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The Structures of Two Tricyclic Phosphoranes Displaying Facial Placement of the Fused Bicyclic System

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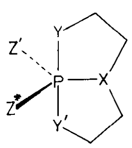
Abstract

The crystal structures of two tricyclic phosphoranes displaying facial placement of the fused bicyclus have been determined. 2′,3′-Diphenylspiro[[1,3,2λ^5]dioxaphospholane-2,10′-[1,3,2λ^5]oxazaphospholo[2,3-*b*]-[1,3,2λ^5]benzoxazaphosphole] (1) is monoclinic, $P2_1/n$, with $a = 10{\cdot}173\,(2)$, $b = 8{\cdot}988\,(2)$, $c = 21{\cdot}053\,(4)$ Å, $\beta = 101{\cdot}69\,(2)°$, $Z = 4$; 1′,2,3′-trimethyl-3-phenylspiro[[1,2λ^5]azaphospholo[2,1-*b*][1,3,2λ^5]benzoxazaphosphole-4(1*H*),2′-[1,3,2λ^5]diazaphospholidine] (2) is triclinic, $P\bar{1}$, with $a = 12{\cdot}257\,(5)$, $b = 18{\cdot}038\,(3)$, $c = 9{\cdot}336\,(2)$ Å, $\alpha = 111{\cdot}40\,(1)$, $\beta = 90{\cdot}86\,(2)$, $\gamma = 95{\cdot}05\,(5)°$, $Z = 4$. The structures were refined to $R = 0{\cdot}053$ and $0{\cdot}062$ for respectively 2602 and 4857 reflections. The deviations from the ideal trigonal-bipyramidal geometry are found to lie on the Berry pseudorotation pathway for both (1) and (2). A 34·9% distortion in the direction of a square-pyramidal geometry is observed for (1) and respectively 12·7 and 22·5% distortions for the two independent molecules of (2). The axial P—N bond of the bicyclus in (1) is 0·055 Å shorter than the average value for the equivalent bond in (2) as a result of polarization of the N—P—O axial bond in comparison to the N—P—N axial bond. Increased ring strain in the benzoxaphosphole ring of the independent molecules of (2) leads to an average lengthening of their axial P—N bonds of 0·075 Å in comparison to the opposite P—N bonds of the saturated diazaphospholidine rings.

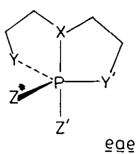
Introduction

The current interest in the dynamic stereochemistry of pentacoordinate P species (Hellwinkel, 1972; Luckenbach, 1973) has been accompanied by a substantial increase to more than 50 in the number of phosphoranes which have been characterized by X-ray diffraction (Sheldrick, 1978). Most of these derivatives owe their stability to the inclusion of a P atom in one or more small rings.

We have recently studied a series of phosphorane derivatives with fused bicyclic systems. Extension to these systems of the principle of preferred axial–equatorial placement observed for mono- and spirobicyclic derivatives leads to two possible structural representations for a trigonal-bipyramidal geometry, namely with either meridional (*aea*) or facial (*eae*) placement of the bicyclus,



aea



eae

that is equatorial or axial annelation, which are capable of interconversion by Berry (1960) pseudorotation about the pivot bond marked with an asterisk. As yet only the *aea* configuration has been observed for those bicyclic derivatives studied by X-ray diffraction in which P does not participate in a further small ring. Indeed, when the bridgehead atom *X* is N, as in the majority of fused bicyclic derivatives studied, and the apicophilicities of *X*, *Y*(*Y*′) and *Z*(*Z*′) are similar, so that the polarity rule is not structure-determinative, then the *aea* configuration would be expected to be relatively more stable because only an equatorially substituted N is capable of adopting the preferred planar trigonal coordination. This geometry has been confirmed by X-ray structural analysis for the acyclic equatorial N in 2,2-bis(*p*-bromophenoxy)-2-dimethylamino-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^5-dioxaphospholane (Barlow, Bone, Russell, Trippett & Whittle, 1976), and by electron diffraction for the three acyclic equatorial N atoms in $(Me_2N)_3PF_2$

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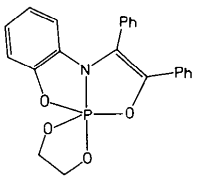
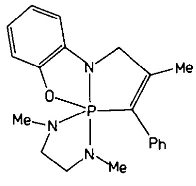
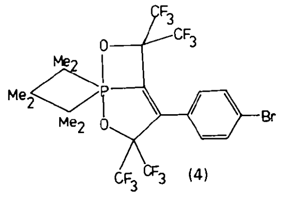
(Oberhammer & Schmutzler, 1976). In favourable heterocyclic ring systems π delocalization over the ring members may further stabilize the *aea* arrangement. However, the alternative *eae* configuration might be expected to be preferred for derivatives in which, for instance, X and Z' are considerably more electronegative than Y and Y' or in which the ligands Z and Z' belong to a further small (four- or five-membered) ring system. In the latter case, adoption of the energetically more favourable *ae* placement by the third ring will force the fused bicyclic system to adopt an *eae* configuration. Axial annelation has indeed been reported for the tricyclic derivatives (1) and (2), preliminary reports of which have previously appeared (Schmidpeter, Schomburg, Sheldrick & Weinmaier, 1976; Schmidpeter, Weinmaier, Sheldrick & Schomburg, 1979). A reduction of the equatorial angle Z–P–Z' to 106–117° has, however, been observed for fused bicyclic systems (Sheldrick, 1978), which suggests that this angle might be capable of narrowing still further to accommodate an *ee*-placed small ring. This possibility has recently been realized in (4), in which the four-membered phosphetane ring is diequatorially placed with an endocyclic C—P—C angle of 82·9 (9)° (Aly, Barlow, Russell, Smith, Swindles & Trippett, 1976). The full structural details for (1) and (2) are presented in this work.



(1)



(2)



(4)

Experimental

Crystal and refinement data for (1) and (2) are summarized in Table 1. Cell parameters were determined by least squares from the settings for 15 reflexions $\pm(hkl)$ on a Syntex $P2_1$ diffractometer. Intensities were collected with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Measurements were carried out in the θ–2θ mode for $3{\cdot}0 < 2\theta < 55{\cdot}0°$ at scan speeds varying linearly between 2·93 and 29·30° min^{-1}. The net intensity of each reflexion (scaled to counts per minute) was assigned an e.s.d. based on the counting statistics, of $\sigma(I) = t(N_s + N_b)^{1/2}$, where t is the scan rate, N_s the gross count and N_b the total background count. Lorentz and polarization but no absorption corrections were made.

Table 1. *Crystal and refinement data*

Compound	(1)	(2)
Stoichiometry	$C_{22}H_{18}NO_4P$	$C_{20}H_{24}N_3OP$
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	10·173 (2)	12·257 (5)
b (Å)	8·988 (2)	18·038 (3)
c (Å)	21·053 (4)	9·336 (2)
α (°)		111·40 (1)
β (°)	101·69 (2)	90·86 (2)
γ (°)		95·05 (5)
U (Å^3)	1885·1 (5)	1911·9 (8)
Z	4	4
M_r	391·4	353·4
D_c (Mg m^{-3})	1·38	1·23
Radiation	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0·131	0·118
2θ range (°)	3·0–55·0	3·0–55·0
F rejection criterion	4·0	4·0
Number of reflexions	2602	4857
R	0·053	0·062
$R_w = (\sum w^{1/2}\Delta/\sum w^{1/2}F_o)$	0·046	0·050
k	2·1286	2·1760
g	0·000193	0·000114
Highest peak in difference map (e Å^{-3})[*]	0·24	0·44

[*] Refers to the last refinement cycle.

Structure solution and refinement

All reflexions were included in the direct-methods solutions, those with $I < 0{\cdot}5\sigma(I)$ being assigned a value of $0{\cdot}25\sigma(I)$. The structures were solved by the automatic multisolution routine of *SHELX* 76 (G. M. Sheldrick) and refined by blocked full-matrix least squares, $\sum w\Delta^2$ being minimized. For (2) there are two independent molecules in the cell. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Difference syntheses revealed the positions of all H atoms, which were then freely refined with individual isotropic temperature factors. Weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed for the non-hydrogen atoms. The final atom coordinates are listed in Table 2.[*] Bond lengths and angles are presented in Tables 3 and 4. Figs. 1 and 2 which show the molecules of (1) and (2) respectively with the numbering scheme were drawn by *RSPLOT* (W. S. Sheldrick) which was also used for all molecular-geometry calculations.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35348 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional parameters* ($\times 10^4$)

	x	*y*	*z*
Compound 1			
P	7489 (1)	2321 (1)	4622 (0)
O(4)	8702 (2)	2938 (2)	5192 (1)
O(5)	6254 (2)	3116 (2)	4117 (1)
O(2)	8422 (2)	2651 (2)	4079 (1)
O(3)	7582 (2)	557 (2)	4561 (1)
N(1)	6468 (2)	2226 (2)	5200 (1)
C(2)	8500 (3)	2662 (3)	5826 (1)
C(3)	7225 (3)	2290 (3)	5837 (1)
C(16)	5160 (3)	2739 (3)	4968 (1)
C(11)	5046 (3)	3213 (3)	4331 (1)
C(12)	3873 (3)	3704 (3)	3959 (2)
C(13)	2760 (3)	3771 (3)	4241 (2)
C(14)	2850 (3)	3350 (4)	4873 (2)
C(15)	4042 (3)	2825 (3)	5250 (2)
C(4)	9275 (4)	1414 (4)	4045 (2)
C(5)	8457 (4)	71 (5)	4139 (2)
C(31)	6630 (3)	1883 (3)	6400 (1)
C(36)	5887 (3)	574 (4)	6377 (2)
C(35)	5330 (4)	162 (5)	6899 (2)
C(34)	5502 (4)	1042 (5)	7440 (2)
C(33)	6248 (3)	2338 (4)	7476 (1)
C(32)	6806 (3)	2765 (4)	6951 (1)
C(21)	9728 (3)	2784 (3)	6328 (1)
C(26)	10738 (3)	3751 (3)	6227 (2)
C(25)	11937 (4)	3850 (5)	6669 (2)
C(24)	12131 (4)	3026 (6)	7224 (2)
C(23)	11154 (4)	2076 (5)	7349 (2)
C(22)	9930 (3)	1937 (4)	6893 (1)
Compound 2			
P	5164 (1)	7545 (1)	4720 (1)
C(4)	6410 (2)	7688 (2)	5972 (3)
C(21)	6877 (3)	7034 (2)	6324 (3)
C(22)	7934 (3)	6876 (2)	5935 (4)
C(23)	8414 (4)	6276 (3)	6241 (5)
C(24)	7843 (4)	5836 (3)	6952 (5)
C(25)	6798 (5)	5986 (2)	7369 (5)
C(26)	6301 (3)	6581 (2)	7052 (4)
C(2)	6828 (2)	8450 (2)	6628 (3)
C(19)	7743 (3)	8793 (3)	7845 (5)
C(3)	6296 (3)	9035 (2)	6114 (5)
N(1)	5493 (2)	8576 (1)	4888 (3)
C(11)	5373 (2)	7918 (2)	2272 (4)
C(12)	5427 (3)	7826 (3)	766 (4)
C(13)	5689 (3)	8511 (3)	426 (6)
C(14)	5892 (3)	9250 (3)	1591 (5)
C(15)	5829 (3)	9334 (2)	3135 (5)
C(16)	5567 (2)	8660 (2)	3479 (3)
O(5)	5160 (2)	7297 (1)	2787 (2)
N(3)	3958 (2)	7712 (2)	5505 (3)
N(2)	4876 (2)	6538 (1)	4424 (3)
C(5)	3309 (3)	7018 (2)	5618 (6)
C(6)	3716 (3)	6304 (2)	4408 (6)
C(18)	3631 (5)	8475 (3)	6528 (7)
C(17)	5468 (4)	5933 (2)	3315 (5)
P′	292 (1)	7459 (1)	2719 (1)
C(4)′	1416 (2)	7517 (2)	1459 (3)
C(12)′	1743 (3)	6819 (2)	134 (4)
C(22)′	1058 (3)	6437 (2)	−1178 (4)
C(23)′	1393 (4)	5828 (2)	−2426 (5)
C(24)′	2415 (4)	5583 (2)	−2400 (5)
C(25)′	3107 (4)	5944 (2)	−1127 (5)
C(26)′	2769 (3)	6566 (2)	142 (5)
C(2)′	1867 (3)	8260 (2)	1736 (3)
C(19)′	2726 (4)	8513 (3)	835 (6)
C(3)′	1442 (3)	8901 (2)	3061 (4)
N(1)′	648 (2)	8515 (1)	3749 (3)
C(11)′	490 (2)	8069 (2)	5735 (3)
C(12)′	499 (3)	8127 (2)	7240 (4)
C(13)′	675 (3)	8894 (3)	8382 (5)
C(14)′	855 (3)	9553 (3)	8003 (5)
C(15)′	849 (3)	9492 (2)	6480 (5)
C(16)′	662 (2)	8736 (2)	5324 (3)
O(5)′	363 (2)	7365 (1)	4476 (2)
N(3)′	−977 (2)	7556 (1)	2207 (3)
N(2)′	21 (2)	6428 (1)	1857 (3)
C(5)′	−1672 (3)	6817 (2)	1415 (5)
C(6)′	−1151 (3)	6182 (2)	1781 (4)
C(18)′	−1328 (5)	8259 (4)	1964 (11)
C(17)′	703 (4)	5907 (2)	2249 (5)

Table 3. *Bond lengths* (Å)

Compound 1			
O(4)–P	1·635 (2)	O(5)–P	1·637 (2)
O(2)–P	1·654 (2)	O(3)–P	1·595 (2)
N(1)–P	1·755 (2)	C(2)–O(4)	1·413 (3)
C(11)–O(5)	1·395 (4)	C(4)–O(2)	1·421 (4)
C(5)–O(3)	1·446 (5)	C(3)–N(1)	1·406 (3)
C(16)–N(1)	1·400 (3)	C(3)–C(2)	1·343 (4)
C(21)–C(2)	1·467 (3)	C(31)–C(3)	1·482 (4)
C(11)–C(16)	1·388 (4)	C(15)–C(16)	1·388 (4)
C(12)–C(11)	1·362 (4)	C(13)–C(12)	1·381 (5)
C(14)–C(13)	1·368 (5)	C(15)–C(14)	1·391 (4)
C(5)–C(4)	1·503 (6)	C(36)–C(31)	1·394 (4)
C(32)–C(31)	1·386 (4)	C(35)–C(36)	1·396 (5)
C(34)–C(35)	1·368 (6)	C(33)–C(34)	1·385 (6)
C(32)–C(33)	1·395 (4)	C(26)–C(21)	1·395 (4)
C(22)–C(21)	1·393 (4)	C(25)–C(26)	1·379 (5)
C(24)–C(25)	1·363 (6)	C(23)–C(24)	1·376 (7)
C(22)–C(23)	1·415 (5)		
Compound 2			
C(4)–P	1·850 (3)	N(1)–P	1·818 (3)
O(5)–P	1·694 (2)	N(3)–P	1·662 (3)
N(2)–P	1·737 (3)	C(21)–C(4)	1·491 (5)
C(2)–C(4)	1·335 (4)	C(22)–C(21)	1·377 (5)
C(26)–C(21)	1·395 (5)	C(23)–C(22)	1·390 (7)
C(24)–C(23)	1·364 (7)	C(25)–C(24)	1·365 (8)
C(26)–C(25)	1·398 (6)	C(19)–C(2)	1·502 (5)
C(3)–C(2)	1·500 (6)	N(1)–C(3)	1·447 (4)
C(16)–N(1)	1·381 (5)	C(12)–C(11)	1·358 (6)
C(16)–C(11)	1·398 (4)	O(5)–C(11)	1·378 (5)
C(13)–C(12)	1·397 (8)	C(14)–C(13)	1·378 (6)
C(15)–C(14)	1·397 (7)	C(16)–C(15)	1·380 (6)
C(5)–N(3)	1·461 (5)	C(18)–N(3)	1·454 (5)
C(6)–N(2)	1·445 (5)	C(17)–N(2)	1·458 (5)
C(6)–C(5)	1·501 (6)	C(4)′–P′	1·845 (3)
N(1)′–P′	1·803 (2)	O(5)′–P′	1·711 (2)
N(3)′–P′	1·664 (3)	N(2)′–P′	1·734 (2)
C(21)′–C(4)′	1·498 (4)	C(2)′–C(4)′	1·334 (4)
C(22)′–C(21)′	1·390 (4)	C(26)′–C(21)′	1·377 (5)
C(23)′–C(22)′	1·376 (5)	C(24)′–C(23)′	1·366 (6)
C(25)′–C(24)′	1·365 (6)	C(26)′–C(25)′	1·400 (5)
C(19)′–C(2)′	1·499 (7)	C(3)′–C(2)′	1·491 (4)
N(1)′–C(3)′	1·438 (5)	C(16)′–N(1)′	1·376 (4)
C(12)′–C(11)′	1·370 (5)	C(16)′–C(11)′	1·391 (5)
O(5)′–C(11)′	1·374 (3)	C(13)′–C(12)′	1·400 (5)
C(14)′–C(13)′	1·359 (8)	C(15)′–C(14)′	1·385 (7)
C(16)′–C(15)′	1·393 (4)	C(5)′–N(3)′	1·453 (4)
C(18)′–N(3)′	1·465 (9)	C(6)′–N(2)′	1·459 (4)
C(17)′–N(2)′	1·449 (6)	C(6)′–C(5)′	1·497 (6)

Table 4. *Bond angles* (°)

Compound 1			
O(5)–P–O(4)	134·0 (1)	O(2)–P–O(4)	89·6 (1)
O(2)–P–O(5)	86·9 (1)	O(3)–P–O(4)	110·4 (1)
O(3)–P–O(5)	115·6 (1)	O(3)–P–O(2)	94·1 (1)
N(1)–P–O(4)	88·4 (1)	N(1)–P–O(5)	89·3 (1)
N(1)–P–O(2)	172·4 (1)	N(1)–P–O(3)	93·5 (1)
C(2)–O(4)–P	113·7 (1)	C(11)–O(5)–P	115·3 (2)
C(4)–O(2)–P	109·7 (2)	C(5)–O(3)–P	113·8 (2)
C(3)–N(1)–P	111·9 (2)	C(16)–N(1)–P	113·3 (2)
C(16)–N(1)–C(3)	128·2 (2)	C(3)–C(2)–O(4)	112·6 (2)
C(21)–C(2)–O(4)	113·6 (2)	C(21)–C(2)–C(3)	133·7 (2)
C(2)–C(3)–N(1)	109·8 (2)	C(31)–C(3)–N(1)	121·2 (2)
C(31)–C(3)–C(2)	128·8 (2)	C(11)–C(16)–N(1)	109·0 (2)
C(15)–C(16)–N(1)	132·3 (2)	C(15)–C(16)–C(11)	118·7 (2)
C(16)–C(11)–O(5)	112·8 (2)	C(12)–C(11)–O(5)	124·1 (3)
C(12)–C(11)–C(16)	123·1 (3)	C(13)–C(12)–C(11)	117·8 (3)
C(14)–C(13)–C(12)	120·4 (3)	C(15)–C(14)–C(13)	121·9 (3)
C(14)–C(15)–C(16)	118·0 (3)	C(5)–C(4)–O(2)	105·2 (3)
C(4)–C(5)–O(3)	105·3 (3)	C(36)–C(31)–C(3)	119·2 (2)
C(32)–C(31)–C(3)	121·6 (2)	C(32)–C(31)–C(36)	119·2 (3)
C(35)–C(36)–C(31)	120·3 (3)	C(34)–C(35)–C(36)	120·1 (4)
C(33)–C(34)–C(35)	120·5 (4)	C(32)–C(33)–C(34)	119·7 (3)
C(33)–C(32)–C(31)	120·1 (3)	C(26)–C(21)–C(2)	118·9 (2)
C(22)–C(21)–C(2)	122·0 (3)	C(22)–C(21)–C(26)	119·0 (2)
C(25)–C(26)–C(21)	121·0 (3)	C(24)–C(25)–C(26)	119·9 (4)
C(23)–C(24)–C(25)	121·1 (4)	C(22)–C(23)–C(24)	119·7 (3)
C(23)–C(22)–C(21)	119·2 (3)		
Compound 2			
N(1)–P–C(4)	86·5 (1)	O(5)–P–C(4)	124·4 (1)
O(5)–P–N(1)	87·0 (1)	N(3)–P–C(4)	119·6 (1)
N(3)–P–N(1)	93·9 (1)	N(3)–P–O(5)	115·9 (1)
N(2)–P–C(4)	94·8 (1)	N(2)–P–N(1)	175·9 (1)
N(2)–P–O(5)	89·1 (1)	N(2)–P–N(3)	88·9 (1)
C(21)–C(4)–P	124·3 (2)	C(2)–C(4)–P	113·7 (3)
C(2)–C(4)–C(21)	121·9 (3)	C(22)–C(21)–C(4)	118·5 (3)
C(26)–C(21)–C(4)	123·2 (3)	C(26)–C(21)–C(22)	118·2 (3)
C(23)–C(22)–C(21)	121·1 (4)	C(24)–C(23)–C(22)	120·2 (4)
C(25)–C(24)–C(23)	120·1 (5)	C(26)–C(25)–C(24)	120·4 (4)
C(25)–C(26)–C(21)	120·0 (4)	C(19)–C(2)–C(4)	127·9 (3)
C(3)–C(2)–C(4)	115·6 (3)	C(3)–C(2)–C(19)	116·5 (3)
N(1)–C(3)–C(2)	107·2 (3)	C(3)–N(1)–P	114·5 (2)
C(16)–N(1)–P	113·1 (2)	C(16)–N(1)–C(3)	118·7 (3)
C(16)–C(11)–C(12)	123·1 (4)	O(5)–C(11)–C(12)	124·4 (3)
O(5)–C(11)–C(16)	112·5 (3)	C(13)–C(12)–C(11)	117·7 (3)
C(14)–C(13)–C(12)	120·5 (5)	C(15)–C(14)–C(13)	120·9 (5)
C(16)–C(15)–C(14)	118·8 (3)	C(11)–C(16)–N(1)	110·9 (3)
C(15)–C(16)–N(1)	130·2 (3)	C(15)–C(16)–C(11)	118·9 (3)
C(11)–O(5)–P	116·5 (2)	C(5)–N(3)–P	116·1 (2)
C(18)–N(3)–P	126·9 (3)	C(18)–N(3)–C(5)	113·7 (3)
C(6)–N(2)–P	112·7 (2)	C(17)–N(2)–P	120·8 (3)
C(17)–N(2)–C(6)	113·9 (3)	C(6)–C(5)–N(3)	105·3 (4)
C(5)–C(6)–N(2)	103·3 (3)	N(1)′–P′–C(4)′	86·5 (1)
O(5)′–P′–C(4)′	128·7 (1)	O(5)′–P′–N(1)′	86·4 (1)
N(3)′–P′–C(4)′	119·2 (2)	N(3)′–P′–N(1)′	94·9 (1)
N(3)′–P′–O(5)′	112·0 (1)	N(2)′–P′–C(4)′	94·2 (1)
N(2)′–P′–N(1)′	174·7 (1)	N(2)′–P′–O(5)′	89·1 (1)
N(2)′–P′–N(3)′	89·4 (1)	C(21)′–C(4)′–P′	124·4 (2)
C(2)′–C(4)′–P′	114·0 (2)	C(2)′–C(4)′–C(21)′	121·3 (3)
C(22)′–C(21)′–C(4)′	121·8 (3)	C(26)′–C(21)′–C(4)′	120·5 (3)
C(26)′–C(21)′–C(22)′	117·6 (3)	C(23)′–C(22)′–C(21)′	121·2 (4)
C(24)′–C(23)′–C(22)′	120·4 (4)	C(25)′–C(24)′–C(23)′	119·8 (4)
C(26)′–C(25)′–C(24)′	119·9 (4)	C(25)′–C(26)′–C(21)′	121·0 (3)
C(19)′–C(2)′–C(4)′	126·9 (3)	C(3)′–C(2)′–C(4)′	115·8 (3)
C(3)′–C(2)′–C(19)′	117·2 (3)	N(1)′–C(3)′–C(2)′	107·0 (3)
C(3)′–N(1)′–P′	116·0 (2)	C(16)′–N(1)′–P′	113·5 (2)
C(16)′–N(1)′–C(3)′	119·9 (2)	C(16)′–C(11)′–C(12)′	122·3 (3)
O(5)′–C(11)′–C(12)′	125·2 (3)	O(5)′–C(11)′–C(16)′	112·4 (3)
C(13)′–C(12)′–C(11)′	117·6 (4)	C(14)′–C(13)′–C(12)′	120·9 (4)
C(15)′–C(14)′–C(13)′	121·4 (4)	C(16)′–C(15)′–C(14)′	118·7 (4)
C(11)′–C(16)′–N(1)′	111·0 (2)	C(15)′–C(16)′–N(1)′	130·0 (3)
C(15)′–C(16)′–C(11)′	119·0 (3)	C(11)′–O(5)′–P′	115·9 (2)
C(5)′–N(3)′–P′	116·2 (2)	C(18)′–N(3)′–P′	125·3 (3)
C(18)′–N(3)′–C(5)′	114·6 (4)	C(6)′–N(2)′–P′	111·2 (2)
C(17)′–N(2)′–P′	120·4 (2)	C(17)′–N(2)′–C(6)′	113·8 (3)
C(6)′–C(5)′–N(3)′	105·7 (3)	C(5)′–C(6)′–N(2)′	103·8 (3)

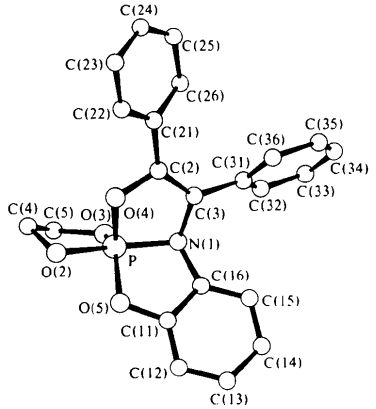

Fig. 1. The molecule of (1) in perspective.

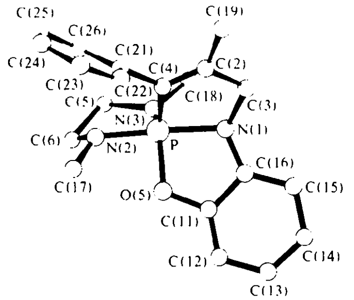

Fig. 2. The molecule of (2) in perspective.

Discussion

In the following discussion, the derivative (3) (Fig. 3) (Sheldrick, Schmidpeter & Weinmaier, 1975; Sheldrick, 1976), which contains an identical fused bicyclic system to that in (1), will be included for comparison. The molecular dimensions of the fused bicyclic ring systems in derivatives (1)–(3) are compared in Fig. 5.

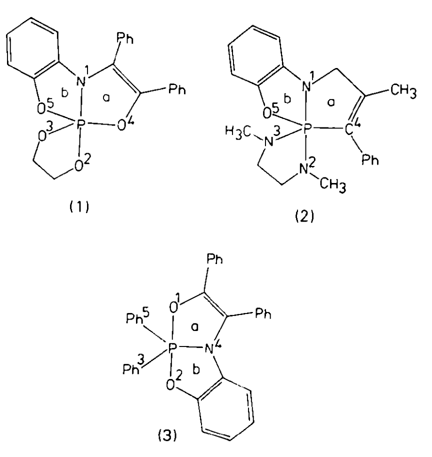

Fig. 3. The numbering scheme for derivatives (1)–(3).

In an analysis of structures of 16 phosphoranes, Holmes & Deiters (1977) were able to demonstrate that the dihedral angles between polyhedral faces (Muetterties & Guggenberger, 1974) provide a better measure of the degree of distortion from the idealized trigonal bipyramid (TBP) or square pyramid (SP) than do the bond angles at the central P atom. The results of analogous calculations for the derivatives (1) to (3) are presented in Table 5. The estimated degree of distortion of the idealized trigonal-bipyramidal geometry is given here by definition (1)

$$C_{2v}\,\text{distortion} = \sum_i \left\{ 1 - \frac{|\delta_i(\text{SP}) - \delta_i(M)|}{|\delta_i(\text{SP}) - \delta_i(\text{TBP})|} \right\} \times 100\% \qquad (1)$$

in which the original expression of Holmes & Deiters has been modified to allow for the possibility of anti-Berry distortions as depicted in Fig. 4. Such distortions, for which local C_{2v} symmetry is preserved, have been observed in several monocyclic and fused bicyclic phosphoranes containing four-membered rings (Schmidpeter, Luber, Schomburg & Sheldrick 1976; Schmidpeter, Weinmaier & Sheldrick, 1980). The $\delta_i(M)$ in (1) are the observed interfacial angles, *i.e.* δ_{14} is the dihedral angle between the polyhedral faces 134 and 145 which share the edge 1–4. The numbering of the substituents for the interfacial angle calculations on derivatives (1) to (3) may be taken from Figs. 3 and 4.

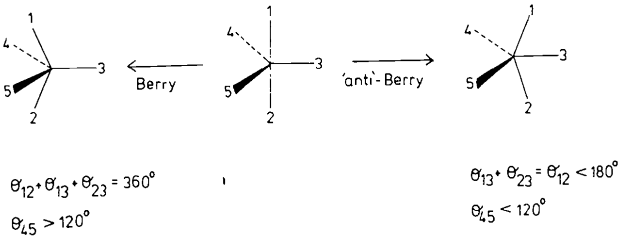

Fig. 4. Berry and anti-Berry distortions of the trigonal-bipyramidal geometry (θ_{45} is, for instance, the bond angle 4—P—5). For the Berry distortion θ_{12} > 180°, for the anti-Berry distortion $\theta_{12} < 180°$.

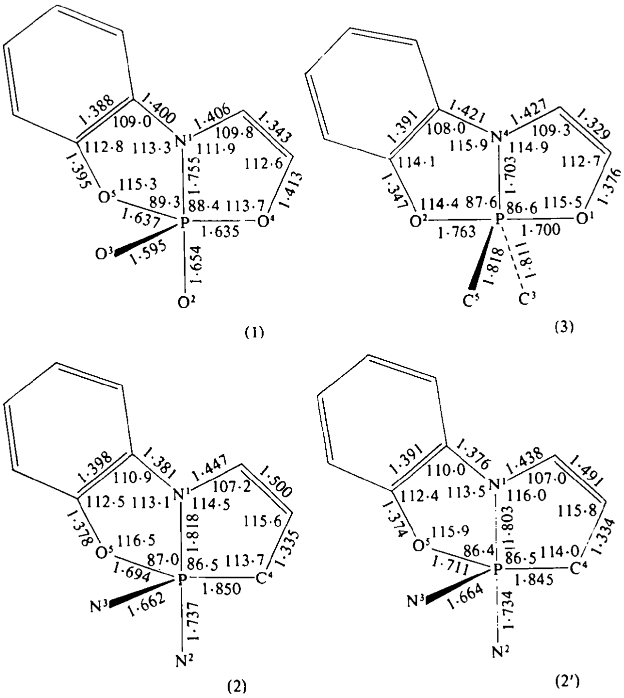

Fig. 5. Molecular dimensions of the fused bicyclic systems in derivatives (1)–(3). Bond lengths and bond angles in (3) have e.s.d.'s of respectively 0·005–0·009 Å and 0·3–0·6°. Lengths are in Å and angles in degrees.

Table 5. *Interfacial dihedral angles and degree of* C_{2v} *distortion from the idealized trigonal-bipyramidal geometry for* (1)–(3) (°)

Compound	(1)	(2)	(2′)	(3)	TBP	SP[a]
θ_{12}	172·4 (1)	175·9 (1)	174·7 (1)	171·6 (3)	180	150
θ_{45}	134·0 (1)	124·4 (1)	128·7 (1)	130·6 (4)	120	150
$\theta_{13} + \theta_{23}$	187·6	128·8	184·3	188·0	180	210
$\theta_{12} + \theta_{13} + \theta_{23}$	360·0	358·7	359·0	359·6	360	360
$\theta_{34} + \theta_{35} + \theta_{45}$	360·0	359·9	359·9	359·9	360	360
δ_{14}	108·2	107·9	109·9	105·8	101·5	118·5
δ_{15}	110·5	103·4	104·4	104·1	101·5	118·5
δ_{24}	106·2	104·3	106·6	105·9	101·5	118·5
δ_{25}	109·9	102·7	103·1	103·5	101·5	118·5
δ_{13}	93·7	96·2	92·7	93·3	101·5	76·9
δ_{23}	91·6	99·4	96·6	91·2	101·5	76·9
δ_{34}	60·6	56·0	57·2	59·4	53·1	76·9
δ_{35}	56·5	52·4	56·1	65·5	53·1	76·9
δ_{45}	34·5	47·2	43·0	39·9	53·1	0·0
$\sum_i \lvert\delta_i(M) - \delta_i(\text{TBP})\rvert$	76·0	29·1	49·0	63·7	0	217·9
$\sum_i [\lvert\delta_i(\text{SP}) - \delta_i(\text{TBP})\rvert - \lvert\delta_i(\text{SP}) - \delta_i(M)\rvert]$	76·0	27·7	49·0	63·7	0	217·9
% C_{2v} distortion	34·9	12·7	22·5	29·2	0	100
φ (angular discrepancy)	8·6	7·5	9·6	9·5	0	0

(*a*) For SP (square-pyramidal) geometry $\theta_{12} = \theta_{45}$ is taken to be (180° + 120°)/2 = 150°.

It is, however, apparent from Table 5 that the distortion of the interfacial angles for derivatives with strained ring systems may not always follow the C_{2v} constraint. Thus $\sum_i|\delta_i(M) - \delta_i(\mathrm{TBP})|$ and $\sum_i[|\delta_i(\mathrm{SP}) - \delta_i(\mathrm{TBP})| - |\delta_i(\mathrm{SP}) - \delta_i(M)|]$ may not be equal in magnitude as in (2) [although they are equal for (2′)] or they may be equal in magnitude but may contain individual components which differ markedly in magnitude from one another. In order to give a measure of the goodness-of-fit we may calculate the average angular discrepancy φ

$$\varphi = \tfrac{1}{9}\sum_i \left\{ \frac{|\delta_i(M) - \delta_i(C)|}{|\delta_i(\mathrm{SP}) - \delta_i(\mathrm{TBP})|} \right\} \times 100\% \qquad (2)$$

where the $\delta_i(C)$ are the interfacial angles calculated for the % C_{2v} distortion given by (1). For (2), calculations for the pivot axes P–4 and P–5 yield values for φ of 14·4 and 13·6% in comparison to that of 7·5% for P–3, indicating thereby the correctness of the choice of the latter axis as pivot.

The more pronounced Berry distortion in the direction of an *aea* placement of the bicyclus in (1) in comparison to (2) may be explained on the basis of the polarity rule. Whereas, on the basis of electronegativities alone, the ligand pair O(4)/O(5) should occupy the axial sites for (1), no such clear prediction is possible for the two possible ligand pairs N(1)/N(2) (*eae*) or C(4)/O(5) (*aea*) in (2). The difference of 9·8% between the degrees of C_{2v} distortion of the two crystallographically independent molecules of (2) provides a measure of the importance of intermolecular interactions for the observed coordination geometry in the crystal lattice. We have previously reported a similar difference of 19·0% between the two chemically equivalent halves of the spirobicyclic bis-catechol derivative $(C_6H_4O_2)_2PO{-}pC_6H_4O{-}P(C_6H_4O_2)_2$ (Schmidpeter, von Criegern, Sheldrick & Schomburg, 1978). The more pronounced Berry distortion of (2′) in comparison to (2) is reflected in other molecular dimensions. The pyramidal geometry of N(1) is flatter (sum of angles 349·4 *vs* 346·3°), the P—N(1) bond shorter [1·803 (2) *vs* 1·818 (2) Å] and the P—O(5) bond longer [1·711 (2) *vs* 1·694 (2) Å], the former distance being indicative of more equatorial, the latter more axial character. The P—C(4) lengths are not significantly different from one another [1·845 (2) *vs* 1·850 (3) Å]. On the basis of the polarity rule, a Berry distortion of derivative (3) would not be expected, *i.e.* a distortion in which P—N(4) and P—C(5) adopt a degree of axial, P—O(1) and P—O(2) a degree of equatorial character. An explanation of the observed positive distortion of 29·2% must be sought in the reduction of ring strain which may be obtained at the expense of the loss of total planarity of the bicyclus by a bending of the O(1)—P—O(2) axis into the N(4)—P—C(5) angle which is consequently widened to 130·6 (4)°. Planarity of the benzoxazaphospholine system and of the bridgehead coordination at N(3) are thereby retained, whereas the second five-membered ring (*a*) adopts an envelope conformation with P as flap.

Ring geometries

The geometries of the fused bicyclic systems for (1)—(3) are presented in Table 6 and allow an analysis of the changes in ring geometry which occur upon going from a facial to a meridional placement of the bicyclus. Extended π-delocalization over both rings is not possible for axial annelation. The deviations from planarity of the benzoxazaphospholine ring *b* in (1) are more marked than those in (3). As in derivative (3), the other five-membered ring *a* in (1) adopts an envelope conformation with the P atom as flap displaced 0·351 Å [*vs* 0·186 Å in (3)] from the plane of the remaining ring atoms [distances N(1) 0·007, C(3) −0·012, C(2) 0·012, O(4) −0·007 Å]. The ring conformations of the two independent molecules of (2) are not identical. The ring *b* is no longer planar in the more Berry-distorted molecule (2′) and adopts an envelope conformation with P displaced 0·167 Å from the plane of the other ring atoms [distances N(1) 0·002, C(16) −0·003, C(11) 0·003, O(5) −0·002 Å]. Ring *a* is puckered in both independent molecules with P 0·306 Å in (2) [distances N(1) −0·013, C(3) 0·034, C(2) −0·025, C(4) 0·015 Å] and 0·168 Å in (2′) [distances N(1) −0·006, C(3) 0·010, C(2) −0·011, C(4) 0·007 Å] from the least-squares plane of the four remaining atoms. It may be seen from this discussion that all the non-planar rings in fused bicyclic systems adopt an envelope conformation with P as flap displaced at distances of between 0·167 and 0·351 Å from the plane of the other atoms.

Table 6. *Geometries of the fused bicyclic system in (1)–(3)*

		(1)		(2)	(2′)		(3)
Deviations from least-squares plane[a] (Å)							
Ring *a*							
	P	0·109	P	0·086	0·047	P	0·054
	N^1	−0·095	N^1	−0·013	−0·085	N^4	−0·053
	C	0·040	C	0·071	0·034	C	0·028
	C	0·060	C	0·015	0·010	C	0·025
	O^4	−0·133	C^4	−0·069	−0·039	O^1	−0·053
Ring *b*							
	P	−0·028	P	−0·003	−0·048	P	−0·010
	N^1	0·018	N^1	0·003	0·046	N^4	0·010
	C	0·000	C	−0·002	−0·022	C	−0·005
	C	−0·026	C	−0·002	−0·027	C	−0·004
	O^5	0·035	O^5	0·004	0·051	O^2	0·010
Sum of angles at bridgehead N atom (°)		353·4		346·3	349·4		360·0

(*a*) Calculated with unit weights for all atoms; e.s.d.'s are 0·002–0·007 Å.

The alterations in the molecular dimensions of the bicyclic system on going from a facial placement in (1) to a meridional placement in (3) are depicted in Fig. 5. The P—O bonds are axial and therefore longer, the P—N bond is equatorial and therefore shorter in (3). A more detailed discussion of these bond-length changes follows in the next section. In contrast, the bond angles in the ring systems of (1) and (3) display relatively minor differences. As the C=C double bonds in both derivatives are also similar, the alterations in the P—O and P—N distances are taken up in the opposite formally single N—C and O—C bonds of the five-membered rings. The O—C distances opposite the 0·052 Å shorter P—N bond in (3) are respectively 0·037 (O^1—C) and 0·048 Å (O^2—C) shorter than in (1). Respective increases of 0·021 and 0·021 Å are observed for the N^4—C bonds in (3). A marked lengthening of both P—N^1 and P—O^5 of respectively 0·063/0·048 and 0·057/0·074 Å is observed on going from (1) to (2)/(2′), which is reflected in a shortening of the N^1—C and O^5—C distances by 0·019/0·024 and 0·017/0·021 Å. This is presumably a result of a decrease in the π-bonding component in the longer P—N and P—O bonds in (2) which leads to a corroborative strengthening of the N—C and O—C bonds in the benzoxazaphospholine system. The reduction in the importance of extended π-delocalization over the members of ring *b* in derivative (2) may be reflected in its non-planarity in (2′) with puckering at P.

Bond distances to phosphorus

Several factors have been shown to influence the bond distances to pentacoordinate phosphorus:

(1) the electronegativities of the remaining substituents at P,

(2) the degree of square-pyramidal character of the configuration at P (Holmes & Deiters, 1977; Sheldrick, 1978),

(3) the degree of ring strain (Sheldrick, 1978; Roesky, Ambrosius & Sheldrick, 1979),

(4) the mutual polarization of the two axial bonds (Roesky, Ambrosius & Sheldrick, 1979).

As these factors are often simultaneously operative it is not straightforward to quantify their influence. The large difference of 0·081/0·069 Å between the two P—N_{ax} distances in (2)/(2′) may, however, be readily accounted for in terms of the increased strain in the planar (or near-planar) ring *b* in comparison to the saturated ring containing N(2). It has, for instance, been established that the P—O_{ax} bond may increase by up to 0·25 Å in length on going from an acyclic O atom to an O atom participating in a strained planar four-membered ring. Characteristic values are: acyclic 1·60–1·71, non-planar five-membered rings 1·63–1·77, planar five-membered rings 1·75–1·79, and four-membered rings 1·79–1·85 Å (Sheldrick, 1978). A value of 1·743 (2) Å similar to that of 1·737/1·734 Å in (2)/(2′) has been reported for the P—N_{ax} bond in the saturated non-planar five-membered ring of a spirobicyclic phosphorane containing axial N—P—N bonds (Roesky, Ambrosius & Sheldrick, 1979). The opposite P—N_{ax} bond in this derivative belongs to a planar four-membered ring and, at 1·867 (3) Å, is 0·132 Å longer, underlining the role of ring strain. A shortening of P—N^1 in (1) in comparison to (2)/(2′) is observed, the bond being 1·755 (2) Å as compared to 1·818/1·803 Å in (2). This indicates that the polarization of the N—P—O axial bonds leads to an average shortening of 0·055 Å in P—N^1 in comparison to the N—P—N axial bonds. A similar shortening of a P—N_{ax} bond opposite to a P—O_{ax} bond of 0·068 Å has been reported for the four-membered ring of another fused bicyclic system (Schmidpeter, Luber, Schomburg & Sheldrick, 1976) in this case in comparison to the above-mentioned spirobicyclic phosphorane. It may also be noted that the exocyclic equatorial P—O^3 length of 1·595 (2) in (1) is significantly shorter than the two endocyclic equatorial bond lengths of 1·635 (2) and 1·637 (2) Å.

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Structures of Three Forms of the Purine Base Precursor 5(4)-Amino-1*H*-imidazole-4(5)-carboxamide (AICA): AICA.C_3H_7OH, AICA.H_2O and HAICA$^+$.$H_2PO_4^-$

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Abstract

$C_4H_6N_4O.C_3H_7OH$ is monoclinic, space group $P2_1/c$, with $a = 11{\cdot}111$ (4), $b = 6{\cdot}153$ (1), $c = 14{\cdot}904$ (6) Å, $\beta = 105{\cdot}2$ (1)°, $Z = 4$. $C_4H_6N_4O.H_2O$ is monoclinic, space group $P2_1/a$, with $a = 6{\cdot}586$ (5), $b = 9{\cdot}972$ (6), $c = 9{\cdot}499$ (5) Å, $\beta = 91{\cdot}3$ (1)°, $Z = 4$. $C_4H_7N_4O^+.H_2PO_4^-$ is monoclinic, space group $P2_1/c$, with $a = 12{\cdot}238$ (2), $b = 5{\cdot}465$ (1), $c = 12{\cdot}875$ (1) Å, $\beta = 92{\cdot}7$ (1)°, $Z = 4$. The structures were refined to $R = 0{\cdot}091$ for 1363 reflexions, $R = 0{\cdot}055$ for 849 reflexions, and $R = 0{\cdot}071$ for 1215 reflexions respectively. The tautomers AICA.C_3H_7OH (2-propanol) and AICA.H_2O can be distinguished from each other and from the protonated form on the basis of the internal bond angles. The geometry of the HAICA$^+$ cation resembles the corresponding part of the purine nucleotide precursor 5-amino-1-β-D-ribofuranosylimidazole-4-carboxamide 5′-(dihydrogen phosphate) (AICAR 5′-P). Similarly the geometry of AICA in AICA.C_3H_7OH resembles the AICA part in the corresponding nucleoside (AICAR). In each molecule the 4-carboxamide moiety is oriented so that a strong intramolecular hydrogen bond is formed to the 5-amino group of the heterocycle.

Introduction

5-Amino-1-β-D-ribofuranosylimidazole-4-carboxamide 5′-(dihydrogen phosphate) (AICAR 5′-P), synthesized enzymatically in living cells, is a key substance of purine nucleotides (Henderson & Paterson, 1973). To elucidate the formation of such purine nucleotides the molecular structures of their building blocks (precursors), the ambivalent 5(4)-amino-1*H*-imidazole-4(5)-carboxamide (AICA) (Zimmerman, 1979, and references therein), crystallized from two different solvents (2-propanol and water), and a protonated AICA molecule (HAICA$^+$.$H_2PO_4^-$) have been determined. These structural parameters fit systematically in the picture which has been inferred from the structure determinations of AICAR 5′-P and its nucleoside AICAR (Adamiak & Saenger, 1979). Beyond this, it is worth noting that HAICA$^+$.$H_2PO_4^-$ is an effective liver regenerating agent (Szepesházi *et al.*, 1978).

First, stable crystals of AICA.H_2O could be obtained which (Kálmán & Simon, 1975), unlike the analogous 5-amino-1*H*-1,2,3-triazole-4-carboxamide (Kálmán, Simon, Schawartz & Horváth, 1974), exhibited the tautomeric form 5-amino-3*H*-imidazole-4-carboxamide (if positions are defined not in relation to the protonated N atoms but in relation to the substituents on the ring; the canonical notation is, however, 4-amino-1*H*-imidazole-5-carboxamide). This phenomenon was mainly attributed to the role of H_2O in forming a complicated hydrogen-bond network with AICA molecules. New, but less stable, crystals of AICA could be obtained from absolute 2-propanol. The structure analysis revealed the co-crystallization of the expected tautomeric form 5-amino-1*H*-imidazole-4-carboxamide with one molecule of 2-propanol per asymmetric unit (hereafter AICA.C_3H_7OH). They are

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