ARTICLE

REVISED

Synthesis of optically pure (+)-puraquinonic acid, and assignment of absolute configuration to natural (-)-puraquinonic acid. Use of radical cyclization for asymmetric generation of a quaternary center

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SUPPORTING INFORMATION

X-ray data for 41	S2-S15
¹³ C NMR spectra of the following compounds: 9-11, 21-31, 33-38, 40-41, 42 (more polar), 42 (less polar), 43-45, 47, 49-52	S16-S48
General experimental procedures	S49
Experimental procedures for compounds 9-11, 41, and for 2-bromo-5-methoxy-4-methylbenzaldehyde.	S49-S54

University of Alberta Department of Chemistry
X-Ray Crystallography Laboratory

STRUCTURE REPORT

XCL Code: DLC0305

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Compound: 3-[3-(*t*-Butyldimethylsiloxy)-3-(2,5-dimethoxy-6-ethyl-3-(2-hydroxyethyl)-4-methylphenyl)-2-methylpropanoyl]-4-isopropyl-1,3-oxazolidin-2-one, hemi(*n*-pentane) solvate

Formula: C_{31.5}H₅₅NO₇Si (C₂₉H₄₉NO₇Si•0.5C₅H₁₂)

Supervisor: D. L. J. Clive

Crystallographer: R. McDonald

Figure Legends

Figure 1. Perspective view of the 3-[3-(*t*-butyldimethylsiloxy)-3-(2,5-dimethoxy-6-ethyl-3-(2-hydroxyethyl)-4-methylphenyl)-2-methylpropanoyl]-4-isopropyl-1,3-oxazolidin-2-one molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. The hydrogen atoms attached to O7, C2, C3, C8, and C9 are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

Figure 2. Alternate view of the molecule.

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Table 1. Crystallographic Experimental Details**A. Crystal Data**

formula	C _{31.5} H ₅₅ NO ₇ Si
formula weight	587.86
crystal dimensions (mm)	0.91 × 0.35 × 0.05
crystal system	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
unit cell parameters ^a	
<i>a</i> (Å)	11.6156 (6)
<i>b</i> (Å)	13.2406 (6)
<i>c</i> (Å)	24.0810 (12)
<i>V</i> (Å ³)	3703.6 (3)
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.054
μ (mm ⁻¹)	0.103

B. Data Collection and Refinement Conditions

diffractometer	Bruker PLATFORM/SMART 1000 CCD ^b
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	-80
scan type	ω scans (0.2°) (15 s exposures)
data collection 2θ limit (deg)	52.76
total data collected	23633 (-14 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 16, -30 ≤ <i>l</i> ≤ 29)
independent reflections	7538 (<i>R</i> _{int} = 0.0537)
number of observed reflections (<i>NO</i>)	5713 [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]
structure solution method	direct methods (<i>SHELXS</i> -86 ^c)
refinement method	full-matrix least-squares on <i>F</i> ² (<i>SHELXL</i> -93 ^d)
absorption correction method	multi-scan (<i>SADABS</i>)
range of transmission factors	0.9949–0.9121
data/restraints/parameters	7538 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)] / 8 ^e / 361
Flack absolute structure parameter ^f	-0.1 (2)
goodness-of-fit (<i>S</i>) ^g	1.038 [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]
final <i>R</i> indices ^h	
<i>R</i> ₁ [<i>F</i> _o ² ≥ 2σ(<i>F</i> _o ²)]	0.0753
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3σ(<i>F</i> _o ²)]	0.2259
largest difference peak and hole	1.167 and -0.271 e Å ⁻³

^aObtained from least-squares refinement of 7080 reflections with 4.57° < 2θ < 51.71°.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

^cSheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

(continued)

Table 1. Crystallographic Experimental Details (continued)

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R -factors wR_2 and all goodnesses of fit S are based on F_o^2 ; conventional R -factors R_1 are based on F_o , with F_o set to zero for negative F_o^2 . The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 , and is not relevant to the choice of reflections for refinement. R -factors based on F_o^2 are statistically about twice as large as those based on F_o , and R -factors based on ALL data will be even larger.

^eDistances within the solvent *n*-pentane molecule were given fixed idealized values: $d(\text{C1S}-\text{C2S}) = d(\text{C2S}-\text{C3S}) = d(\text{C3S}-\text{C4S}) = d(\text{C4S}-\text{C5S}) = 1.54 \text{ \AA}$; $d(\text{C1S}\cdots\text{C3S}) = d(\text{C2S}\cdots\text{C4S}) = d(\text{C3S}\cdots\text{C5S}) = 2.52 \text{ \AA}$. An idealized geometry was imposed upon the hydrogen-bonded $\text{C25}-\text{O7}-\text{H7O}\cdots\text{O3}'$ (related to O3 by the symmetry operation $[1/2+x, 1/2-y, \bar{z}]$) unit by constraining these atoms to be virtually coplanar (here, by requiring the C25, O7, H7O, and O3' positions to define a tetrahedral volume of not more than $0.001 \text{ \AA}^3$).

^fFlack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst.* **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. In this case the large values of the Flack parameter and its standard uncertainty indicate that the X-ray data alone may not be used for unambiguous assignment of absolute stereochemistry; however, the known stereochemistry of the precursor compounds may be coupled with the relative stereochemistry hereby established in order to assign absolute configuration.

^g $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1454P)^2 + 0.9704P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^h $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters*(a) atoms of 3-[3-(*t*-butyldimethylsiloxy)-3-(2,5-dimethoxy-6-ethyl-3-(2-hydroxyethyl)-4-methylphenyl)-2-methylpropanoyl]-4-isopropyl-1,3-oxazolidin-2-one*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
Si	0.31131(10)	-0.18224(8)	0.06804(5)	0.0310(3)*
O1	0.7495(3)	0.2013(2)	0.18559(14)	0.0456(8)*
O2	0.6299(3)	0.0825(2)	0.21777(14)	0.0538(9)*
O3	0.4169(3)	0.2113(2)	0.09593(12)	0.0367(7)*
O4	0.4024(2)	-0.11143(19)	0.10378(11)	0.0293(6)*
O5	0.4830(2)	0.09764(19)	-0.00748(11)	0.0295(6)*
O6	0.8606(2)	-0.0665(2)	0.09762(13)	0.0384(7)*
O7	0.7592(3)	0.3004(2)	0.00179(14)	0.0483(8)*
N	0.5743(3)	0.1966(2)	0.14859(13)	0.0313(7)*
C1	0.6490(4)	0.1516(3)	0.18701(18)	0.0385(10)*
C2	0.7494(4)	0.2740(3)	0.1414(2)	0.0432(11)*
C3	0.6231(4)	0.2893(3)	0.12623(18)	0.0340(9)*
C4	0.5667(4)	0.3852(3)	0.14955(19)	0.0422(11)*
C5	0.6209(5)	0.4780(3)	0.1217(3)	0.0641(16)*
C6	0.5740(6)	0.3936(4)	0.2110(2)	0.0653(16)*
C7	0.4705(3)	0.1596(3)	0.12749(16)	0.0302(9)*
C8	0.4300(3)	0.0540(3)	0.14344(16)	0.0284(8)*
C9	0.4383(3)	-0.0116(3)	0.09018(16)	0.0274(8)*
C10	0.3074(4)	0.0588(3)	0.16567(19)	0.0430(11)*
C11	0.1903(4)	-0.1057(4)	0.0406(2)	0.0507(12)*
C12	0.3903(5)	-0.2448(4)	0.0101(2)	0.0572(14)*
C13	0.2588(4)	-0.2788(3)	0.11923(18)	0.0403(10)*
C14	0.1682(6)	-0.3456(4)	0.0915(3)	0.0719(18)*
C15	0.2033(6)	-0.2289(4)	0.1692(2)	0.0671(17)*
C16	0.3563(6)	-0.3447(5)	0.1396(3)	0.0744(19)*
C17	0.5592(3)	-0.0062(3)	0.06611(16)	0.0249(7)*
C18	0.5770(3)	0.0554(3)	0.01938(15)	0.0272(8)*
C19	0.6866(4)	0.0798(3)	-0.00105(16)	0.0290(8)*
C20	0.7826(3)	0.0397(3)	0.02556(17)	0.0309(9)*
C21	0.7648(3)	-0.0233(3)	0.07199(18)	0.0303(8)*
C22	0.6570(3)	-0.0481(3)	0.09240(16)	0.0272(8)*
C23	0.4369(4)	0.0358(3)	-0.05019(18)	0.0401(10)*
C24	0.6965(4)	0.1502(3)	-0.05016(17)	0.0371(10)*
C25	0.6747(4)	0.2598(3)	-0.03496(19)	0.0425(11)*
C26	0.9034(4)	0.0591(4)	0.0049(2)	0.0463(11)*
C27	0.9130(4)	-0.0030(4)	0.1377(2)	0.0489(12)*
C28	0.6486(4)	-0.1217(3)	0.14073(17)	0.0318(9)*
C29	0.6659(4)	-0.2315(3)	0.1210(2)	0.0446(11)*

Table 2. Atomic Coordinates and Displacement Parameters (continued)

(b) solvent n-pentane atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
C1S ^a	0.2100(9)	0.3571(9)	0.2036(7)	0.0915(19)
C2S ^a	0.0805(8)	0.3339(6)	0.2082(5)	0.0915(19)
C3S ^a	0.0623(11)	0.2203(7)	0.2185(4)	0.0915(19)
C4S ^a	0.1074(13)	0.1916(7)	0.2765(4)	0.0915(19)
C5S ^a	0.0763(14)	0.0810(7)	0.2895(5)	0.0915(19)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$. ^aCarbon atoms of the solvent *n*-pentane molecule were refined with a common isotropic displacement parameter.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Si	O4	1.655(3)	C4	C5	1.535(7)
Si	C11	1.854(5)	C4	C6	1.486(7)
Si	C12	1.864(5)	C7	C8	1.525(5)
Si	C13	1.878(4)	C8	C9	1.552(5)
O1	C1	1.340(5)	C8	C10	1.523(6)
O1	C2	1.435(6)	C9	C17	1.521(5)
O2	C1	1.197(5)	C13	C14	1.529(6)
O3	C7	1.198(5)	C13	C15	1.517(7)
O3	H7O ^a	2.25 ^b	C13	C16	1.512(8)
O4	C9	1.424(4)	C17	C18	1.405(5)
O5	C18	1.386(5)	C17	C22	1.413(5)
O5	C23	1.420(5)	C18	C19	1.403(6)
O6	C21	1.395(5)	C19	C20	1.391(6)
O6	C27	1.417(5)	C19	C24	1.511(5)
O7	C25	1.427(6)	C20	C21	1.410(6)
N	C1	1.402(5)	C20	C26	1.510(6)
N	C3	1.455(5)	C21	C22	1.385(6)
N	C7	1.397(5)	C22	C28	1.521(5)
C2	C3	1.526(6)	C24	C25	1.517(6)
C3	C4	1.535(6)	C28	C29	1.543(6)

^aAt $-1/2+x, 1/2-y, \bar{z}$. ^bNonbonded distance.

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
O4	Si	C11	111.1(2)	O4	C9	C17	113.7(3)
O4	Si	C12	109.0(2)	C8	C9	C17	110.3(3)
O4	Si	C13	104.60(17)	Si	C13	C14	109.3(3)
C11	Si	C12	110.4(3)	Si	C13	C15	111.3(3)
C11	Si	C13	111.1(2)	Si	C13	C16	111.3(3)
C12	Si	C13	110.4(2)	C14	C13	C15	107.9(5)
C1	O1	C2	110.4(3)	C14	C13	C16	108.9(5)
Si	O4	C9	126.4(2)	C15	C13	C16	108.2(5)
C18	O5	C23	113.7(3)	C9	C17	C18	117.9(3)
C21	O6	C27	113.6(3)	C9	C17	C22	123.6(3)
C1	N	C3	111.2(3)	C18	C17	C22	117.9(3)
C1	N	C7	128.7(3)	O5	C18	C17	119.5(3)
C3	N	C7	119.8(3)	O5	C18	C19	117.3(3)
O1	C1	O2	123.5(4)	C17	C18	C19	123.2(3)
O1	C1	N	108.2(4)	C18	C19	C20	118.6(3)
O2	C1	N	128.2(4)	C18	C19	C24	119.0(4)
O1	C2	C3	105.5(4)	C20	C19	C24	122.4(4)
N	C3	C2	100.0(3)	C19	C20	C21	118.2(4)
N	C3	C4	113.3(4)	C19	C20	C26	121.9(4)
C2	C3	C4	115.7(4)	C21	C20	C26	119.9(4)
C3	C4	C5	109.1(4)	O6	C21	C20	118.4(4)
C3	C4	C6	113.7(4)	O6	C21	C22	117.9(3)
C5	C4	C6	110.5(4)	C20	C21	C22	123.6(4)
O3	C7	N	118.6(4)	C17	C22	C21	118.4(3)
O3	C7	C8	121.6(4)	C17	C22	C28	122.9(3)
N	C7	C8	119.8(3)	C21	C22	C28	118.7(3)
C7	C8	C9	106.6(3)	C19	C24	C25	112.9(3)
C7	C8	C10	109.8(3)	O7	C25	C24	113.3(4)
C9	C8	C10	111.9(3)	C22	C28	C29	111.1(3)
O4	C9	C8	108.1(3)				

Table 5. Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C11	Si	O4	C9	-39.3(4)	O3	C7	C8	C10	-54.6(5)
C12	Si	O4	C9	82.6(3)	N	C7	C8	C9	-111.2(4)
C13	Si	O4	C9	-159.2(3)	N	C7	C8	C10	127.4(4)
O4	Si	C13	C14	176.9(4)	C7	C8	C9	O4	179.2(3)
O4	Si	C13	C15	57.9(4)	C7	C8	C9	C17	54.4(4)
O4	Si	C13	C16	-62.8(4)	C10	C8	C9	O4	-60.7(4)
C11	Si	C13	C14	57.0(4)	C10	C8	C9	C17	174.5(3)
C11	Si	C13	C15	-62.1(4)	O4	C9	C17	C18	135.6(3)
C11	Si	C13	C16	177.2(4)	O4	C9	C17	C22	-53.5(5)
C12	Si	C13	C14	-65.9(5)	C8	C9	C17	C18	-102.8(4)
C12	Si	C13	C15	175.1(4)	C8	C9	C17	C22	68.0(4)
C12	Si	C13	C16	54.4(5)	C9	C17	C18	O5	-8.7(5)
C2	O1	C1	O2	175.1(4)	C9	C17	C18	C19	169.2(3)
C2	O1	C1	N	-6.7(5)	C22	C17	C18	O5	180.0(3)
C1	O1	C2	C3	18.0(5)	C22	C17	C18	C19	-2.2(5)
Si	O4	C9	C8	133.0(3)	C9	C17	C22	C21	-168.6(3)
Si	O4	C9	C17	-104.2(3)	C9	C17	C22	C28	13.5(5)
C23	O5	C18	C17	-89.4(4)	C18	C17	C22	C21	2.2(5)
C23	O5	C18	C19	92.6(4)	C18	C17	C22	C28	-175.6(3)
C27	O6	C21	C20	85.3(5)	O5	C18	C19	C20	179.1(3)
C27	O6	C21	C22	-97.1(4)	O5	C18	C19	C24	0.5(5)
C3	N	C1	O1	-8.2(5)	C17	C18	C19	C20	1.1(5)
C3	N	C1	O2	169.9(4)	C17	C18	C19	C24	-177.5(3)
C7	N	C1	O1	165.8(4)	C18	C19	C20	C21	-0.2(5)
C7	N	C1	O2	-16.1(7)	C18	C19	C20	C26	177.7(4)
C1	N	C3	C2	18.0(4)	C24	C19	C20	C21	178.3(3)
C1	N	C3	C4	-105.7(4)	C24	C19	C20	C26	-3.7(6)
C7	N	C3	C2	-156.6(3)	C18	C19	C24	C25	75.3(5)
C7	N	C3	C4	79.7(5)	C20	C19	C24	C25	-103.3(5)
C1	N	C7	O3	177.7(4)	C19	C20	C21	O6	177.8(3)
C1	N	C7	C8	-4.2(6)	C19	C20	C21	C22	0.4(6)
C3	N	C7	O3	-8.7(5)	C26	C20	C21	O6	-0.2(6)
C3	N	C7	C8	169.4(3)	C26	C20	C21	C22	-177.6(4)
O1	C2	C3	N	-20.9(4)	O6	C21	C22	C17	-178.8(3)
O1	C2	C3	C4	101.2(4)	O6	C21	C22	C28	-0.9(5)
N	C3	C4	C5	-177.8(4)	C20	C21	C22	C17	-1.4(6)
N	C3	C4	C6	58.3(6)	C20	C21	C22	C28	176.5(4)
C2	C3	C4	C5	67.5(5)	C17	C22	C28	C29	100.3(4)
C2	C3	C4	C6	-56.3(6)	C21	C22	C28	C29	-77.5(5)
O3	C7	C8	C9	66.8(5)	C19	C24	C25	O7	65.2(5)

Table 6. Anisotropic Displacement Parameters (U_{ij} , Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	0.0291(5)	0.0302(5)	0.0335(6)	-0.0013(4)	-0.0010(5)	-0.0051(5)
O1	0.0384(17)	0.0419(16)	0.057(2)	-0.0027(15)	-0.0163(15)	0.0045(15)
O2	0.071(2)	0.0448(18)	0.0454(19)	0.0091(15)	-0.0250(17)	-0.0035(17)
O3	0.0430(17)	0.0279(13)	0.0390(15)	-0.0001(12)	-0.0098(14)	0.0041(13)
O4	0.0266(14)	0.0257(12)	0.0356(14)	0.0029(11)	-0.0014(12)	-0.0062(11)
O5	0.0282(14)	0.0301(13)	0.0300(14)	0.0026(11)	-0.0015(11)	0.0044(11)
O6	0.0278(15)	0.0405(16)	0.0470(17)	-0.0017(14)	-0.0057(13)	0.0082(12)
O7	0.0450(18)	0.0454(17)	0.0545(19)	-0.0090(15)	0.0126(16)	-0.0171(15)
N	0.0363(18)	0.0280(16)	0.0296(17)	0.0013(13)	-0.0009(15)	0.0012(15)
C1	0.043(3)	0.035(2)	0.038(2)	-0.0062(19)	-0.010(2)	0.0006(19)
C2	0.038(3)	0.040(2)	0.051(3)	0.002(2)	-0.002(2)	-0.002(2)
C3	0.034(2)	0.033(2)	0.035(2)	0.0001(17)	-0.0026(18)	-0.0016(17)
C4	0.043(3)	0.031(2)	0.053(3)	-0.0083(19)	-0.003(2)	0.0050(19)
C5	0.058(3)	0.028(2)	0.107(5)	0.005(3)	-0.017(3)	-0.005(2)
C6	0.091(5)	0.048(3)	0.058(3)	-0.019(2)	-0.003(3)	0.016(3)
C7	0.031(2)	0.032(2)	0.027(2)	-0.0055(16)	0.0013(17)	0.0020(17)
C8	0.031(2)	0.0269(17)	0.0277(19)	0.0001(15)	-0.0008(16)	0.0047(16)
C9	0.030(2)	0.0237(17)	0.0280(19)	0.0046(15)	0.0002(16)	-0.0033(16)
C10	0.042(3)	0.037(2)	0.049(3)	-0.0028(19)	0.016(2)	0.003(2)
C11	0.033(2)	0.053(3)	0.066(3)	0.009(2)	-0.013(2)	-0.005(2)
C12	0.069(4)	0.054(3)	0.049(3)	-0.015(2)	0.010(3)	-0.004(3)
C13	0.041(2)	0.038(2)	0.042(2)	0.0023(18)	-0.002(2)	-0.014(2)
C14	0.080(4)	0.056(3)	0.080(4)	0.007(3)	-0.017(3)	-0.046(3)
C15	0.086(4)	0.054(3)	0.062(3)	0.004(3)	0.022(3)	-0.022(3)
C16	0.064(4)	0.064(4)	0.096(5)	0.040(3)	0.003(3)	-0.002(3)
C17	0.0256(19)	0.0258(16)	0.0232(18)	-0.0035(15)	-0.0041(15)	0.0015(15)
C18	0.028(2)	0.0246(17)	0.029(2)	-0.0020(15)	0.0005(16)	-0.0005(16)
C19	0.034(2)	0.0267(17)	0.0266(19)	-0.0018(15)	0.0014(18)	0.0018(17)
C20	0.023(2)	0.0312(19)	0.039(2)	-0.0049(17)	0.0044(16)	-0.0032(16)
C21	0.026(2)	0.0272(17)	0.037(2)	-0.0046(16)	-0.0020(17)	0.0017(15)
C22	0.029(2)	0.0245(17)	0.0275(19)	-0.0012(15)	0.0011(16)	-0.0013(15)
C23	0.040(2)	0.045(2)	0.035(2)	-0.0031(18)	-0.0078(19)	0.003(2)
C24	0.041(2)	0.042(2)	0.028(2)	-0.0003(16)	0.0044(19)	-0.006(2)
C25	0.041(3)	0.039(2)	0.047(3)	0.0089(19)	0.007(2)	0.000(2)
C26	0.029(2)	0.055(3)	0.055(3)	0.008(2)	0.006(2)	0.002(2)
C27	0.033(2)	0.059(3)	0.054(3)	-0.011(2)	-0.014(2)	0.009(2)
C28	0.029(2)	0.032(2)	0.034(2)	0.0036(16)	-0.0011(17)	0.0023(16)
C29	0.044(3)	0.033(2)	0.056(3)	0.009(2)	-0.001(2)	0.0049(19)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H7O	0.8218	0.3072	-0.0152	0.072
H2A	0.7933	0.2484	0.1091	0.052
H2B	0.7844	0.3384	0.1539	0.052
H3	0.6150	0.2890	0.0849	0.041
H4	0.4833	0.3836	0.1392	0.051
H5A	0.5852	0.5395	0.1364	0.077
H5B	0.6084	0.4746	0.0815	0.077
H5C	0.7037	0.4792	0.1294	0.077
H6A	0.5391	0.3339	0.2281	0.078
H6B	0.5329	0.4543	0.2232	0.078
H6C	0.6550	0.3983	0.2222	0.078
H8	0.4820	0.0257	0.1726	0.034
H9	0.3835	0.0163	0.0621	0.033
H10A	0.3056	0.1007	0.1992	0.052
H10B	0.2809	-0.0095	0.1747	0.052
H10C	0.2568	0.0882	0.1374	0.052
H11A	0.2199	-0.0560	0.0140	0.061
H11B	0.1521	-0.0706	0.0713	0.061
H11C	0.1349	-0.1501	0.0219	0.061
H12A	0.4171	-0.1935	-0.0162	0.069
H12B	0.3387	-0.2920	-0.0090	0.069
H12C	0.4565	-0.2817	0.0250	0.069
H14A	0.1406	-0.3961	0.1181	0.086
H14B	0.2024	-0.3798	0.0594	0.086
H14C	0.1034	-0.3038	0.0791	0.086
H15A	0.1768	-0.2810	0.1952	0.080
H15B	0.1376	-0.1881	0.1571	0.080
H15C	0.2598	-0.1854	0.1878	0.080
H16A	0.3264	-0.3943	0.1662	0.089
H16B	0.4145	-0.3026	0.1578	0.089
H16C	0.3911	-0.3801	0.1080	0.089
H23A	0.3711	0.0699	-0.0674	0.048
H23B	0.4116	-0.0287	-0.0343	0.048
H23C	0.4961	0.0233	-0.0783	0.048
H24A	0.6404	0.1294	-0.0789	0.044
H24B	0.7745	0.1441	-0.0663	0.044
H25A	0.6733	0.3007	-0.0694	0.051
H25B	0.5980	0.2653	-0.0173	0.051
H26A	0.9081	0.0424	-0.0347	0.056
H26B	0.9578	0.0170	0.0257	0.056

Table 7. Derived Parameters for Hydrogen Atoms (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
H26C	0.9227	0.1305	0.0103	0.056
H27A	0.9794	-0.0376	0.1540	0.059
H27B	0.8572	0.0131	0.1669	0.059
H27C	0.9387	0.0596	0.1198	0.059
H28A	0.5722	-0.1152	0.1585	0.038
H28B	0.7079	-0.1048	0.1688	0.038
H29A	0.6602	-0.2773	0.1528	0.054
H29B	0.7421	-0.2382	0.1038	0.054
H29C	0.6065	-0.2486	0.0937	0.054
H1SA ^a	0.2210	0.4295	0.1971	0.110
H1SB ^a	0.2431	0.3188	0.1727	0.110
H1SC ^a	0.2485	0.3377	0.2382	0.110
H2SA ^a	0.0467	0.3731	0.2391	0.110
H2SB ^a	0.0412	0.3541	0.1734	0.110
H3SA ^a	-0.0207	0.2039	0.2158	0.110
H3SB ^a	0.1037	0.1808	0.1898	0.110
H4SA ^a	0.0728	0.2366	0.3047	0.110
H4SB ^a	0.1920	0.2002	0.2777	0.110
H5SA ^a	0.1051	0.0633	0.3265	0.110
H5SB ^a	0.1116	0.0366	0.2618	0.110
H5SC ^a	-0.0075	0.0728	0.2886	0.110

^aIncluded with an occupancy factor of 0.5.

85.51
X

AU230F.1
AU PROG
X25. AU
DATE 2-11-99
TIME 19:11

SF 7: 69
SY 112.0
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SI 6583
TD 3276
SW 2000(000
HZ/PT 10

PW (000
RD (000
AG 800
RG 4800
NS 297
TE

FW 25000
O2 5200(000
DP 18H 000

LB 1 00
GB 36 00
CX 7 00
CY 210 00
F1 210 00
F2 210 00
HZ/CM 452 00
PPM/CM 5 00
SR 708 00

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D2 1.50 00
D3 1.50 00
D4 1.50 00
D5 1.50 00
D6 1.50 00
D7 1.50 00
D8 1.50 00
D9 1.50 00
D10 1.50 00
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D75 1.50 00
D76 1.50 00
D77 1.50 00
D78 1.50 00
D79 1.50 00
D80 1.50 00
D81 1.50 00
D82 1.50 00
D83 1.50 00
D84 1.50 00
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D95 1.50 00
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D97 1.50 00
D98 1.50 00
D99 1.50 00
D100 1.50 00

101501 S 13C(4H) APT ON MS-7-15 IN CD2CL2

149.073
145.869
143.508

128.726
127.048
125.148
123.828
120.394

54.523
54.183
53.802
53.443
53.081

13.804

MS-7-19

BRUKER

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APTXH.AU
DATE 26-8-
TIME 8:37

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SI 12300.
SI 32768
TD 32768
SW 29411.
HZ/PT 1.

PW 0.
RG 400.
RG 14535
TE 237

FW 36800
O2 7200.
DP 15H CP

LB 2.
GB 0.
CY 36.
CY 10.
F1 210.
F2 5.
HZ/CM 603.
PR/CM 27.

D1 2.000 0
S2 15H 95.
P9 .001 0
D2 .001 0
P0 .007 0
D3 .007 0
P6 .000 0
D4 .000 0
RD 0.0
PW 0
DE 23
NS 1453
DS

MSC743.001
AU PROG
APT/H AU
DATE 10-11-
TIME 9:44

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TO 32768
SW 29411.7
HZ/PT 1.7

PW 0.0
RG 400
NS 14402
TE 297

FW 36800
O2 6300.0
DP 15H CPO

LB 2.0
GB 36.0
CX 0.0
CY 0.0
F1 200.0
F2 -15.9

HZ/CM 603.6
PPM/CM 6.0
SR -133.4

D1 2.0000
S2 15H
P9 95.
D2 .0010
P0 2.
D3 .0070
P6 13.
D4 .0001
RD 0.0
RM 0.
NO 23.
NS 14402
DS 2

S19

100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
 CH, CH₃ positive; C, CH₂ negative
 date: Jul 9 2001 seqfil: apt hz/mm: 87.63 sweep width [Hz]: 40000 spectrometer: lbd5 file: /mnt/d600/clivenmrdata/Maol1n/pl1-c-5-1.fld
 acq.time[s]: 2.0 relax.time[s]: 0.5 dig.res.[Hz/pt]: 0.61 # of scans: 112
 Pulse Sequence: apt

Pulse Sequence: apt

125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe CH, CH3 positive; C, CH2 negative
 date: Jun 3 2001 seqfil: apt
 acq.time [s]: 2.0 relax.time [s]: 0.5 sweep width [Hz]: 34965 dig.res. [Hz/pt]: 0.53
 spectrometer: lbd5
 hz/mm: 145.68
 file: exp

100 MHz APT in CDCl₃ (ref. to CDC13 @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
 CH, CH3 positive; C, CH2 negative
 date: Jul 12 2001 seqfil: apt
 acq.time[s]: 2.0 relax.time[s]: 0.5
 hz/mm: 89.82 sweep width [Hz]: 50000. spectrometer: lbd5 file: /mnt/d600/clivenmrdata/Mao1in/pl-c-7-1.fld
 dig.res. [Hz/pt]: 0.76 # of scans: 488
 Pulse Sequence: apt

S 22

Pulse Sequence: apt

100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe

CH, CH3 positive; C, CH2 negative

date: Jul 13 2001 seqfil: apt

acq.time[s]: 2.0 relax.time[s]: 0.5

hz/mm: 95.56 sweep width [Hz]: 50000 spectrometer: u500

file: /mnt/d600/clivemrdata/Maolin/pl-c-8-2.fid

dig.res. [Hz/pt]: 0.76 # of scans: 1072

100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
 CH, CH₃ positive; C, CH₂ negative
 date: Jun 27 2001 seq11: apt
 acq.time[s]: 2.0 relax.time[s]: 0.5
 file: /mnt/d600/clivenmrdata/Mao1in/p1-c-11-1.fid
 spectrometer: 1300
 sweep width [Hz]: 30019
 dig.res. [Hz/pt]: 0.46
 # of scans: 1200
 Pulse Sequence: apt

S24

Pulse Sequence: apt

100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe

CH, CH3 positive; C, CH2 negative

date: Feb 18 2002 seqfil: apt

hz/mm: 83.33 sweep width [Hz]: 20000 spectrometer: 300 file: /mnt/d600/clivenmrdata/Maolin/p1-c-13.fid

acq.time[s]: 2.0 relax.time[s]: 0.5 dig.res.[Hz/pt]: 0.31 # of scans: 224

100 MHz APT 1h CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asv400 probe
 CH, CH₃ positive; C, CH₂ negative
 date: Jul 17 2001 seqf11: apt hz/mm: 89.23 sweep width [Hz]: 30019 spectrometer: u500 file: /mnt/d600/clivemrdata/Mao11n/pi-c-13-1.fld
 acq.time[s]: 2.0 relax.time[s]: 0.5 dig.res.[Hz/pt]: 0.46 # of scans: 1176
 Pulse Sequence: apt

125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe CH, CH3 positive; C, CH2 negative
 date: Jul 4 2001 seqfil: apt hz/mm: 104.17 sweep width [Hz]: 25000 spectrometer: 1300 file: /mnt/d800/clivenmrdata/Maolin/p1-c-14-3.fid
 acq.time [s]: 2.0 relax.time [s]: 0.5 dig.res. [Hz/pt]: 0.38 # of scans: 1096 Pulse Sequence: apt

100 MHz APT in CDCl₃ (ref. to CDC13 @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asv400 probe
 CH, CH3 positive; C, CH2 negative
 date: Aug 2 2001 seqfil: apt hz/mm: 94.72 sweep width [Hz]: 30019 spectrometer: 1300 file: /mnt/d600/clivemrdata/Maol/n/p1-c-17-1.fid
 acq.time [s]: 2.0 relax.time [s]: 0.5 dig.res. [Hz/pt]: 0.46 # of scans: 14088

100 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
 CH, CH3 positive; C, CH2 negative
 date: Oct 9 2001 seqfil: apt file: /mnt/d600/clivenmrdata/Mao11n/pi-c-20-2.f1d
 acq.time[s]: 2.0 relax.time[s]: 0.5 hz/mm: 91.71 sweep width[Hz]: 40000 spectrometer: u500 # of scans: 2032
 Pulse Sequence: apt
 dig.res.[Hz/pt]: 0.61

532

Pulse Sequence: apt

100 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe

CH, CH3 positive; C, CH2 negative

date: Oct 15 2001 seqfil: apt hz/mm: 92.29 sweep width [Hz]: 40000 spectrometer: i300 file: /mnt/d600/clivemrdata/Mao11n/pl1-c-20-3.fld

acq.time[s]: 2.0 relax.time[s]: 0.5 dig.res. [Hz/pt]: 0.61 # of scans: 2440

100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
CH, CH₃ positive; C, CH₂ negative
date: Aug 22 2001 seqfil: apt
acq.time[s]: 2.0 relax.time[s]: 0.5
hz/mm: 97.71 sweep width [Hz]: 50000 spectrometer: 1300 file: /mnt/d600/clivenmrdata/Mao1in/p1-c-21-1.fid
dig.res. [Hz/pt]: 0.76 # of scans: 13792
Pulse Sequence: apt

Pulse Sequence: apt

535

Pulse Sequence: apt

100 MHz APT in acetone (ref. to acetone @ 29.8 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe

CH, CH3 positive; C, CH2 negative

date: Mar 25 2002 seq1: apt file: /mnt/d600/clivemrdata/Mao11n/p1-c-24-0.fid

hz/mm: 104.17 sweep width [Hz]: 25000 spectrometer: u500

acq.time[s]: 2.0 relax.time[s]: 0.5 dig.res.[Hz/pt]: 0.38 # of scans: 296

100 MHz APT 1n CDC13 (ref. to CDC13 @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
 CH, CH3 positive; C, CH2 negative
 date: Mar 31 2002 seq11: apt hz/mm: 83.33 sweep width [Hz]: 20000 spectrometer: u500 file: /mnt/4600/clivenmrdata/Mao11n/pl-c-26-iso1.fid
 acq. time [s]: 2.0 relax. time [s]: 0.5 dig. res. [Hz/pt]: 0.31 # of scans: 616

Pulse Sequence: apt

14.972
14.490
12.283

33.021
27.773

77.303
76.987
76.668
72.777
69.608
63.795
61.424
58.456

82.903

98.578

151.338
146.769
146.150
138.586
135.177
132.296
128.253
127.494
127.476
127.394
126.322
123.545

less polar

180 160 140 120 100 80 60 40 20 ppm

100 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.8 C -> actual temp = 27.0 C, asw400 probe
 CH, CH₃ positive; C, CH₂ negative
 date: Mar 31 2002 seqf1: apt hz/mm: 83.33 sweep width [Hz]: 20000 spectrometer: 1300 file: /mnt/d800/clivenmrdata/Maol1n/p1-c-26-iso2.fid
 acq.time[s]: 2.0 relax.time[s]: 0.5 dig.res.[Hz/pt]: 0.31 # of scans: 504

Pulse Sequence: apt

125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe CH, CH3 positive; C, CH2 negative
 date: Dec 4 2001 seqfil: apt hz/mm: 104.17 sweep width [Hz]: 25000 spectrometer: i300 file: /mnt/d600/clivenmrdata/Maolin/p1-c-27-1.fid
 acq: time [s]: 2.0 relax. time [s]: 0.5 dig. res. [Hz/pt]: 0.38 # of scans: 1728
 Pulse Sequence: apt