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2-Methyl-2,2′-spirobi[1,3,2λ⁵-benzoxazarsoline]

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Abstract. $(C_6H_4ONH)_2AsCH_3$, monoclinic, $P2_1/c$, $a = 12{\cdot}285$ (5), $b = 9{\cdot}508$ (3), $c = 10{\cdot}848$ (2) Å, $\beta = 104{\cdot}66$ (2)°, $M_r = 304{\cdot}1$, $Z = 4$, $D_x = 1{\cdot}651$ Mg m^{-3}, μ(Mo $K\alpha$) = 2·9 mm^{-1}. Final $R = 0{\cdot}06$. With an axial O—As—O angle of 169·6° and three equatorial angles of 125·9 (N—As—N), 118·9 and 115·2° (N—As—C), the geometry of the pentacoordinate As atom can be described as a 72% trigonal bipyramid with the two O atoms at the axial positions. This structural distortion from the idealized geometries deviates considerably from the Berry exchange coordinate.

Introduction. The title compound was prepared and crystallized from ethanol by Mallon & Wieber (1979). From systematic absences the space group $P2_1/c$ was determined. A colorless plate, 0·35 × 0·38 × 0·1 mm, was used for data collection and determination of the lattice parameters (15 high-order reflections). The intensities of all 2794 symmetry-independent reflections within $4 \leq 2\theta \leq 55°$ (Mo $K\alpha$, crystal monochromator) were measured with an ω scan on a computer-controlled diffractometer (Syntex $P2_1$). 2105 reflections were classified as observed ($I > 1{\cdot}96\sigma_I$) and were used for the structure determination. During the refinement 27 reflections showed unusually high discrepancies with $F_o > F_c$. This could only be explained by *Umweganregung*; thus, these reflections were eliminated and the final refinement was based on 2078 reflections. The structure was solved by the heavy-atom method. All H atoms could be located in difference syntheses and were included with isotropic temperature factors. Refinement (215 parameters) converged at $R = 0{\cdot}063$ (0·085) and $R_w = 0{\cdot}078$ (0·082) for the observed (all) reflections. Weights were derived from counting statistics by $1/w = \sigma_F^2 + (0{\cdot}03F)^2$. Scattering factors were taken from Cromer & Waber (1974), those of the As atom being corrected for anomalous dispersion. The final atomic parameters are listed in Tables 1 and 2.* The anisotropic temperature factors

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35093 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* (×10⁴) *of the non-*H *atoms with e.s.d.'s from the least-squares refinement in parentheses*

The equivalent isotropic temperature factors B_{eq} (Å²) have been calculated by $B_{eq} = \frac{1}{3}(B_{11}a^{*2}a^2 + B_{12}a^*b^*ab\cos\gamma + \cdots)$.

	x	y	z	B_{eq}
As	1409 (1)	1894 (1)	1611 (1)	2·49
N(1)	269 (5)	3032 (7)	859 (6)	3·28
O(2)	468 (4)	1237 (5)	2584 (5)	3·32
N(3)	2463 (5)	2267 (6)	3032 (5)	3·07
O(4)	2332 (4)	2884 (5)	748 (4)	3·30
C(5)	1562 (9)	119 (11)	834 (11)	4·73
C(11)	−604 (5)	1708 (6)	2124 (6)	2·56
C(12)	−743 (5)	2728 (7)	1155 (6)	2·58
C(13)	−1792 (6)	3312 (8)	654 (7)	3·19
C(14)	−2709 (6)	2825 (8)	1082 (8)	3·63
C(15)	−2568 (7)	1786 (9)	1986 (8)	3·76
C(16)	−1515 (6)	1230 (8)	2521 (6)	3·08
C(21)	3277 (5)	3393 (6)	1591 (6)	2·43
C(22)	3373 (5)	3050 (7)	2866 (6)	2·50
C(23)	4308 (6)	3478 (7)	3790 (6)	3·00
C(24)	5128 (6)	4263 (9)	3436 (7)	3·76
C(25)	5026 (6)	4605 (8)	2167 (8)	3·67
C(26)	4087 (6)	4167 (8)	1245 (6)	3·04

Table 2. *Positional parameters* (×10³) *and isotropic temperature factors* (Å²), *with e.s.d.'s in parentheses, of the* H *atoms bonded to the* C *and* N *atoms with the same numbering*

H(51), H(52), and H(53) belong to the methyl group.

	x	y	z	B
H(1)	25 (4)	338 (5)	28 (5)	0 (1)
H(3)	233 (7)	225 (9)	379 (8)	5 (2)
H(13)	−188 (5)	395 (6)	23 (5)	1 (1)
H(14)	−352 (10)	333 (11)	37 (11)	9 (3)
H(15)	−323 (6)	140 (8)	203 (7)	3 (1)
H(16)	−135 (5)	43 (8)	324 (6)	3 (2)
H(23)	442 (8)	317 (10)	466 (9)	6 (2)
H(24)	581 (6)	453 (8)	410 (7)	4 (2)
H(25)	558 (6)	509 (9)	207 (7)	4 (2)
H(26)	406 (5)	429 (7)	49 (6)	2 (1)
H(51)	184 (9)	17 (12)	30 (11)	7 (3)
H(52)	222 (8)	−27 (10)	137 (8)	5 (2)
H(53)	70 (8)	−26 (11)	51 (9)	7 (3)

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B_{ii} do not show any unusual features and are distributed between 1·7 and 5·2 Å^2. All calculations were carried out with the program system *EXTL* (Syntex) on an Eclipse computer (Data General).

Discussion. Both the geometries and dynamics of pentacoordinate compounds of Group V*a* elements have been studied during recent years. The main interest in these elements concerns phosphorus (Sheldrick, 1978). The stereochemistries of spirocyclic phosphoranes $(C_6H_4O_2)_2PY$ reveal a continuous series of angular geometries at P between the idealized trigonal-bipyramidal (tbp, symmetry D_{3h}) and square-pyramidal (sp, symmetry C_{4v}) forms, the latter of which is reduced by chelation of the P to a rectangular pyramid (rp, symmetry C_{2v}). As was pointed out by Holmes & Deiters (1977), the intermediate states follow closely the Berry exchange coordinate (Berry, 1960). From the crystal structure of the phosphorane with $Y = H$ (Wunderlich & Wussow, 1978), showing tbp geometry, it is evident that there is no influence on the tbp by the ring constraints in an individual compound of this kind. Only the different electronegativities and steric hindrance seem to determine the geometry.

Several structures of spirophosphoranes with N and O at the P atom have been published: $(C_6H_4ONH)_2PH$ and $(CH_2CH_2ONH)_2PH$ (Meunier, Day, Devillers & Holmes, 1978), $(C_9H_{10}ONCH_3)_2PH$ (Newton, Collier & Wolf, 1974), and $C_{18}H_{21}N_2O_3P$ (Devillers, Garrigues, Wolf & Bonnet, 1979). In all these structures the geometry is very close to tbp with the two O atoms at axial sites.

Compounds of the heavier homologues of P are expected to show similar stereochemical properties, but only a few experimental results exist.

Crystal structures of the following spiroarsoranes have been reported: $(C_2Me_4O_2)_2AsC_6H_5$ and $(C_2H_4O_2)_2AsOH$ (Goldwhite & Teller, 1978), $(C_6H_4O_2)_2AsCH_3$ (Wunderlich, 1978*a*). The structure

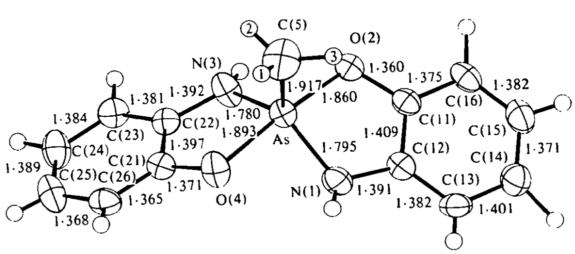

Fig. 1. The molecule of $(C_6H_4ONH)_2AsCH_3$ in an arbitrary crystallographic orientation with bond lengths (Å). The non-H atoms are represented by thermal ellipsoids of 50% probability (*ORTEP* II, Johnson, 1976). The radius of the H atoms was set to $B = 1·0$ Å^2. The H atoms of the methyl group are identified by their last digit. The e.s.d.'s are: As—O,N 0·005–0·006, As—C 0·011, C—O,N 0·008–0·009, and C—C 0·009–0·011 Å.

Table 3. *Bond angles* (°) *of* $(C_6H_4ONH)_2AsCH_3$ *not involving* H *atoms*

(*a*) Angles at the As atom
The e.s.d.'s are 0·2–0·4°

	N(1)	O(2)	N(3)	O(4)
O(2)	86·3			
N(3)	125·9	89·8		
O(4)	88·4	169·6	86·2	
C(5)	118·9	95·6	115·2	94·8

(*b*) Other angles in the five-membered rings
The e.s.d.'s are 0·4–0·6°

As—N(1)—C(12)	114·2	As—N(3)—C(22)	115·2
N(1)—C(12)—C(11)	111·6	N(3)—C(22)—C(21)	112·6
C(12)—C(11)—O(2)	115·1	C(22)—C(21)—O(4)	115·1
C(11)—O(2)—As	111·4	C(21)—O(4)—As	110·9

(*c*) Angles in the benzene rings
The e.s.d.'s are 0·6–0·7°.

	$n = 1$	$n = 2$
C(n1)—C(n2)—C(n3)	119·6	119·8
C(n2)—C(n3)—C(n4)	119·0	119·2
C(n3)—C(n4)—C(n5)	120·5	120·8
C(n4)—C(n5)—C(n6)	120·8	119·7
C(n5)—C(n6)—C(n1)	119·4	119·7
C(n6)—C(n1)—C(n2)	120·5	120·9

under study extends this series and introduces a further possible influence on the geometry of the As atom by a hetero substitution of the type $AsX_2X'_2Y$ with different atoms X, X', and Y.

Fig. 1 shows all bond lengths involving the non-H atoms; Table 3 contains the corresponding bond angles. The geometry of the H atoms is in the usual range (av. N—H 0·79, C—H 0·94 Å). The geometry of the pentacoordinate As atom is closer to a tbp, with the two O atoms at axial positions, than to an rp. The As—O distances of 1·893 (5) and 1·860 (5) Å are enlarged in comparison with corresponding values in the structures cited above and underline the axial character of the atoms of highest electronegativity in a tbp. Also, the angles at the As atom (Table 3) are more characteristic of a tbp than an rp. From a criterion of a least-squares plane defined by N(1), O(2), N(3), and O(4) (Wunderlich, 1978*b*) the geometry is 71% tbp, while from an angle criterion (Holmes, 1974) it is 73% tbp. The dihedral angle δ_{24} (Table 4) between the two triangular faces defined by O(2), N(1), N(3) and N(1), N(3), O(4) has to be 53·1° in a tbp and 0° in an rp (Muetterties & Guggenberger, 1974) with the two O atoms in axial and basal positions, respectively. The value of 38·0° in the present structure again shows the predominance of the tbp geometry (72% by linear interpolation).

Table 4. *Analysis of the dihedral angles* (°)

The angles δ are defined by the two adjacent triangular faces with the listed common edge. Nomenclature of δ and angles of idealized tbp and rp are according to Holmes & Deiters (1977). The e.s.d.'s are *ca* 0·5°.

Edge	δ	tbp	Δ(tbp)	Observed	rp	Δ(rp)
O(2),N(3)	45	101·5	1·4	102·9	117·6	14·7
N(1),O(2)	25	101·5	5·0	106·5	119·3	12·8
N(3),O(4)	14	101·5	2·7	104·2	119·3	15·1
N(1),O(4)	12	101·5	4·1	105·6	117·6	12·0
O(2),C(5)	35	101·5	3·8	97·7	76·9	10·8
O(4),C(5)	13	101·5	3·7	97·8	76·9	10·9
N(1),C(5)	23	53·1	4·1	57·2	76·9	19·7
N(3),C(5)	34	53·1	7·0	60·1	76·9	16·8
N(1),N(3)	24	53·1	15·1	38·0	0·0	38·0
$\sum\Delta$			46·9			150·8

The sums of the absolute differences between the nine dihedral angles formed by all pairs of adjacent triangular faces and the corresponding angles of the idealized polyhedra (Table 4) are 46·9° (tbp) and 150·8° (rp). From these values the compound again is much closer to a tbp than to an rp. The corresponding sum of the differences between the idealized tbp and rp is 217·7°. The discrepancy between the values of 46·9° and 217·7 − 150·8 = 66·9° indicates a geometry which does not closely follow the Berry exchange coordinate, but gives an averaged percentage of (46·9 + 66·9)/(2 × 217·7) = 26·1% along the Berry coordinate.

The two six-membered rings and the five-membered ring involving N(3) and O(4) are planar within 0·02 Å, while the other five-membered ring shows atomic displacements of up to 0·07 Å from its least-squares plane. No C—C length differs significantly from the average of 1·385 Å. There is one intermolecular contact <3·2 Å which can be accepted as a hydrogen bond: N(3)—H(3)···O(4) with N···O and H···O at 2·994 (7) and 2·13 (9) Å, respectively, and an N—H···O angle of 169 (8)°.

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