suggestions. ZJ thanks the Department of Chemistry, University of Saskatchewan, for financial support through a graduate scholarship.

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Structure of a Chiral Chloropropyl Bicyclic Phosphonamide

By Francine Bélanger-Gariépy, Youssef L. Bennani, Stephen Hanessian* and François Brisse*

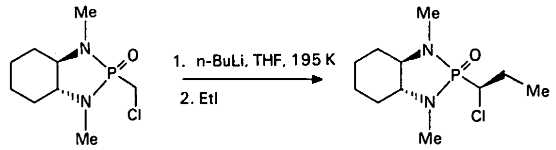
Département de Chimie, Université de Montréal, CP 6128, *Succ. 'A', Montréal, Québec, Canada H*3*C* 3*J*7

(*Received* 15 *June* 1988; *accepted* 21 *September* 1988)

Abstract. 2-(1-Chloropropyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1*H*-1,3,2-benzodiazaphosphole 2-oxide, $C_{11}H_{22}ClN_2OP$, $M_r = 264{\cdot}74$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}862$ (3), $b = 9{\cdot}492$ (4), $c = 18{\cdot}976$ (7) Å, $V = 1416{\cdot}11$ Å^3, $D_x = 1{\cdot}242$ Mg m^{-3}, $Z = 4$, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\,K\bar{\alpha}) = 3{\cdot}381$ mm^{-1}, $F(000) = 568$, $T = 293$ K, $R = 0{\cdot}077$, $wR = 0{\cdot}049$ for 1554 observed reflections. The title compound contains a five-membered ring of the envelope type including a tetrahedrally coordinated P atom. A chloropropyl group and an O atom are attached to the phosphorus. The cyclohexane ring, in the chair conformation, is *trans*-fused to the five-membered ring.

Introduction. Chiral, non-racemic phosphonamides (Hanessian, Delorme, Beaudoin & Leblanc, 1985) can be obtained from chloromethyl phosphonamides by anion formation and alkylation (Hanessian & Bennani, 1989). Although alkyl phosphonamides behave similarly and the products can be rationalized based on precedents (Hanessian, Delorme, Beaudoin & Leblanc, 1984), definitive evidence for the structure of the alkylchloro phosphonamides was not available. We now report the crystal structure of the product (2) resulting from the treatment of the chloromethyl phosphonamide (1) with ethyl iodide.

It is of interest to note that very high selectivity results from this alkylation, since the product (2) has an optical purity in excess of 90%. Previously, we had also resorted to X-ray crystallography to elucidate the structure and stereochemistry of related alkyl phosphonamides (Bélanger-Gariépy, Delorme, Hanessian & Brisse, 1986).



(1) (2)

Experimental. Crystals of $C_{11}H_{22}ClN_2OP$ recrystallized from hexane solution, bounded by {001}, {010}, {100}, dimensions 0·04 × 0·09 × 0·42 mm. Unit-cell dimensions from 25 well centered reflections in the range $40 \leq 2\theta \leq 50°$. Nonius CAD-4 diffractometer, graphite-monochromatized $\mathrm{Cu}\,K\bar{\alpha}$ radiation, ω–2θ scan, $\Delta\omega = (1{\cdot}00 + 0{\cdot}14\tan\theta)°$, $2\theta_{\max} = 140{\cdot}0°$, $-9 \leq h \leq 9$, $0 \leq k \leq 11$, $0 \leq l \leq 23$. Orientation monitored every 200 measurements, the intensities of seven standard reflections (checked every hour) decreased regularly by about 15% over the duration of the data collection. This is due to the slow decomposition of the compound. 2679 measured reflections of which 1554

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* Authors to whom correspondence should be addressed.

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Table 1. *Final atomic coordinates and their e.s.d.'s* ($\times 10^4$) *and* U_{eq} ($Å^2 \times 10^4$) *for* $C_{11}H_{22}ClN_2OP$

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl	10303 (3)	7980 (3)	8019 (1)	878
P	8018 (3)	7989 (2)	9265 (1)	460
O	7740 (6)	7194 (5)	9916 (3)	554
N(1)	8369 (7)	9695 (5)	9362 (3)	541
N(2)	6427 (7)	8145 (6)	8691 (3)	457
C(1)	7355 (9)	10481 (7)	8849 (4)	529
C(2)	6818 (10)	11972 (8)	9078 (4)	723
C(3)	5721 (10)	12611 (7)	8487 (5)	739
C(4)	4215 (10)	11683 (8)	8323 (4)	792
C(5)	4727 (9)	10152 (7)	8142 (4)	599
C(6)	5733 (9)	9596 (7)	8756 (4)	508
C(7)	5124 (9)	7030 (8)	8669 (4)	634
C(8)	10041 (10)	10298 (8)	9517 (4)	753
C(9)	9808 (9)	7151 (8)	8831 (4)	566
C(10)	9570 (10)	5571 (8)	8720 (4)	774
C(11)	11170 (12)	4774 (9)	8635 (5)	1117

with $I \geq 1{\cdot}96\sigma(I)$ were retained for structure determination and refinement. Data corrected for Lp and absorption effects (transmission range 0·57–0·89).

The structure was solved by direct methods using *MULTAN*80.* Full-matrix weighted least-squares refinement based on F (*SHELX*), all non-H atoms anisotropic. The thermal motion was found to be very high for the methyl group C(11), suggesting that this group could be disordered among two or more sites. Attempts to resolve this disorder could not yield coherent sets of alternate positions. All H atoms found on difference Fourier synthesis. All attempts to refine the coordinates of methyl H atoms led to meaningless C—H distances and very high temperature factors. These H atoms were held at a fixed distance, 1·08 Å, from C(7), C(8) and C(11) and given isotropic temperature factors of 8·0 Å^2. Function minimized: $\sum w(|F_o| - |F_c|)^2$. Final $R = 0{\cdot}0768$, $wR = 0{\cdot}0492$ [weights derived from the counting statistics $w = 1/\sigma^2(F)$] and $S = 1{\cdot}937$ for 234 parameters. Maximum $\Delta/\sigma = 0{\cdot}32$, average $\Delta/\sigma = 0{\cdot}04$, residual electron density fluctuation on final difference Fourier synthesis $+0{\cdot}62$ and $-0{\cdot}57$ 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 $C_{11}H_{22}ClN_2OP$ was established using the real and imaginary parts of anomalous dispersion of Cl and P atoms (Cromer & Liberman, 1970). Structure-factor calculations were performed for each configuration by changing x, y, z into $\bar{x}, \bar{y}, \bar{z}$. After two refinement cycles for the other configuration: $R = 0{\cdot}0819$, $wR = 0{\cdot}0531$ and $S = 2{\cdot}091$. The R ratios ($w\mathcal{R} = 1{\cdot}079$, $\mathcal{R} = 1{\cdot}066$) are clearly larger than 1·0 (Hamilton, 1965). The relatively high value of the final R factor is attributed to the steady decomposition of the crystal as the data collection proceeded. The final atomic coordinates for $C_{11}H_{22}ClN_2OP$, given in Table 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 and previous works (Hanessian *et al.*, 1984).

The five-membered ring has the usual envelope conformation folded along C(1)–N(2). The atoms C(1), N(1), N(2) and P are coplanar (plane 1) and the atom C(6) is at the flap. This atom is $-0{\cdot}488$ (6) Å away from 1. The fold angle, *i.e.* the dihedral angle between plane 1 and plane 2 [N(2), C(1), C(6)], is 31·5°. In two other bicyclic phosphonamides, $C_{12}H_{25}N_2OP$ (3) and $C_{13}H_{25}N_2OP$ (4), which differ by the substituents on P, the corresponding dihedral angles were both 40° (Bélanger-Gariépy *et al.*, 1986).

The environment of the two N atoms of the five-membered ring is not planar. The distortion, measured by the sum of the three N atom bond angles ($\sum$N), indicates $\sum N(1) = 348{\cdot}4°$ and $\sum N(2) = 340{\cdot}6°$ instead of $\sum N = 360°$ for a planar group. Consequently, N(1) and N(2) are away from the planes formed by their three neighbours by as much as $-0{\cdot}227$ (5) Å for N(1) and $0{\cdot}295$ (4) Å for N(2). These values correspond to those found in the above mentioned bicyclic phosphonamides: $\sum N(1) = 340{\cdot}2°$ and

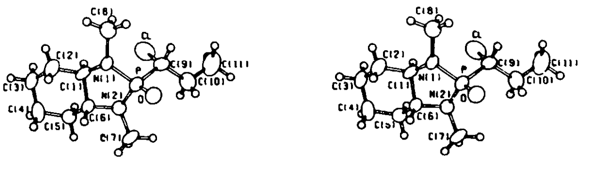

Fig. 1. Stereopair showing the molecular conformation and the atomic numbering of $C_{11}H_{22}ClN_2OP$.

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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 *et al.*, 1980); *SHELX*, program for structure determination (Sheldrick, 1976) and *ORTEP*, stereodrawings (Johnson, 1965).

* 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 51393 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles and torsion angles* (°) *with their e.s.d.'s for* $C_{11}H_{22}ClN_2OP$

P—O	1·464 (5)	C(9)—Cl	1·773 (7)
P—N(1)	1·653 (6)	C(9)—C(10)	1·526 (10)
N(1)—C(1)	1·463 (9)	C(10)—C(11)	1·477 (12)
C(1)—C(6)	1·537 (10)	C(1)—C(2)	1·540 (10)
C(6)—N(2)	1·487 (9)	C(2)—C(3)	1·539 (11)
P—N(2)	1·665 (6)	C(3)—C(4)	1·508 (11)
N(1)—C(8)	1·464 (10)	C(4)—C(5)	1·547 (11)
N(2)—C(7)	1·474 (9)	C(5)—C(6)	1·504 (10)
P—C(9)	1·814 (8)		
O—P—N(1)	115·8 (3)	N(2)—P—N(1)	96·4 (3)
O—P—N(2)	119·1 (3)	P—N(1)—C(8)	123·7 (5)
O—P—C(9)	105·8 (3)	C(1)—N(1)—C(8)	115·1 (6)
N(1)—P—N(2)	96·4 (3)	P—N(2)—C(7)	118·5 (5)
N(1)—P—C(9)	110·5 (3)	C(6)—N(2)—C(7)	114·4 (5)
N(2)—P—C(9)	109·0 (3)	C(1)—C(2)—C(3)	108·1 (6)
P—C(9)—Cl	111·7 (4)	C(2)—C(3)—C(4)	111·1 (6)
P—C(9)—C(10)	113·5 (5)	C(3)—C(4)—C(5)	113·0 (6)
Cl—C(9)—C(10)	110·1 (5)	C(4)—C(5)—C(6)	107·1 (6)
C(9)—C(10)—C(11)	114·5 (7)	C(5)—C(6)—C(1)	109·5 (6)
P—N(1)—C(1)	109·6 (5)	C(6)—C(1)—C(2)	107·9 (6)
N(1)—C(1)—C(6)	104·5 (5)	C(2)—C(1)—N(1)	115·5 (6)
C(1)—C(6)—N(2)	102·2 (5)	C(5)—C(6)—N(2)	117·0 (6)
C(6)—N(2)—P	107·7 (4)		
C(11)—C(10)—C(9)—Cl	76·7 (8)	N(1)—P—N(2)—C(7)	−151·8 (5)
C(11)—C(10)—C(9)—P	−157·3 (6)	N(2)—P—N(1)—C(8)	−149·2 (6)
C(10)—C(9)—P—O	54·1 (6)	C(2)—C(1)—N(1)—C(8)	−64·5 (8)
C(10)—C(9)—P—N(1)	−179·7 (5)	C(5)—C(6)—N(2)—C(7)	−66·6 (8)
C(10)—C(9)—P—N(2)	−75·0 (6)	C(1)—C(6)—N(2)—C(7)	173·9 (5)
Cl—C(9)—P—O	179·3 (4)	C(6)—C(1)—N(1)—C(8)	177·2 (6)
Cl—C(9)—P—N(1)	−54·6 (5)	P—N(1)—C(1)—C(6)	32·4 (6)
Cl—C(9)—P—N(2)	50·1 (5)	N(1)—C(1)—C(6)—N(2)	−44·9 (6)
C(9)—P—N(1)—C(8)	−36·2 (7)	C(1)—C(6)—N(2)—P	40·0 (6)
C(9)—P—N(2)—C(7)	93·9 (5)	C(6)—N(2)—P—N(1)	−20·1 (5)
C(9)—P—N(1)—C(1)	104·9 (5)	N(2)—P—N(1)—C(1)	−8·1 (5)
C(9)—P—N(2)—C(6)	−134·4 (5)	C(1)—C(2)—C(3)—C(4)	56·3 (8)
O—P—N(1)—C(8)	84·2 (6)	C(2)—C(3)—C(4)—C(5)	−54·8 (9)
O—P—N(2)—C(7)	−27·5 (6)	C(3)—C(4)—C(5)—C(6)	56·7 (8)
O—P—N(1)—C(1)	−134·8 (5)	C(4)—C(5)—C(6)—C(1)	−62·1 (7)
O—P—N(2)—C(6)	104·3 (5)	C(5)—C(6)—C(1)—C(2)	67·0 (7)
P—N(1)—C(1)—C(2)	150·8 (5)	C(6)—C(1)—C(2)—C(3)	−61·7 (7)
P—N(2)—C(6)—C(5)	159·5 (5)	N(1)—C(1)—C(2)—C(3)	−178·1 (6)
N(1)—C(1)—C(6)—C(5)	−169·6 (6)	N(2)—C(6)—C(5)—C(4)	−177·7 (6)
N(2)—C(6)—C(1)—C(2)	−168·3 (5)		

$\sum$N(2) = 352·4° for phosphonamide (3) and $\sum$N(1) = 342·7° and $\sum$N(2) = 353·7° for phosphonamide (4). The distances, *D*, of the N atoms to the corresponding planes were *D*(1) = 0·390 (3) Å and *D*(2) = 0·238 (3) Å for (3) and, *D*(1) = 0·406 (2) Å and *D*(2) = 0·221 (2) Å for (4), respectively.

Because of the influence of the phosphorus, the angles P—N(1)—C(8) and P—N(2)—C(7) with values of 123·7 (5) and 118·5 (5)° respectively, are significantly larger than C(1)—N(1)—C(8) = 115·1 (6)° and C(6)—N(2)—C(7) = 114·4 (5)°. Atom C(8) is at 0·460 (7) Å from plane 1 while C(7) is at −0·503 (6) and 0·813 (5) Å from planes 1 and 2 respectively.

The coordination at the P atom is approximately tetrahedral since the average of the six angles involving P is 109·4°. However, the coordination is clearly distorted since the O—P—N bond angles, averaging 117·5°, are much larger than the N(1)—P—N(2) angle whose value is 96·4 (3)°. Such a distortion may be associated with the fact that P is part of a five-membered ring.

The P—O bond length is 1·466 (4) Å, in good agreement with the P—O distances in the two other bicyclic phosphonamides, 1·467 (3) and 1·478 (4) Å for (3) and (4) respectively. All distances and angles in the 1-chloropropyl group are normal. The O—P—C(9)—Cl torsion angle is *trans* [τ = 179·3 (4)°].

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 −44·9 (6) and 67·0 (7)° respectively. The cyclohexane adopts a chair conformation. The atoms C(1), C(6), C(3) and C(4) (plane 3) are nearly coplanar while atoms C(2) and C(5) are symmetrically displaced to opposite sides of plane 3 by −0·519 (5) and 0·517 (5) Å respectively. The endocyclic torsion angles have an average of 59·8° showing a clear deviation from the 'standard' torsion angle, τ = 55·8°, for a cyclohexane ring in the chair conformation (Bucourt & Hainault, 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 109·5° and although the ring C—C distances average 1·529 Å, the two distances C(3)—C(4) and C(5)—C(6) are quite short.

The molecules are held together by van der Waals interactions since there are no contacts shorter than 3·3 Å. The shortest intramolecular contact between P and Cl is 2·970 (3) Å.

We thank the Ministère de l'Education du Québec for its financial support of this research, and Mr M. Simard for the collection of the X-ray intensities.

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