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Structure of a Chiral Azidopropyl Bicyclic Phosphonamide

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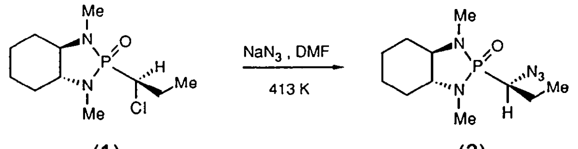
Abstract. Compound (2), 2-[(*R*)-1-azidopropyl]-2,3,-3a,4,5,6,7a-octahydro-1,3-dimethyl-1*H*-1,3,2-benzodiazaphosphole 2-oxide, $C_{11}H_{22}N_5OP$, $M_r = 271{\cdot}30$, triclinic, $P1$, $a = 5{\cdot}488\,(3)$, $b = 8{\cdot}140\,(3)$, $c = 8{\cdot}664\,(3)$ Å, $\alpha = 85{\cdot}68\,(3)$, $\beta = 74{\cdot}52\,(4)$, $\gamma = 72{\cdot}50\,(4)°$, $V = 355{\cdot}7$ Å^3, $D_x = 1{\cdot}266$ Mg m^{-3}, $Z = 1$, $\lambda(\text{Cu }K\bar{\alpha}) = 1{\cdot}54178$ Å, $\mu = 1{\cdot}697$ mm^{-1}, $F(000) = 146$, $T = 173$ K, $R = 0{\cdot}047$, $wR = 0{\cdot}045$, for 2500 observed reflections. The title compound, $C_{11}H_{22}N_5OP$, contains a five-membered ring of the half-chair type including a tetrahedrally coordinated P atom, with an azidopropyl group and an oxygen attached to the phosphorus. The five membered ring is *trans*-fused to a cyclohexyl group, which is in the chair conformation.

Introduction. Chiral, non racemic phosphonamides can be obtained by azide substitution of α-chloroalkyl phosphonamides (Hanessian & Bennani, 1989). Although the products can be rationalized based on chemical and spectroscopic methods, definitive evidence for the structure of azidoalkyl phosphonamides was not available. We now report the crystal structure of the product (2) resulting from the treatment of the chloropropyl bicyclic phosphonamide (1) with sodium azide.

It is of interest to note the inversion of the stereochemistry at the carbon center α to phosphorus in (1) leading to (2), since (1) has an optical purity in excess of 90%. Previously, we had reported the X-ray structure of (1) (Bélanger-Gariépy, Bennani, Hanessian & Brisse, 1989).



(1) (2)

Experimental. Crystals of $C_{11}H_{22}N_5OP$ recrystallized from petroleum ether, bounded by {011}, {001}, {100}, dimensions 0·08 × 0·14 × 0·40 mm. Unit-cell dimensions from 25 well-centered reflections in the range $40 \leq 2\theta \leq 47°$. Nonius CAD-4 diffractometer, graphite monochromatized Cu $K\bar{\alpha}$ radiation, ω scan, $\Delta\omega = (3{\cdot}00 + 0{\cdot}14\tan\theta)°$, $-6 \leq h \leq 6$, $-9 \leq k \leq 9$, $-10 \leq l \leq 10$. Max. $2\theta = 140°$. Orientation monitored every 200 measurements, intensities of five standard reflections (checked every hour) decreased regularly by about 28% over the duration of the data collection. This is due to the slow decomposition of the material. 2632 measured reflections, 2500 unique with $I \geq 1{\cdot}96\,\sigma(I)$ were retained for structure determination and refinement. Data corrected for Lp. The structure was solved by direct-methods using *MULTAN*80.† Block-diagonal least-squares refinement based on *F*, all non-H atoms anisotropic. H-atoms found on difference Fourier synthesis isotropically refined. Function minimized: $\sum w(|F_o| - |F_c|)^2$. The displacements calculated after each refinement cycle were dampened by a factor of 0·30. Final $R = 0{\cdot}047$, $wR = 0{\cdot}045$ (weights derived from the counting statistics), $w = 1/\sigma^2(F)$ and $S = 2{\cdot}894$ for 249 parameters. Maximum $(\Delta/\sigma) = 0{\cdot}09$, average $(\Delta/\sigma) = 0{\cdot}02$, residual electron-density fluctuations on final difference Fourier synthesis $+0{\cdot}38$ and $-0{\cdot}64$ e Å^{-3} near the P atom.

The scattering curves for the non-H atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965). The absolute configuration for $C_{11}H_{22}N_5OP$ was established using the real and imaginary parts of anomalous dispersion of the P atom (Cromer & Liberman, 1970). Structure-factor calculations were performed for each configuration by changing x, y, z to $-x$, $-y$, $-z$. After one refinement cycle for the other configuration: $R = 0{\cdot}060$, $wR = 0{\cdot}056$ and $S = 3{\cdot}647$. The ratios (for R 1·277, for wR 1·244) are clearly larger than 1·0 (Hamilton, 1965). The final atomic coordinates for $C_{11}H_{22}N_5OP$, given in Table

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† The programs used here are modified versions of: *NRC*-2, data reduction, *NRC*-10, bond distances and angles and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *FORDAP*, Fourier and Patterson maps (A. Zalkin, unpublished); *MULTAN*80, multisolution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *NUCLS*, least-squares refinement (Doedens & Ibers, 1967); and *ORTEP*, stereodrawings (Johnson, 1965).

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Table 1. *Final atomic coordinates* ($\times 10^4$; P $\times 10^5$) *and* U_{eq} ($\times 10^3$) *for the azidopropyl bicyclic phosphonamide with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
P	50620	51972	53174	39
O	3215 (5)	4269 (3)	5161 (3)	50
N(1)	4265 (5)	7322 (3)	5005 (3)	40
N(2)	5470 (5)	5307 (3)	7138 (3)	39
N(3)	8878 (6)	2342 (3)	3969 (3)	48
N(4)	7868 (7)	1732 (4)	3121 (4)	54
N(5)	7135 (8)	983 (4)	2380 (4)	74
C(1)	3635 (7)	8215 (4)	6535 (4)	39
C(2)	3816 (7)	10039 (4)	6450 (4)	45
C(3)	3148 (7)	10690 (4)	8160 (4)	48
C(4)	4881 (8)	9510 (4)	9164 (4)	53
C(5)	4827 (8)	7636 (4)	9132 (4)	50
C(6)	5545 (7)	7058 (4)	7408 (4)	39
C(7)	7354 (7)	3871 (4)	7736 (4)	45
C(8)	2529 (7)	8057 (4)	3944 (4)	50
C(9)	8299 (7)	4249 (4)	3925 (4)	40
C(10)	8542 (7)	4970 (4)	2225 (4)	46
C(11)	11314 (8)	4260 (5)	1140 (5)	57

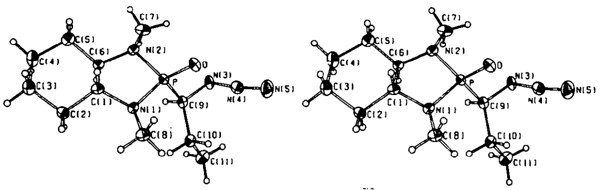

Fig. 1. Stereopair showing the molecular conformation and the atomic numbering of $C_{11}H_{22}N_5OP$. The ellipsoids correspond to 50% probability, except for the hydrogens which are shown as spheres of arbitrary sizes.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with their e.s.d.'s for* (2)

P—O	1·472 (3)	C(9)—N(3)	1·488 (4)
P—N(1)	1·671 (2)	C(9)—C(10)	1·531 (5)
N(1)—C(1)	1·468 (4)	C(10)—C(11)	1·524 (6)
C(1)—C(6)	1·510 (5)	C(1)—C(2)	1·513 (4)
C(6)—N(2)	1·476 (4)	C(2)—C(3)	1·524 (5)
P—N(2)	1·663 (3)	C(3)—C(4)	1·533 (5)
N(1)—C(8)	1·467 (1)	C(4)—C(5)	1·537 (5)
N(2)—C(7)	1·474 (4)	C(5)—C(6)	1·513 (5)
P—C(9)	1·838 (4)	N(3)—N(4)	1·238 (5)
		N(4)—N(5)	1·136 (5)

O—P—N(1)	118·3 (1)	C(9)—N(3)—N(4)	115·6 (3)
O—P—N(2)	117·0 (1)	P—N(1)—C(8)	118·5 (2)
O—P—C(9)	109·1 (2)	C(1)—N(1)—C(8)	116·7 (3)
N(1)—P—N(2)	95·4 (1)	P—N(2)—C(7)	120·0 (2)
N(1)—P—C(9)	106·8 (1)	C(6)—N(2)—C(7)	116·4 (3)
N(2)—P—C(9)	109·1 (1)	C(1)—C(2)—C(3)	107·8 (3)
P—C(9)—N(3)	108·5 (2)	C(2)—C(3)—C(4)	112·9 (3)
P—C(9)—C(10)	113·8 (2)	C(3)—C(4)—C(5)	111·8 (3)
C(9)—C(10)—C(11)	112·3 (3)	C(4)—C(5)—C(6)	108·9 (3)
P—N(1)—C(1)	109·1 (2)	C(5)—C(6)—C(1)	110·3 (3)
N(1)—C(1)—C(6)	103·9 (3)	C(6)—C(1)—C(2)	111·1 (3)
C(1)—C(6)—N(2)	104·2 (3)	C(2)—C(1)—N(1)	116·8 (3)
C(6)—N(2)—P	109·1 (2)	C(5)—C(6)—N(2)	116·6 (3)
C(10)—C(9)—N(3)	112·8 (3)	N(5)—N(4)—N(3)	171·7 (4)

C(11)—C(10)—C(9)—N(3)	−60·4 (4)	N(1)—P—N(2)—C(7)	−150·6 (3)
C(11)—C(10)—C(9)—P	175·5 (3)	N(2)—P—N(1)—C(8)	−151·5 (3)
C(10)—C(9)—P—O	84·7 (3)	C(2)—C(1)—N(1)—C(8)	63·4 (4)
C(10)—C(9)—P—N(1)	−44·3 (3)	C(5)—C(6)—N(2)—C(7)	63·7 (4)
C(10)—C(9)—P—N(2)	−146·4 (2)	C(1)—C(6)—N(2)—C(7)	174·5 (3)
N(3)—C(9)—P—O	−41·7 (3)	C(6)—C(1)—N(1)—C(8)	173·9 (3)
N(3)—C(9)—P—N(1)	−170·7 (2)	N(4)—N(3)—C(9)—C(10)	44·2 (4)
N(3)—C(9)—P—N(2)	87·3 (2)	N(4)—N(3)—C(9)—P	82·8 (3)
C(9)—P—N(1)—C(8)	96·6 (3)	C(9)—P—N(2)—C(7)	40·7 (3)
C(9)—P—N(1)—C(1)	−126·6 (2)	C(9)—P—N(2)—C(6)	97·4 (2)
O—P—N(1)—C(8)	−26·8 (3)	C(1)—C(2)—C(3)—C(4)	55·0 (4)
O—P—N(2)—C(7)	87·7 (3)	C(2)—C(3)—C(4)—C(5)	−53·5 (4)
O—P—N(2)—C(6)	−138·2 (2)	C(4)—C(5)—C(6)—C(1)	−58·6 (4)
P—N(1)—C(1)—C(2)	158·9 (2)	C(5)—C(6)—C(1)—C(2)	63·8 (4)
P—N(2)—C(6)—C(5)	156·6 (3)	C(6)—C(1)—C(2)—C(3)	−59·9 (4)
N(1)—C(1)—C(6)—C(5)	−169·9 (3)	N(1)—C(1)—C(2)—C(3)	−178·7 (3)
N(2)—C(6)—C(1)—C(2)	−170·3 (3)	N(2)—C(6)—C(5)—C(4)	−177·1 (3)
N(5)—N(4)—N(3)—C(9)	169·0 (3)		

1,[*] are those of the unambiguously established absolute configuration, *i.e.* that having the smaller values of R, wR and S.

Discussion. A stereopair showing the molecular conformation and the atomic numbering is given in Fig. 1. The bond distances, angles and torsion angles calculated from the final refined coordinates are given in Table 2. The absolute configuration established by X-ray diffraction is in agreement with that deduced from a prediction based on molecular models, stereochemistry of compound (1) and chemical data from further manipulations on compound (2).

$C_{11}H_{22}N_5OP$ contains a five-membered ring including a tetrahedrally coordinated P atom and a *trans*-fused cyclohexane. The five-membered-ring torsion angles in (2) are compared with those in (1), the chloropropyl bicyclic phosphonamide (Bélanger-Gariépy *et al.*, 1989), compounds (3) and (4), the *sec*-butyl and 4-penten-2-yl bicyclic phosphonamides respectively (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986) and the values computed by Pitzer & Donath (1959) for two conformations of minimum energy of cyclopentane, the half-chair and the envelope conformation. The five-membered-ring torsion angles of (2) conform to those tabulated for the half-chair conformation. For (2), the average deviation is only 3·0° from the computed values for the half-chair conformation while the average deviation is 10·4° from the values for the envelope conformation. For (1), the conformation of the five-membered ring is between the half-chair and the envelope. The average deviation is 4·6° from the computed values for the half-chair conformation while the average deviation is 5·4° from the values for the envelope conformation. In the five-membered rings of (3) and (4), four atoms N(2), P, N(1) and C(1) are nearly coplanar and the atom C(6) is at the flap. These five-membered rings are both of the envelope type; the average deviation is only 3·0 and 4·0° for (3) and (4) respectively, from the computed values for this form.

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52468 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Torsion angles* (°) *for the five-membered ring of* (1) (*Bélanger-Gariépy et al.*, 1989); *compound* (2) (*this work*); *compounds* (3) *and* (4) (*Bélanger-Gariépy et al.*, 1986) *and computed values for the half-chair and the envelope conformation of cyclopentane* (*Pitzer et al.*, 1959)

Torsion angles	(1)	(2)	(3)	(4)	Half-chair	Envelope
N(1)—C(1)—C(6)—N(2)	−44·9 (6)	−44·0 (3)	−43·2 (3)	41·2 (2)	−48·0	−46·1
C(1)—C(6)—N(2)—P	40·0 (6)	34·8 (3)	42·6 (3)	41·2 (2)	39·5	46·1
C(6)—N(2)—P—N(1)	−20·1 (5)	−12·5 (2)	−24·5	23·7 (2)	−15·2	−28·6
N(2)—P—N(1)—C(1)	−8·1 (5)	−14·7 (2)	−2·6 (2)	1·9 (2)	−15·2	0·0
P—N(1)—C(1)—C(6)	32·4 (6)	36·3 (3)	27·4 (3)	−25·7 (2)	39·5	28·6

The nature of the substituent on the carbon *α* to the phosphorus causes the pseudorotation of the flexible forms of the five-membered ring. The torsion angle N(2)—P—N(1)—C(1) is more affected. The angle varies from 1·9 (2)° for compound (4) (envelope form) where the substituent on the *α*-carbon is the 4-penten-2-yl, to −14·7 (2)° for (2) (half-chair form) where the substituent on the *α*-carbon is the azido group.

The azido group is in a nearly linear conformation with the angle N(5)—N(4)—N(3) 171·7 (4)°. This is in accordance with values reported by Baird, Dho, Fleet, Peach, Prout & Smith (1987). The dihedral angles C(9)—N(3)—N(4) and C(10)—C(9)—N(3) are 115·5 (7) and 112·7 (5)°, respectively. The C(9)—N(3), N(3)—N(4) and N(4)—N(5) bond lengths of 1·448 (4), 1·238 (5) and 1·136 (5) Å, respectively, indicate that the $\mathrm{C{-}\overset{-}{N}{-}\overset{+}{N}{\equiv}N}$ resonance form predominates and that there is also some contribution from the $\mathrm{C{-}N{=}\overset{+}{N}{=}\overset{-}{N}}$ resonance form (Birnbaum, Giziewicz, Gabe, Lin & Prusoff, 1987). The torsion angle O—P—C(9)—N(3) is −41·6 (8)°.

The five-membered ring is *trans*-fused to the cyclohexane ring. The torsion angles N(1)—C(1)—C(6)—N(2) and C(2)—C(1)—C(6)—C(5) are −47·9 (5) and 63·7 (8)° respectively.

The cyclohexane adopts a chair conformation. The atoms C(1), C(6), C(3) and C(4) (plane 1) are nearly coplanar while atoms C(2) and C(5) are symmetrically displaced to opposite sides of plane 1 by 0·705 (5) and −0·694 (1) Å, respectively. The endocyclic torsion angles average 57·9° showing a deviation from the 'standard' torsion angle, τ = 55·8°, for a cyclohexane ring in the chair conformation (Bucourt & Hainaut, 1965). The largest deviations involve the C(1)—C(6) bond which is also part of the five-membered ring. The mean value of the ring valency angles is 110·5° and the C—C distances average 1·521 Å. A comparison of torsion angles for (1), (2), (3), (4) and cyclopentane is given in Table 3.

The environment of the two N atoms of the five-membered ring is not planar. The distortion, measured by the three N-atom bond angles (ΣN), indicates ΣN(1) = 344·3° and ΣN(2) = 345·5° instead of ΣN = 360° for a planar group. Consequently, N(1) and N(2) are away from the plane formed by their three neighbors by 0·355 (3) and 0·341 (3) Å, respectively.

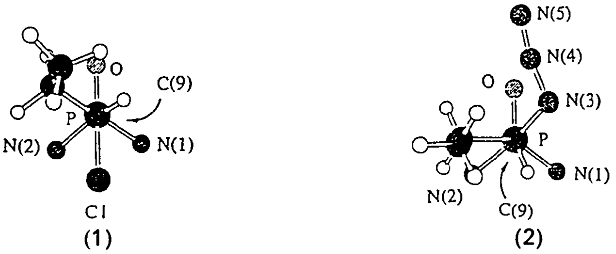

Fig. 2. Newman projections along C(9)—P for phosphonamides (1) and (2).

Because of the influence of the phosphorus, the angles P—N(1)—C(8) and P—N(2)—C(7) with values of 118·5 (5) and 120·0 (2)° respectively are significantly larger than C(1)—N(1)—C(8) = 116·7 and C(6)—N(2)—C(7) = 116·4 (4)°.

The coordination at the P atom is approximately tetrahedral since the average of the six angles involving P is 109·3°. However, the coordination is clearly distorted since the O—P—N bond angles, averaging 117·7°, are much larger than the N(1)—P—N(2) angle whose value is 95·4 (1)°. Such distortion might be due to the fact that the phosphorus is part of the five-membered ring.

The P—O bond length is 1·472 (3) Å, in good accordance with the P—O distances in the other bicyclic phosphonamides, 1·466 (4), 1·467 (3) and 1·478 (4) Å for (1), (3) and (4) respectively. All the bond lengths in azidopropyl phosphonamide (2) seem to be normal.

A close examination of the Newman projection along the C(9)—P bond (Fig. 2) reveals that the azido group is *gauche* to the oxygen. The torsion angles O—P—C(9)—N(3) and O—P—C(9)—C(10) are −41·7 (3) and 84·7 (3)° respectively. The torsion angle O—P—C(9)—H(90) is −159·4 (2)°, which shows that O is *anti* to H(90). By comparison, the torsion angles O—P—C(9)—H(90), O—P—C(9)—C(10) and O—P—C(9)—Cl in chloropropylphosphonamide (1) are −60·1 (2), 54·1 (6) and 179·3 (4)° respectively; O—P—C(9)—C(10) and O—P—C(9)—C(11) are 174·4 (3), 45·8 (3)° in (3) and −175·8 (2),

−46·5 (2)° in (4). These three systems [(1), (3) and (4)] are in an almost perfect staggered conformation. This difference in conformation between phosphonamide (2) and [(1), (3) and (4)] is most probably due to electronic effects caused by the presence of an azido group.

The molecules are held together by van der Waals forces. The closest approach is observed between O and C(9) at 3·162 (5) Å.

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Structures of Two Carbon-to-Boron Bridged *o*-Carboranes

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Abstract. The structures of two substituted *o*-carboranes, icosahedral cages in which two adjacent positions are CH and the remaining vertices BH, are described. These carboranes [(1) and (2)] are the first molecules in which one C atom is attached to an adjacent framework B atom through a carbocyclic bridge. In (1) the C—B bridge is CH_2—CH_2—CO—CH_2, in (2) it is CH_2—CO—CH_2. The cage C—C bond in (1) can be assigned unambiguously because of the absence of rotational disorder. Compound (1): 1,4-[1,2-dicarbadodecaborane(12)-1,4-diyl]-2-butanone, $C_6H_{16}B_{10}O$, $M_r = 212{\cdot}3$, monoclinic, $C2/c$, $a = 21{\cdot}702\,(6)$, $b = 8{\cdot}662\,(2)$, $c = 13{\cdot}610\,(4)$ Å, $\beta = 102{\cdot}11\,(2)°$, $V = 2501\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}13$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 4{\cdot}1$ cm^{-1}, $F(000) = 880$, $T = 293$ K, $R = 0{\cdot}056$ for 1283 reflections. Compound (2): 1,3-[1,2-dicarbadodecaborane(12)-1,4-diyl]-2-propanone, $C_5H_{14}B_{10}O$, $M_r = 198{\cdot}3$, orthorhombic, $Pbca$, $a = 22{\cdot}822\,(7)$, $b = 10{\cdot}797\,(4)$, $c = 9{\cdot}280\,(3)$ Å, $V = 2286\,(1)$ Å^3, $Z = 8$, $D_x = 1{\cdot}15$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 4{\cdot}22$ cm^{-1}, $F(000) = 816$, $T = 293$ K, $R = 0{\cdot}067$ for 1096 reflections.

Introduction. Although myriad *o*-carboranes are known (Muetterties, 1975; Olah, Prakash, Williams, Field & Wade, 1987) and many substitution patterns have been examined by X-ray crystallography, simple compounds in which one of the framework carbons is linked to one of the borons through a simple bridge were unknown until recently. Until 1986, when we reported a synthesis of such compounds using an intramolecular insertion reaction of a ketocarbene (Wu & Jones, 1986), only relatively exotic metallocycles were known [C—P—Ir—B: Hoel & Hawthorne (1975), NMR analysis; C—P—Pt—B: Manojlovic-Muir, Muir & Solomun (1980), X-ray analysis; C—C—N—Pd—B: Kalinin, Usatov & Zakharkin (1985), NMR analysis]. In addition, X-ray structure determination of *o*-carboranes has been plagued with problems of rotational disorder resulting in a general inability to

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