Reactivity of Nitrovinylquinones With Cyclic and Acyclic Enol Ethers – Supporting Information

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REFERENCE NUMBER: 99158

CRYSTAL STRUCTURE REPORT

Report prepared for:
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DATA COLLECTION

A colourless crystal of approximate dimensions 0.24 x 0.22 x 0.19 mm³ was attached onto the tip of a 0.1 mm diameter glass capillary and mounted on a Siemens SMART system for a data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 217 reflections. Final cell constants were calculated from the xyz centroids of 2096 strong reflections from the actual data collection after integration (SAINT 6.0, 1999). Please refer to Table 1 for additional crystal and refinement information.

The data collection was carried out using MoK α radiation (graphite monochromator) with a detector distance of 4.945 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 1.3 hemispheres and to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω at 3 different ϕ settings and a detector position of -25° in 2θ with a frame time of 50 seconds. The intensity data were corrected for absorption (SADABS, G. Sheldrick 1996).

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved and refined using SHELXS-86 and SHELXL-97 (G. Sheldrick). The space group C2/c was determined based on systematic absences and intensity statistics.¹ A direct-methods solution was calculated which provided all non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located all hydrogen atoms. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined with individual isotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0611$ and $WR2 = 0.1470$ (F^2 , all data).

STRUCTURE DESCRIPTION

The structure was found as suggested. The stereochemistry of the four stereocentres C7, C8, C13, and C14 is S,R,S,S or, for the other enantiomer, R,S,R,R, respectively. Intermolecular hydrogen bonds order the molecules into bilayers along the short axes with hydrophilic ends facing towards each other and hydrophobic ends outward (for details refer to table 3).

Data collection and structure solution were conducted at the X-Ray Crystallographic Laboratory, 160 Kolthoff Hall, Chemistry Department, The University of Minnesota. All calculations were performed using SGI INDY R4400-SC

or Pentium computers using the SHELXTL V5.0 suite of programs. All publications arising from this report MUST either 1) include Maren Pink as a coauthor or 2) acknowledge Maren Pink, Victor G. Young, Jr. and the X-Ray Crystallographic Laboratory.

¹. SHELXTL-Plus V5.0, Siemens Industrial Automation, Inc., Madison, WI.

Some equations of interest:

$$\begin{aligned}
 R_{\text{int}} &= \sum |F_o^2 - \langle F_o^2 \rangle| / \sum |F_o^2| \\
 R_1 &= \sum ||F_o| - |F_c|| / \sum |F_o| \\
 wR_2 &= [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}, \\
 \text{where } w &= 1/\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P \\
 \text{Goof} &= S = [\sum (w(F_o^2 - F_c^2)^2) / (n-p)]^{1/2}
 \end{aligned}$$

Table 1. Crystal data, data collection, and solution and refinement for 99158.

Crystal Data

Empirical formula	$C_{15}H_{17}NO_5$
Crystal Habit, color	block, colourless
Crystal size	0.24 x 0.22 x 0.19 mm
Crystal system	Monoclinic
Space group	C2/c
	$a = 32.579(3) \text{ \AA}$ $\alpha = 90.000(3)^\circ$
	$b = 8.1242(9) \text{ \AA}$ $\beta = 105.955(2)^\circ$
	$c = 10.559(1) \text{ \AA}$ $\gamma = 90.000(3)^\circ$
Volume	$2687.0(5) \text{ \AA}^3$
Z	8
Formula weight	291.30
Density (calculated)	1.440 Mg/m^3
Absorption coefficient	0.109 mm^{-1}
F(000)	1232

Data Collection

Diffractionmeter	Siemens SMART Platform CCD
Wavelength	$0.71073 \text{ \AA}$
Temperature	$173(2) \text{ K}$
θ range for data collection	1.30 to 25.11°
Index ranges	$-38 \leq h \leq 38$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$
Reflections collected	11735
Independent reflections	2388 ($R_{\text{int}} = 0.0844$)

Solution and Refinement

System used	SHELXTL-V5.0
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2(F_o^2) + (AP)^2 + (BP)]^{-1}$, where $P = (Fo^2 + 2Fc^2)/3$, $A = 0.0807$, and $B = 0$
Absorption correction	SADABS, G. Sheldrick (1996)
Max. and min. transmission	1.000000 and 0.781357
Extinction coefficient	$0.0014(6)$
Data / restraints / parameters	2388 / 0 / 259
R indices ($I > 2\sigma(I)$) = 1460	$R1 = 0.0611$, $wR2 = 0.1269$
R indices (all data)	$R1 = 0.1145$, $wR2 = 0.1470$
Goodness-of-fit on F^2	0.996
Largest diff. peak and hole	0.226 and $-0.264 \text{ e\AA}^{-3}$

Table 2. Atomic coordinates [x, y, z] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 99158. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
O(1)	1472(1)	-4354(3)	5698(2)	43(1)	1
O(2)	2529(1)	-3006(3)	2889(2)	42(1)	1
O(3)	1312(1)	2546(3)	3341(2)	48(1)	1
O(4)	1620(1)	663(3)	4725(2)	42(1)	1
O(5)	670(1)	-115(3)	2664(2)	34(1)	1
N(1)	1450(1)	1147(4)	3616(3)	34(1)	1
C(1)	1650(1)	-4367(4)	4824(3)	32(1)	1
C(2)	2046(1)	-5300(4)	4964(3)	37(1)	1
C(3)	2323(1)	-4889(4)	4292(3)	37(1)	1
C(4)	2252(1)	-3465(4)	3395(3)	33(1)	1
C(5)	1836(1)	-2593(4)	3176(3)	25(1)	1
C(6)	1799(1)	-1058(4)	2713(3)	28(1)	1
C(7)	1400(1)	-82(4)	2490(3)	27(1)	1
C(8)	997(1)	-1125(4)	2391(3)	26(1)	1
C(9)	853(1)	-1905(4)	1006(3)	31(1)	1
C(10)	456(1)	-2962(4)	839(3)	36(1)	1
C(11)	531(1)	-4303(4)	1884(3)	37(1)	1
C(12)	680(1)	-3555(5)	3265(3)	36(1)	1
C(13)	1076(1)	-2464(4)	3454(3)	27(1)	1
C(14)	1475(1)	-3489(4)	3510(3)	25(1)	1
C(15)	468(1)	1054(5)	1694(4)	46(1)	1

Table 3. Selected Hydrogen bonds with $H \cdots A < r(A) + 2.000 \text{ \AA}$ and $\angle DHA > 110^\circ$ for 99158.

D-H	d(D-H)	d(H...A)	$\angle DHA$	d(D...A)	A
C2-H2	1.028	2.445	146.7	3.352	O2 [x, -y, 0.5-z]
C3-H3	0.952	2.476	156.4	3.370	O4 [1.5-x, 0.5-y, -1+z]
C14-H14	0.914	2.579	131.7	3.262	O3 [x, 1+y, z]

Table 4. Bond lengths [Å] and angles [°] for 99158.

O(1)-C(1)	1.218(3)	O(2)-C(4)	1.224(4)
O(3)-N(1)	1.228(3)	O(4)-N(1)	1.215(3)
O(5)-C(15)	1.419(4)	O(5)-C(8)	1.435(3)
N(1)-C(7)	1.526(4)	C(1)-C(2)	1.470(4)
C(1)-C(14)	1.524(4)	C(2)-C(3)	1.335(5)
C(2)-H(2)	1.03(4)	C(3)-C(4)	1.473(5)
C(3)-H(3)	0.95(3)	C(4)-C(5)	1.491(4)
C(5)-C(6)	1.333(4)	C(5)-C(14)	1.505(4)
C(6)-C(7)	1.486(4)	C(6)-H(6)	0.92(3)
C(7)-C(8)	1.540(4)	C(7)-H(7)	0.93(3)
C(8)-C(13)	1.533(4)	C(8)-C(9)	1.544(4)
C(9)-C(10)	1.522(4)	C(9)-H(9A)	0.94(3)
C(9)-H(9B)	1.02(3)	C(10)-C(11)	1.522(5)
C(10)-H(10A)	1.00(3)	C(10)-H(10B)	1.03(4)
C(11)-C(12)	1.530(5)	C(11)-H(11A)	0.98(3)
C(11)-H(11B)	1.02(3)	C(12)-C(13)	1.532(4)
C(12)-H(12A)	0.92(3)	C(12)-H(12B)	0.94(3)
C(13)-C(14)	1.531(4)	C(13)-H(13)	0.95(3)
C(14)-H(14)	0.92(3)	C(15)-H(15A)	0.98(5)
C(15)-H(15B)	0.97(5)	C(15)-H(15C)	0.90(4)
C(15)-O(5)-C(8)	117.5(3)	O(4)-N(1)-O(3)	124.6(3)
O(4)-N(1)-C(7)	117.5(3)	O(3)-N(1)-C(7)	117.9(3)
O(1)-C(1)-C(2)	121.1(3)	O(1)-C(1)-C(14)	123.4(3)
C(2)-C(1)-C(14)	115.5(3)	C(3)-C(2)-C(1)	121.4(3)
C(3)-C(2)-H(2)	121(2)	C(1)-C(2)-H(2)	118(2)
C(2)-C(3)-C(4)	121.9(3)	C(2)-C(3)-H(3)	125(2)
C(4)-C(3)-H(3)	113(2)	O(2)-C(4)-C(3)	121.0(3)
O(2)-C(4)-C(5)	122.3(3)	C(3)-C(4)-C(5)	116.7(3)
C(6)-C(5)-C(4)	119.3(3)	C(6)-C(5)-C(14)	122.7(3)
C(4)-C(5)-C(14)	118.0(3)	C(5)-C(6)-C(7)	123.0(3)
C(5)-C(6)-H(6)	119(2)	C(7)-C(6)-H(6)	118(2)
C(6)-C(7)-N(1)	108.9(2)	C(6)-C(7)-C(8)	114.1(3)
N(1)-C(7)-C(8)	108.7(2)	C(6)-C(7)-H(7)	112(2)
N(1)-C(7)-H(7)	105(2)	C(8)-C(7)-H(7)	108(2)
O(5)-C(8)-C(13)	104.1(2)	O(5)-C(8)-C(7)	109.7(2)
C(13)-C(8)-C(7)	111.9(2)	O(5)-C(8)-C(9)	112.1(2)
C(13)-C(8)-C(9)	110.3(3)	C(7)-C(8)-C(9)	108.7(2)
C(10)-C(9)-C(8)	111.6(3)	C(10)-C(9)-H(9A)	113(2)
C(8)-C(9)-H(9A)	107(2)	C(10)-C(9)-H(9B)	114(2)
C(8)-C(9)-H(9B)	108(2)	H(9A)-C(9)-H(9B)	104(2)
C(11)-C(10)-C(9)	111.0(3)	C(11)-C(10)-H(10A)	108(2)
C(9)-C(10)-H(10A)	113(2)	C(11)-C(10)-H(10B)	109(2)
C(9)-C(10)-H(10B)	111(2)	H(10A)-C(10)-H(10B)	104(2)
C(10)-C(11)-C(12)	110.6(3)	C(10)-C(11)-H(11A)	111(2)
C(12)-C(11)-H(11A)	108(2)	C(10)-C(11)-H(11B)	110(2)
C(12)-C(11)-H(11B)	112(2)	H(11A)-C(11)-H(11B)	105(2)
C(11)-C(12)-C(13)	112.9(3)	C(11)-C(12)-H(12A)	107(2)
C(13)-C(12)-H(12A)	111(2)	C(11)-C(12)-H(12B)	104(2)
C(13)-C(12)-H(12B)	114(2)	H(12A)-C(12)-H(12B)	108(3)
C(14)-C(13)-C(12)	111.5(3)	C(14)-C(13)-C(8)	112.6(2)
C(12)-C(13)-C(8)	110.4(3)	C(14)-C(13)-H(13)	106(2)
C(12)-C(13)-H(13)	110(2)	C(8)-C(13)-H(13)	106(2)
C(5)-C(14)-C(1)	108.6(2)	C(5)-C(14)-C(13)	116.0(3)
C(1)-C(14)-C(13)	112.9(2)	C(5)-C(14)-H(14)	107(2)
C(1)-C(14)-H(14)	101(2)	C(13)-C(14)-H(14)	110(2)
O(5)-C(15)-H(15A)	106(3)	O(5)-C(15)-H(15B)	113(3)
H(15A)-C(15)-H(15B)	104(3)	O(5)-C(15)-H(15C)	116(2)
H(15A)-C(15)-H(15C)	108(3)	H(15B)-C(15)-H(15C)	109(4)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for 99158. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [(\text{ha})^2 U_{11} + \dots + 2\text{hka} \cdot b U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	58(2)	55(2)	23(1)	10(1)	20(1)	3(1)
O(2)	37(1)	50(2)	42(1)	-5(1)	19(1)	-1(1)
O(3)	70(2)	25(1)	49(2)	-3(1)	15(1)	2(1)
O(4)	50(1)	51(2)	23(1)	-3(1)	7(1)	4(1)
O(5)	39(1)	31(1)	35(1)	1(1)	15(1)	6(1)
N(1)	39(2)	37(2)	26(2)	-2(1)	10(1)	-3(1)
C(1)	43(2)	29(2)	23(2)	-1(2)	9(2)	-5(2)
C(2)	44(2)	45(2)	20(2)	2(2)	3(2)	6(2)
C(3)	37(2)	44(2)	26(2)	-5(2)	2(2)	9(2)
C(4)	35(2)	39(2)	23(2)	-12(2)	7(1)	-2(2)
C(5)	32(2)	33(2)	12(1)	-4(1)	7(1)	-3(1)
C(6)	31(2)	38(2)	18(2)	-6(1)	11(1)	-7(2)
C(7)	40(2)	28(2)	14(2)	-3(1)	10(1)	-3(1)
C(8)	32(2)	25(2)	22(2)	-1(1)	8(1)	3(1)
C(9)	37(2)	31(2)	22(2)	-2(2)	5(1)	-1(2)
C(10)	34(2)	36(2)	37(2)	-5(2)	5(2)	2(2)
C(11)	31(2)	30(2)	50(2)	-4(2)	9(2)	-3(2)
C(12)	39(2)	36(2)	39(2)	4(2)	18(2)	0(2)
C(13)	38(2)	29(2)	17(2)	-2(1)	12(1)	-3(1)
C(14)	33(2)	25(2)	16(2)	0(1)	7(1)	0(1)
C(15)	46(2)	35(2)	52(3)	10(2)	6(2)	11(2)

Table 6. Torsion angles [$^\circ$] for 99158.

O(1)-C(1)-C(2)-C(3)	-155.3(3)	C(14)-C(1)-C(2)-C(3)	26.7(4)
C(1)-C(2)-C(3)-C(4)	1.2(5)	C(2)-C(3)-C(4)-O(2)	172.6(3)
C(2)-C(3)-C(4)-C(5)	-5.5(4)	O(2)-C(4)-C(5)-C(6)	-17.7(4)
C(3)-C(4)-C(5)-C(6)	160.3(3)	O(2)-C(4)-C(5)-C(14)	163.1(3)
C(3)-C(4)-C(5)-C(14)	-18.9(4)	C(4)-C(5)-C(6)-C(7)	-178.7(2)
C(14)-C(5)-C(6)-C(7)	0.4(4)	C(5)-C(6)-C(7)-N(1)	102.4(3)
C(5)-C(6)-C(7)-C(8)	-19.2(4)	O(4)-N(1)-C(7)-C(6)	-42.1(3)
O(3)-N(1)-C(7)-C(6)	138.7(3)	O(4)-N(1)-C(7)-C(8)	82.7(3)
O(3)-N(1)-C(7)-C(8)	-96.4(3)	C(15)-O(5)-C(8)-C(13)	-168.0(3)
C(15)-O(5)-C(8)-C(7)	72.1(3)	C(15)-O(5)-C(8)-C(9)	-48.8(4)
C(6)-C(7)-C(8)-O(5)	158.9(2)	N(1)-C(7)-C(8)-O(5)	37.1(3)
C(6)-C(7)-C(8)-C(13)	43.9(3)	N(1)-C(7)-C(8)-C(13)	-77.8(3)
C(6)-C(7)-C(8)-C(9)	-78.2(3)	N(1)-C(7)-C(8)-C(9)	160.0(2)
O(5)-C(8)-C(9)-C(10)	-58.7(3)	C(13)-C(8)-C(9)-C(10)	56.8(3)
C(7)-C(8)-C(9)-C(10)	179.8(3)	C(8)-C(9)-C(10)-C(11)	-57.1(4)
C(9)-C(10)-C(11)-C(12)	55.2(4)	C(10)-C(11)-C(12)-C(13)	-54.9(4)
C(11)-C(12)-C(13)-C(14)	-71.1(4)	C(11)-C(12)-C(13)-C(8)	54.8(4)
O(5)-C(8)-C(13)-C(14)	-168.9(2)	C(7)-C(8)-C(13)-C(14)	-50.6(3)
C(9)-C(8)-C(13)-C(14)	70.6(3)	O(5)-C(8)-C(13)-C(12)	65.8(3)
C(7)-C(8)-C(13)-C(12)	-175.9(2)	C(9)-C(8)-C(13)-C(12)	-54.7(3)
C(6)-C(5)-C(14)-C(1)	-135.9(3)	C(4)-C(5)-C(14)-C(1)	43.2(3)
C(6)-C(5)-C(14)-C(13)	-7.5(4)	C(4)-C(5)-C(14)-C(13)	171.7(2)
O(1)-C(1)-C(14)-C(5)	135.4(3)	C(2)-C(1)-C(14)-C(5)	-46.7(4)
O(1)-C(1)-C(14)-C(13)	5.2(4)	C(2)-C(1)-C(14)-C(13)	-176.8(3)
C(12)-C(13)-C(14)-C(5)	157.5(2)	C(8)-C(13)-C(14)-C(5)	32.7(4)
C(12)-C(13)-C(14)-C(1)	-76.2(3)	C(8)-C(13)-C(14)-C(1)	159.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 99158.

	x	y	z	U(eq)	SOF
H(2)	2117(11)	-6210(45)	5667(37)	62(11)	1
H(3)	2596(10)	-5382(38)	4401(31)	44(10)	1
H(6)	2036(9)	-545(34)	2580(26)	23(8)	1
H(7)	1350(8)	563(35)	1738(29)	27(8)	1
H(9A)	812(9)	-1036(38)	400(29)	31(8)	1
H(9B)	1107(9)	-2533(37)	861(27)	30(8)	1
H(10A)	199(9)	-2310(37)	885(28)	34(8)	1
H(10B)	368(10)	-3499(41)	-79(35)	52(10)	1
H(11A)	750(10)	-5079(38)	1776(29)	35(9)	1
H(11B)	261(9)	-4996(36)	1757(28)	32(8)	1
H(12A)	734(10)	-4420(43)	3854(33)	45(10)	1
H(12B)	440(10)	-2989(39)	3359(31)	41(10)	1
H(13)	1133(8)	-1904(34)	4271(30)	25(8)	1
H(14)	1404(8)	-4362(37)	2940(28)	26(8)	1
H(15A)	319(12)	1807(54)	2135(43)	83(15)	1
H(15B)	242(15)	588(53)	988(50)	96(16)	1
H(15C)	641(11)	1653(45)	1341(37)	55(12)	1

analysed, dry product

University of Minnesota
Department of Chemistry
VAC-300

User: wacblk
Sample: 24
Spin rate: 24
Date: May. 7, 1997
Solvent: acetone
File: 2401
Starting Time: 14:11:08
Completion Time: 14:18:40
Total acq. time 1 minute
Pulprline-300 "vac300"
Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 3.000 sec
Width 5999.3 Hz
16 repetitions
OBSERVE EL 299.9580314 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536

S15