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(1*R*,3*R*,4*S*,5*R*,6*R*)-6-Cyano-5-diphenylphosphino-3,4-*O*-isopropylidene-2-oxabicyclo[3.2.0]heptane-3,4-diol: X-Ray Crystal Structure and Proton Nuclear Magnetic Resonance Spectrum

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The title compound, $C_{22}H_{22}NO_3P$, crystallizes in space group $P2_1$, with $a = 13.219$ (8), $b = 10.536$ (7), $c = 7.143$ (4) Å, $\beta = 94.87$ (6)°, and $Z = 2$. The structure was solved by the direct method and refined to an R value of 0.0353. A unique structure having a cyclobutane ring fused with a furanoside moiety, and a diphenylphosphine group at the ring juncture, was confirmed by the analysis. A 270 MHz proton nuclear magnetic resonance (^{1}H-NMR) analysis of the compound showed interesting coupling features of the cyclobutane ring protons and phosphorus.

Keywords——D-glucose; (1*R*,3*R*,4*S*,5*R*,6*R*)-6-cyano-5-diphenylphosphino-3,4-*O*-isopropylidene-2-oxabicyclo[3.2.0]heptane-3,4-diol; cyclobutane ring; X-ray analysis; crystal structure; absolute configuration; NMR analysis; phosphorus; sugar conformation

Sugars have several asymmetric carbons, and could be useful for syntheses of chiral natural compounds or synthetic intermediates. Several chelating chiral ligands complexing with transition metals have been developed in connection with homogeneous asymmetric hydrogenation. For example, D-glucose has been used as a chiral ligand for homogeneous asymmetric hydrogenation by *O*-phosphination[1)] as a complex with Rh. In the course of attempts to synthesize sugar bisdiphenyl phosphine ligands having C–P bonding, we have reported the synthesis and catalytic reactions of a novel bicycloheptyl diphenylphosphine (**1**) derived from 1,2,5,6-*O*-diisopropylidene-D-glucofuranoside.[2)] For the structure determination of **1**, X-ray analysis and proton nuclear magnetic resonance (^{1}H-NMR) analysis were carried out, and the results are presented here.

Experimental

(1*R*,3*R*,4*S*,5*R*,6*R*)-6-Cyano-5-diphenylphosphino-3,4-*O*-isopropylidene-2-oxabicyclo[3.2.0]heptane-3,4-diol (1)——Colorless needles, mp 174–176 °C (ether). $[\alpha]_D^{28} = +141°$ ($c = 2.5$, benzene). High resolution mass spectrum, Calcd for $C_{22}H_{22}NO_3P$: m/z (M^+) 379.1335. Found: m/z 379.1300.

Crystallographic Measurement——A computer-controlled Rigaku Denki AFC-5 four-circle auto-diffractometer was used for all measurements. Of the toral of 1734 independent reflections of $2\theta < 120°$ obtained by the use of graphite-monochromated Cu-K_α radiation, 1580 reflections with $|F_0| > 3\sigma(F_0)$ were used in the calculation. No absorption correction was made.

Crystal Data——$C_{22}H_{22}NO_3P$. $M_r = 379.38$. Monoclinic. $a = 13.219$ (8), $b = 10.536$ (7), $c = 7.143$ (4) Å, $\beta = 94.87$ (6)°, $V = 991.2$ (6) Å^3, $D_c = 1.27\,\mathrm{g\,cm^{-3}}$, $Z = 2$, μ (Cu-K_α) $= 1.39\,\mathrm{cm^{-1}}$. Space group $P2_1$. Crystal size, $0.30 \times 0.30 \times 0.30\,\mathrm{mm^3}$.

Structure Analysis and Refinement——The structure was solved by the direct method using MULTAN78[3)] and refined by the block-diagonal least-squares procedure in the UNICS III system[4)] with the assumption of positional and isotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms were located on the difference Fourier maps and were included in the subsequent refinement with isotropic thermal parameters. Final refinement utilized anisotropic thermal parameters for all non-hydrogen atoms and converged to $R = 0.0353$. The atomic

Table I. Positional Parameters ($\times 10^4$) of Non-hydrogen Atoms with Their Estimated Standard Deviations (in Parentheses) and Equivalent Isotropic Thermal Parameters (Å^2) of (1*R*,3*R*,4*S*,5*R*,6*R*)-6-Cyano-5-diphenylphosphino-3,4-*O*-isopropylidene-2-oxabicyclo[3.2.0]heptane-3,4-diol (**1**)

Atom	*X*	*Y*	*Z*	B_{eq}
P(10)	7320 (1)	4868 (1)	8054 (1)	3.03 (0.02)
O(2)	5842 (2)	2396 (3)	4704 (4)	6.10 (0.09)
O(C3)	5757 (2)	873 (3)	6973 (4)	5.53 (0.09)
O(C4)	6657 (2)	2284 (3)	8848 (3)	4.48 (0.08)
N(9)	8809 (3)	1526 (4)	3786 (5)	5.81 (0.12)
C(1)	6268 (2)	3630 (4)	4861 (5)	3.72 (0.10)
C(3)	6392 (3)	1502 (4)	5826 (5)	3.96 (0.10)
C(4)	7154 (2)	2230 (4)	7142 (4)	3.27 (0.09)
C(5)	7226 (2)	3540 (4)	6296 (4)	2.86 (0.09)
C(6)	7899 (2)	3631 (4)	4559 (5)	3.25 (0.09)
C(7)	6929 (3)	3945 (4)	3274 (5)	4.01 (0.11)
C(8)	8407 (3)	2466 (4)	4095 (5)	4.04 (0.11)
C(A)	5955 (3)	1282 (4)	8884 (5)	4.28 (0.11)
C(M1)	6441 (6)	208 (6)	10000 (9)	10.52 (0.25)
C(M2)	5011 (4)	1731 (7)	9620 (7)	8.51 (0.22)
C-11	7539 (2)	6221 (3)	6548 (4)	3.16 (0.09)
C-12	8493 (2)	6649 (4)	6121 (5)	3.39 (0.10)
C-13	8590 (3)	7695 (4)	4970 (5)	4.19 (0.11)
C-14	7729 (3)	8338 (4)	4246 (6)	4.81 (0.13)
C-15	6784 (3)	7941 (4)	4674 (6)	5.23 (0.13)
C-16	6694 (3)	6901 (4)	5826 (6)	4.44 (0.12)
C-17	8582 (2)	4642 (3)	9265 (4)	3.03 (0.09)
C-18	8803 (3)	5414 (4)	10837 (5)	3.98 (0.10)
C-19	9741 (3)	5383 (4)	11843 (5)	4.63 (0.12)
C-20	10466 (3)	4565 (4)	11328 (6)	4.99 (0.13)
C-21	10278 (3)	3773 (5)	9802 (7)	5.73 (0.14)
C-22	9330 (3)	3817 (4)	8780 (6)	4.60 (0.12)

Table II. Bond Lengths of **1** with Their Estimated Standard Deviations (in Parentheses)

Bond	Length Å	Bond	Length Å
P(10)–C(5)	1.876 (4)	P(10)–C-11	1.824 (4)
P(10)–C-17	1.828 (3)	O(2)–C(1)	1.417 (5)
O(2)–C(3)	1.400 (5)	N(9)–C(8)	1.154 (6)
C(1)–C(5)	1.563 (4)	C(1)–C(7)	1.525 (5)
C(3)–C(4)	1.525 (5)	C(3)–O(C3)	1.390 (5)
C(4)–C(5)	1.513 (5)	C(4)–O(C4)	1.433 (4)
C(5)–C(6)	1.590 (5)	C(6)–C(7)	1.548 (5)
C(6)–C(8)	1.451 (6)	C(A)–O(C3)	1.434 (4)
C(A)–O(C4)	1.407 (5)	C(A)–C(M1)	1.497 (7)
C(A)–C(M2)	1.473 (7)	C-11–C-12	1.397 (5)
C-11–C-16	1.389 (5)	C-12–C-13	1.388 (5)
C-13–C-14	1.386 (6)	C-14–C-15	1.377 (6)
C-15–C-16	1.381 (6)	C-17–C-18	1.397 (5)
C-17–C-22	1.382 (5)	C-18–C-19	1.379 (5)
C-19–C-20	1.363 (6)	C-20–C-21	1.378 (6)
C-21–C-22	1.397 (6)		

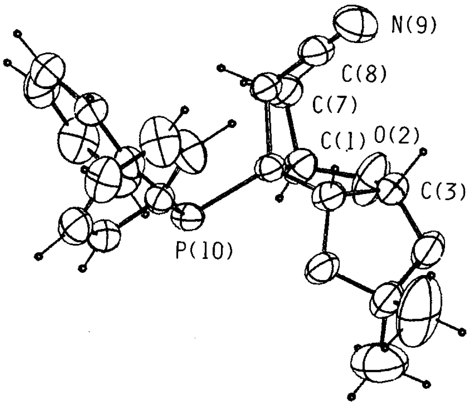

Fig. 1. ORTEP Drawing of **1**

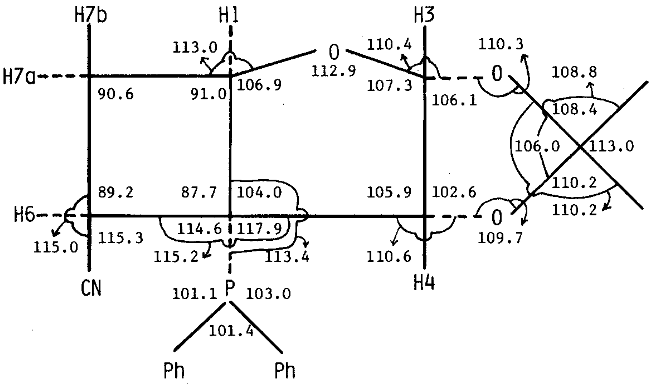

Fig. 2. Bond Angles in **1** (°) with Maximum Standard Deviation 0.5°

parameters, bond lengths, and torsion angles are given in Tables I—III, respectively, and an ORTEP[5)] drawing of the molecule and bond angles are given in Figs. 1 and 2, respectively.

NMR Measurement——NMR spectra were measured on a JEOL JNM-GX270 using $CDCl_3$ as a solvent with tetramethylsilane as an internal standard. Coupling constants were deduced from the results of double resonance experiments. ^{1}H-NMR (270 MHz) δ: 1.33—1.42 (1H, m, H-7a), 1.36 (3H, s, CH_3 protons), 1.62 (3H, s, CH_3 protons), 1.82 (1H, ddd, $J_{7a,7b}=13.9$, $J_{6,7b}=5.1$, $J_{1,7b}=1.5$, H-7b), 3.16 (1H, dddd, $J_{6,P}=8.8$, $J_{6,7b}=5.1$, $J_{1,6}=2.1$, $J_{6,7a}=0.5$, H-6), 4.72 (1H, dddd, $J_{1,7a}=5.1$, $J_{1,P}=5.1$, $J_{1,6}=2.1$, $J_{1,7b}=1.5$, H-1), 5.29 (1H, d, $J=3.7$, H-4), 6.37 (1H, d, $J=$ 3.7 Hz, H-3), 7.30—7.60 ppm (10H, m, phenyl protons).

Calculation of Coupling Constants——A computer program[6)] was applied for the calculation of coupling constants between cyclobutane protons and phosphorus, treating the system as a 5-spin one with an imaginary phosphorus chemical shift (10 ppm).

Results and Discussion

The X-ray analysis established the absolute structure of the compound (**1**) as (1*R*,3*R*,4*S*,5*R*,6*R*)-6-cyano-5-diphenylphosphino-3,4-*O*-isopropylidene-2-oxabicyclo-[3.2.0]heptane-3,4-diol based on the absolute configuration of D-glucose. The cyclobutane ring composed of C(1), C(5), C(6), and C(7) is somewhat distorted, having the longest bond length at C(5)–C(6) of 1.59 Å and the shortest at C(1)–C(7) of 1.53 Å, and the largest bond angle at C(5)–C(1)–C(7) of 91.0 ° and the smallest at C(1)–C(5)–C(6) of 87.7 ° as shown in Table II and in Fig. 2. The furanose ring is in a $_2$E form with slight $_2T^1$ nature (pseudorotation phase angle[7)] $P=340$ °). The displacements of C(3) and C(4) from the plane of the remaining three atoms (C(5), C(1), and O(2)) are 0.01 and 0.26 Å, respectively. The angle between the plane and a plane composed of C(1), C(5), and C(6) is 74.86 °, and the displacement of C(7) from the latter plane is 0.24 Å in a direction opposite to O(2) (Table III, and Fig. 2). The two benzene rings are located nearly perpendicularly, forming an angle of 86.5 °, to each other as shown in Fig. 1.

The NMR analysis showed interesting coupling features between phosphorus and protons (H-1, H-4, and H-6) which are separated by three single bond linkages. The phosphorus of diphenylphosphine coupled with H-1 and H-6 ($J=8.8$ and 5.1 Hz, respectively), but not with H-4. Interestingly, H-7b coupled with H-1 and H-6 ($J=1.5$ and 5.1 Hz, respectively), and H-7a also coupled with them ($J=5.1$ and 0.5 Hz, respectively). The couplings of H-7's with H-1 and H-6 suggest that the conformation in $CDCl_3$ solution is different from what was observed in the crystal, as given in Table III. The chemical shift difference of $\simeq 0.5$ ppm between H-7a and H-7b could be attributed mainly to the anisotropic effect of the CN group which causes the downfield shift of H-7b.[8)] Coupling constants found and calculated for the cyclobutane ring protons and phosphorus are shown in Fig. 3 together

Table III. Torsion Angles (°)

Sugar ring	
C(1)–O(2)–C(3)–C(4)	11.1
O(2)–C(3)–C(4)–C(5)	−17.3
C(3)–C(4)–C(5)–C(1)	16.3
C(4)–C(5)–C(1)–O(2)	−10.2
C(5)–C(1)–O(2)–C(3)	−0.5
Bicycloheptane	
H-3–C(3)–C(4)–H-4	17.5
H-1–C(1)–C(7)–H-7a	14.4
H-1–C(1)–C(7)–H-7b	−106.3
H-6–C(6)–C(7)–H-7a	−12.9
H-6–C(6)–C(7)–H-7b	112.4
P(10)–C(5)–C(1)–H-1	−11.6
P(10)–C(5)–C(6)–H-6	13.7
P(10)–C(5)–C(4)–H-4	−98.8
Conformation around P(10)–C(5)	
C-11–P(10)–C(5)–C(6)	33.3
C-11–P(10)–C(5)–C(1)	−67.1
C-11–P(10)–C(5)–C(4)	173.7
C-17–P(10)–C(5)–C(6)	−71.3
C-17–P(10)–C(5)–C(1)	−171.7
C-17–P(10)–C(5)–C(4)	69.1

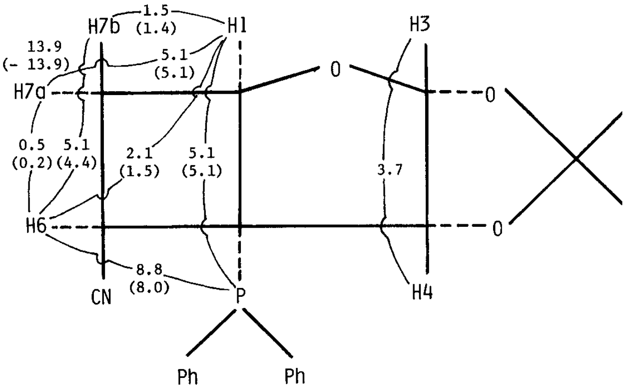

Fig. 3. Coupling Constants, Found and Calcd (in Parentheses) (Hz)

with the found coupling constant between H-3 and H-4.

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References and Notes

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8) Reduction of **1** with $LiAlH_4$ in dry ether gave the 6-aminomethyl compound, mp 125—127 °C. The ^{1}H-NMR spectrum (60 MHz, $CDCl_3$) showed H-7's as a 2H multiplet at 1.17, H-6 as a 1H multiplet at 2.33—3.00, and aminomethyl methylene protons as a 2H doublet with $J = 8$ Hz at 3.73 ppm, besides other signals.