C(1)-C(2)	102.4(3)
C(1)-C(2)-C(3)	118.9(3)
C(7)-C(2)-C(3)	110.1(3)
C(6)-C(7)-C(2)	121.8(3)
C(4)-C(3)-C(2)	109.8(3)
C(3)-C(4)-C(5)	114.6(3)
C(6)-C(5)-C(4)	121.3(3)
C(5)-C(6)-C(7)	117.6(3)
N(1)-C(7)-C(6)	124.5(3)
C(12)-C(1)-C(2)	119.5(3)
O(1)-C(1)-C(12)	109.0(3)
C(13)-C(12)-C(1)	121.0(3)
C(14)-C(13)-C(12)	119.7(3)
C(13)-C(14)-C(15)	120.8(3)
O(2)-C(14)-C(13)	124.6(3)
O(2)-C(14)-C(15)	114.6(3)
C(14)-O(2)-C(18)	117.5(3)
O(3)-C(15)-C(14)	117.9(3)
O(3)-C(15)-C(16)	123.6(3)
C(16)-C(15)-C(14)	118.6(3)
C(15)-C(16)-C(17)	121.3(3)
C(12)-C(17)-C(16)	120.0(4)
C(17)-C(12)-C(13)	119.6(3)
C(17)-C(12)-C(1)	119.4(3)
C(8)-C(6)-C(7)	122.9(3)
C(9)-C(8)-C(6)	120.5(4)
C(8)-C(9)-C(10)	120.3(4)
C(11)-C(10)-C(9)	119.8(4)
C(10)-C(11)-C(5)	121.1(4)
C(11)-C(5)-C(4)	119.9(3)
C(11)-C(5)-C(6)	118.8(4)
C(8)-C(6)-C(5)	119.5(4)
H(1)-C(1)-C(2)-H(2)	-159.6 [16]

lations from -30.0 to 30.0° at $\chi = 45.0°$ and $\phi = 90.0°$. The crystal-to-detector distance was 27.1 mm. The detector swing angle was 0.00°. Cell parameters and additional details of the data collection are reported in Table 1.

Of the 11590 reflections collected, 2558 were unique (R_{int} = 0.1150); equivalent reflections were merged. Data were collected, processed, and corrected for Lorentz-polarization and for absorption using CrystalClear (Rigaku) [12]. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Ideal hydrogen atom coordinates were calculated and the hydrogen atoms were allowed to ride on their respective carbons. The temperature factors of all hydrogen atoms were varied isotropically. The final cycle of full-matrix least-squares refinement on F^2 converged with $R_1 = 0.0827$ (reflections with $I > 2.00\sigma(I)$), wR_2 = 0.2140 (all data). The highest difference peak was 0.264, and the deepest hole was -0.280.

Structure solution, refinement, and the calculation of derived results were performed using the *SHELX-97* [13] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber [14], and the real and imaginary anomalous dispersion corrections were those of Cromer [15].

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