***P*-Heterocyclic Building Blocks: Application to the Stereoselective Synthesis of Phosphono Sugars.**

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General Methods.

All air and moisture sensitive reactions were carried out in flame-dried glassware under argon. THF and CH_2Cl_2 was purified by passage through a purification system employing activated Al_2O_3 . MeOH and HMPA were distilled from CaH_2 . DME was distilled from Na/benzophenone. Flash column chromatography was performed with silica gel (230-400 mesh). Thin layer chromatography was performed out on silica gel 60F₂₅₄ plates. ^1H , ^{13}C and ^{31}P NMR spectra were recorded in CDCl_3 (unless otherwise mentioned) on a DRX-400 spectrometer operating at 400 MHz, 100 MHz, and 162 MHz respectively. High-resolution mass spectrometry (HRMS) and FAB spectra were obtained on a ZAB double-focusing mass spectrometer. Optical rotations were recorded on a Rudolph Automatic Polarimeter.

Compound 17b

Compound 18

Compound 19

Compound 20

Compound 21

Compound 22

Compound 23

Compound 24

Compound 25

Compound 26

Compound 27

Compound 28

Compound 29

Compound 30

Compound 31

Compound 32

d1

Compound 33

Compound 34

Compound 35

Compound 36

Compound 37

Compound 38

Compound 39

Compound 40

Compound 41

Compound 42

Compound 43

X-ray Data:

X-ray Data for azide **23**

Comment

The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A colorless prism-shaped crystal of dimensions 0.21 x 0.17 x 0.05 mm was selected for structural analysis. Intensity data for this compound were collected using a Bruker APEX ccd area detector(1) mounted on a Bruker D8 goniometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data were collected at 100(2) K. The intensity data were measured as a series of ω oscillation frames each of 0.25 ° for 30 sec / frame. The detector was operated in 512 x 512 mode and was positioned 5.04 cm from the sample. Coverage of unique data was 99.5 % complete to 25.99 degrees in q . Cell parameters were determined from a least squares fit of 2072 peaks in the range $2.61 < q < 30.54^\circ$. From 52 peaks that were measured both at the beginning and end of data collection, the crystal showed a decay of 0.08 %. The data were corrected for absorption by the semi-empirical method (2) from equivalent reflections giving minimum and maximum transmission factors of 0.9539 and 0.9888. Lorentz and polarization corrections were applied. The data were merged to form a set of 2635 independent data with $R(\text{int}) = 0.0337$.

The triclinic space group $P\bar{1}$ was determined by statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the displacement parameters of the bonded atoms. A total of 181 parameters were refined against 2635 data to give $wR(F^2) = 0.1570$ and $S = 1.022$ for weights of $w = 1/[s^2(F^2) + (0.1100 P)^2]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0553 for the 2141 observed, $[F > 4s(F)]$, data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.741 and -0.636 e/Å³, respectively.

Acknowledgment

The authors thank the National Science Foundation (grant CHE-0079282) and the University of Kansas for funds to purchase of the X-ray instrument and computers. This structure was determined by Douglas R. Powell.

References

- (1) (a) Data Collection: SMART Software Reference Manual (1994). Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA. (b) Data Reduction: SAINT Software Reference Manual (1995). Bruker-AXS, 6300 Enterprise Dr., Madison, WI 53719-1173, USA.
- (2) G. M. Sheldrick (1996). SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany.
- (3) (a) G. M. Sheldrick (1994). SHELXTL Version 5 Reference Manual. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373, USA. (b) *International Tables for Crystallography, Vol C*, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, Kluwer: Boston (1995).

Table 1. Crystal data and structure refinement for 02038.

Empirical formula	$C_{11} H_{14} N_3 O_5 P$	
Formula weight	299.22	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 8.1636(13) \text{ \AA}$	$a = 79.409(4)^\circ$
	$b = 8.7184(14) \text{ \AA}$	$b = 74.124(4)^\circ$
	$c = 10.1021(16) \text{ \AA}$	$\gamma = 81.613(4)^\circ$
Volume	$676.31(19) \text{ \AA}^3$	
Z, Z'	2, 1	
Density (calculated)	1.469 Mg/m^3	
Wavelength	$0.71073 \text{ \AA}$	
Temperature	$100(2) \text{ K}$	
$F(000)$	312	
Absorption coefficient	0.227 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9888 and 0.9539	
Theta range for data collection	2.12 to 25.99°	

Reflections collected	4187
Independent reflections	2635 [R(int) = 0.0337]
Data / restraints / parameters	2635 / 0 / 181
$wR(F^2 \text{ all data})$	$wR2 = 0.1570$
$R(F \text{ obsd data})$	$R1 = 0.0553$
Goodness-of-fit on F^2	1.022
Observed data [$I > 2s(I)$]	2141
Largest and mean shift / s.u.	0.000 and 0.000
Largest diff. peak and hole	0.741 and -0.636 e/Å ³

$$wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for 02038. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	0.6230(2)	0.69380(18)	0.41110(16)	0.0190(4)
P(2)	0.72952(7)	0.65339(7)	0.52368(6)	0.0170(2)
C(3)	0.9197(3)	0.7519(3)	0.4389(2)	0.0179(5)
C(4)	0.8773(3)	0.9184(3)	0.3690(2)	0.0181(5)
C(5)	0.7669(3)	0.9187(3)	0.2681(2)	0.0200(5)
C(6)	0.5939(3)	0.8554(3)	0.3421(2)	0.0199(5)
O(7)	0.7570(2)	0.48232(19)	0.56259(18)	0.0229(4)
O(8)	0.6352(2)	0.74187(18)	0.65168(16)	0.0188(4)
C(9)	0.4900(3)	0.6915(3)	0.7535(2)	0.0180(5)
C(10)	0.3603(3)	0.6350(3)	0.7184(3)	0.0237(5)
C(11)	0.2172(3)	0.5947(3)	0.8236(3)	0.0296(6)
C(12)	0.2039(3)	0.6109(3)	0.9591(3)	0.0302(6)
C(13)	0.3351(4)	0.6686(3)	0.9923(3)	0.0315(6)
C(14)	0.4802(3)	0.7085(3)	0.8884(3)	0.0244(6)
O(15)	1.0246(2)	0.74969(19)	0.53117(17)	0.0213(4)
O(16)	0.7873(2)	1.01513(19)	0.46859(16)	0.0209(4)
N(17)	0.8673(3)	0.8208(2)	0.1610(2)	0.0237(5)
N(18)	0.8508(3)	0.8680(3)	0.0422(2)	0.0269(5)
N(19)	0.8462(3)	0.8976(3)	-0.0711(2)	0.0422(7)
C(20)	0.4831(3)	0.8476(3)	0.2470(3)	0.0264(6)

Table 3. Bond lengths [Å] and angles [°] for 02038.

O(1)-C(6)	1.469(3)	C(9)-C(10)	1.383(3)
O(1)-P(2)	1.5742(17)	C(10)-C(11)	1.386(3)
P(2)-O(7)	1.4712(17)	C(10)-H(10)	0.9500
P(2)-O(8)	1.5838(16)	C(11)-C(12)	1.375(4)
P(2)-C(3)	1.809(2)	C(11)-H(11)	0.9500
C(3)-O(15)	1.424(3)	C(12)-C(13)	1.389(4)
C(3)-C(4)	1.528(3)	C(12)-H(12)	0.9500
C(3)-H(3)	1.0000	C(13)-C(14)	1.390(3)
C(4)-O(16)	1.411(3)	C(13)-H(13)	0.9500
C(4)-C(5)	1.534(3)	C(14)-H(14)	0.9500
C(4)-H(4)	1.0000	O(15)-H(15)	0.8400
C(5)-N(17)	1.491(3)	O(16)-H(16)	0.8400
C(5)-C(6)	1.535(3)	N(17)-N(18)	1.232(3)
C(5)-H(5)	1.0000	N(18)-N(19)	1.136(3)
C(6)-C(20)	1.505(3)	C(20)-H(20A)	0.9800
C(6)-H(6)	1.0000	C(20)-H(20B)	0.9800
O(8)-C(9)	1.405(3)	C(20)-H(20C)	0.9800
C(9)-C(14)	1.376(3)		
C(6)-O(1)-P(2)	121.37(14)	N(17)-C(5)-H(5)	108.9
O(7)-P(2)-O(1)	110.01(9)	C(4)-C(5)-H(5)	108.9
O(7)-P(2)-O(8)	113.37(9)	C(6)-C(5)-H(5)	108.9
O(1)-P(2)-O(8)	109.01(9)	O(1)-C(6)-C(20)	105.74(18)
O(7)-P(2)-C(3)	116.05(10)	O(1)-C(6)-C(5)	109.41(18)
O(1)-P(2)-C(3)	102.49(10)	C(20)-C(6)-C(5)	114.5(2)
O(8)-P(2)-C(3)	105.18(10)	O(1)-C(6)-H(6)	109.0
O(15)-C(3)-C(4)	111.64(18)	C(20)-C(6)-H(6)	109.0
O(15)-C(3)-P(2)	111.92(15)	C(5)-C(6)-H(6)	109.0
C(4)-C(3)-P(2)	112.13(15)	C(9)-O(8)-P(2)	123.43(14)
O(15)-C(3)-H(3)	106.9	C(14)-C(9)-C(10)	122.0(2)
C(4)-C(3)-H(3)	106.9	C(14)-C(9)-O(8)	116.6(2)
P(2)-C(3)-H(3)	106.9	C(10)-C(9)-O(8)	121.4(2)
O(16)-C(4)-C(3)	111.11(18)	C(9)-C(10)-C(11)	118.1(2)
O(16)-C(4)-C(5)	108.09(18)	C(9)-C(10)-H(10)	120.9
C(3)-C(4)-C(5)	111.06(18)	C(11)-C(10)-H(10)	120.9
O(16)-C(4)-H(4)	108.8	C(12)-C(11)-C(10)	121.1(2)
C(3)-C(4)-H(4)	108.8	C(12)-C(11)-H(11)	119.5
C(5)-C(4)-H(4)	108.8	C(10)-C(11)-H(11)	119.5
N(17)-C(5)-C(4)	107.11(18)	C(11)-C(12)-C(13)	120.0(2)
N(17)-C(5)-C(6)	110.67(19)	C(11)-C(12)-H(12)	120.0
C(4)-C(5)-C(6)	112.33(19)	C(13)-C(12)-H(12)	120.0

C(12)-C(13)-C(14)	119.7(2)
C(12)-C(13)-H(13)	120.1
C(14)-C(13)-H(13)	120.1
C(9)-C(14)-C(13)	119.1(2)
C(9)-C(14)-H(14)	120.5
C(13)-C(14)-H(14)	120.5
C(3)-O(15)-H(15)	109.5
C(4)-O(16)-H(16)	109.5
N(18)-N(17)-C(5)	115.1(2)
N(19)-N(18)-N(17)	172.8(3)
C(6)-C(20)-H(20A)	109.5
C(6)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(6)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 02038. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	13(1)	18(1)	23(1)	-3(1)	0(1)	-4(1)
P(2)	10(1)	16(1)	22(1)	-3(1)	0(1)	-2(1)
C(3)	12(1)	20(1)	20(1)	-3(1)	0(1)	-2(1)
C(4)	13(1)	17(1)	22(1)	-3(1)	2(1)	-4(1)
C(5)	15(1)	19(1)	22(1)	-2(1)	1(1)	-1(1)
C(6)	14(1)	19(1)	24(1)	-4(1)	-2(1)	-1(1)
O(7)	13(1)	20(1)	32(1)	-3(1)	0(1)	-3(1)
O(8)	13(1)	18(1)	22(1)	-3(1)	3(1)	-6(1)
C(9)	12(1)	15(1)	24(1)	-1(1)	1(1)	-2(1)
C(10)	21(1)	26(1)	24(1)	-6(1)	-2(1)	-6(1)
C(11)	17(1)	36(2)	36(1)	-9(1)	1(1)	-11(1)
C(12)	20(1)	35(2)	30(1)	-4(1)	7(1)	-11(1)
C(13)	31(2)	40(2)	21(1)	-2(1)	1(1)	-11(1)
C(14)	19(1)	28(1)	26(1)	-2(1)	-4(1)	-6(1)
O(15)	11(1)	22(1)	30(1)	-6(1)	-4(1)	0(1)
O(16)	16(1)	18(1)	28(1)	-8(1)	1(1)	-3(1)
N(17)	20(1)	28(1)	21(1)	-6(1)	0(1)	-1(1)
N(18)	21(1)	33(1)	25(1)	-4(1)	2(1)	-8(1)
N(19)	45(2)	54(2)	23(1)	0(1)	-2(1)	-10(1)
C(20)	22(1)	29(1)	29(1)	-2(1)	-8(1)	-5(1)

Table 5. Hydrogen coordinates and isotropic displacement parameters for 02038.

	x	y	z	U(eq)
H(3)	0.9881	0.6916	0.3633	0.021
H(4)	0.9865	0.9633	0.3158	0.022
H(5)	0.7459	1.0286	0.2214	0.024
H(6)	0.5299	0.9223	0.4140	0.024
H(10)	0.3690	0.6242	0.6248	0.028
H(11)	0.1269	0.5552	0.8018	0.036
H(12)	0.1050	0.5826	1.0300	0.036
H(13)	0.3257	0.6808	1.0857	0.038
H(14)	0.5713	0.7469	0.9101	0.029
H(15)	1.1065	0.6793	0.5165	0.026
H(16)	0.8468	1.0867	0.4669	0.025
H(20A)	0.5412	0.7752	0.1812	0.040
H(20B)	0.4623	0.9523	0.1955	0.040
H(20C)	0.3737	0.8104	0.3023	0.040

Table 6. Torsion angles [°] for 02038.

C(6)-O(1)-P(2)-O(7)	-172.95(15)
C(6)-O(1)-P(2)-O(8)	62.16(17)
C(6)-O(1)-P(2)-C(3)	-48.94(18)
O(7)-P(2)-C(3)-O(15)	-68.64(18)
O(1)-P(2)-C(3)-O(15)	171.46(15)
O(8)-P(2)-C(3)-O(15)	57.52(17)
O(7)-P(2)-C(3)-C(4)	165.01(14)
O(1)-P(2)-C(3)-C(4)	45.12(17)
O(8)-P(2)-C(3)-C(4)	-68.83(17)
O(15)-C(3)-C(4)-O(16)	-60.6(2)
P(2)-C(3)-C(4)-O(16)	65.9(2)
O(15)-C(3)-C(4)-C(5)	179.05(17)
P(2)-C(3)-C(4)-C(5)	-54.4(2)
O(16)-C(4)-C(5)-N(17)	177.90(17)
C(3)-C(4)-C(5)-N(17)	-60.0(2)
O(16)-C(4)-C(5)-C(6)	-60.4(2)
C(3)-C(4)-C(5)-C(6)	61.7(2)
P(2)-O(1)-C(6)-C(20)	-177.99(15)
P(2)-O(1)-C(6)-C(5)	58.3(2)
N(17)-C(5)-C(6)-O(1)	60.3(2)
C(4)-C(5)-C(6)-O(1)	-59.4(2)
N(17)-C(5)-C(6)-C(20)	-58.2(3)
C(4)-C(5)-C(6)-C(20)	-177.86(19)
O(7)-P(2)-O(8)-C(9)	-45.47(19)
O(1)-P(2)-O(8)-C(9)	77.43(18)
C(3)-P(2)-O(8)-C(9)	-173.26(17)
P(2)-O(8)-C(9)-C(14)	142.29(19)
P(2)-O(8)-C(9)-C(10)	-40.7(3)
C(14)-C(9)-C(10)-C(11)	-0.1(4)
O(8)-C(9)-C(10)-C(11)	-176.9(2)
C(9)-C(10)-C(11)-C(12)	0.3(4)
C(10)-C(11)-C(12)-C(13)	0.1(4)
C(11)-C(12)-C(13)-C(14)	-0.6(4)
C(10)-C(9)-C(14)-C(13)	-0.4(4)
O(8)-C(9)-C(14)-C(13)	176.5(2)
C(12)-C(13)-C(14)-C(9)	0.7(4)
C(4)-C(5)-N(17)-N(18)	-143.3(2)
C(6)-C(5)-N(17)-N(18)	94.0(2)
C(5)-N(17)-N(18)-N(19)	-176(2)

Table 7. Hydrogen bonds for 02038[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(15)-H(15)...O(7)#1	0.84	1.83	2.626(2)	158.7
O(16)-H(16)...O(15)#2	0.84	1.90	2.736(2)	178.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+2, -y+1, -z+1 #2 -x+2, -y+2, -z+1