atoms in the carboxyl plane, are given in Table 4 along with the deviations of individual atoms from the planes. The angle between the two planes is found to be $97.8°$.

The molecular packing seen down **b** is shown in Fig. 2. The molecules, as in other plant-growth hormones (Swaminathan, Vijayalakshmi & Srinivasan, 1976; Karle, Britts & Gum, 1964), exist as dimers. Hydrogen bonds between the acid groups form across the centre of symmetry and are in parallel planes.

The author wishes to express his thanks to Professor R. Srinivasan for helpful discussions.

References

CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN, p. 32. Oxford: Pergamon Press.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Program *UCLALS* 1. Univ. of California.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* 17, 496–499.

MAIN, P. & WOOLFSON, M. M. (1963). *Acta Cryst.* 16, 731–733.

PHILLIPS, D. C. (1954). *Acta Cryst.* 7, 746–751.

ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* 13, 273–274.

SHIONO, R. (1968). Block diagonal least-squares program for the IBM 1130. Department of Crystallography, Univ. of Pittsburgh.

SWAMINATHAN, P., VIJAYALAKSHMI, J. & SRINIVASAN, R. (1976). *Acta Cryst.* B32, 2351–2354.

2-Methyl-2,2'-spirobi(1,3,2-benzodioxaarsole)

BY HARTMUT WUNDERLICH

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1, 4000 Düsseldorf, Federal Republic of Germany

Abstract. $(C_6H_4O_2)_2AsCH_3$, orthorhombic, $Pca2_1$; $a = 18.086$ (2), $b = 8.294$ (1), $c = 8.229$ (1) Å. $M_r = 306.1$, $Z = 4$, $D_x = 1.65$ g cm^{-3}, μ(Mo $K\alpha$) = 29.1 cm^{-1}. The structure was refined to $R = 0.05$. The geometry of the pentacoordinate As atom can be described as a 74% rectangular pyramid with the methyl group in apical position. The molecule contains *trans*-basal angles O—As—O of 158.6 and 143.1° and apical-basal angles C—As—O of 108.6, 108.3, 100.2 and 101.1°.

Introduction. The compound was synthesized by Wieber, Eichhorn & Götz (1973) and recrystallized from CS_2. Photographs showed systematic absences $0kl$ for l odd and $h0l$ for h odd indicative of the space groups *Pcam* (conventional setting: *Pbcm*) and $Pca2_1$. A comparison with the volume of the molecule of the corresponding phosphorane (Wunderlich, 1974) yielded $Z = 4$. The assumption of no crystallographic symmetry of the molecule reduces the alternative to the noncentrosymmetric space group $Pca2_1$ which was later supported by the statistics of the E values. The

intensities of all 1528 symmetry-independent reflections up to $2\theta = 55°$ were collected on a computer-controlled diffractometer (Syntex $P2_1$) in a $\theta:2\theta$ scan mode with Mo $K\alpha$ radiation and a crystal monochromator. 1141 reflections were classified as observed ($F_o \geq 3\sigma_F$). The structure was solved by the heavy-atom method. All H atoms except those of the methyl group could be located from a difference synthesis. The final refinement with fixed (H) and anisotropic (As, O and C) temperature factors converged at $R = 0.050$ (0.074) and $R_w = 0.046$ (0.049) for the observed (all) reflections. Weights were derived from counter statistics by $1/w = \sigma_F^2 + (0.02F_o)^2$; scattering factors were taken from Cromer & Waber (1974). The final atomic parameters are given in Tables 1 and 2.* All calculations were carried out on a Nova 1200 computer with the program system *XTL* (Syntex).

Table 1. *Positional parameters* (×10⁴), *with estimated standard deviations in parentheses*

	x	y	z
As	1622 (0)	2103 (1)	0
O(1)	712 (3)	1479 (8)	616 (7)
O(2)	1672 (4)	3365 (11)	1773 (11)
O(3)	2588 (3)	1749 (6)	343 (8)
O(4)	1607 (3)	250 (8)	−1215 (8)
C(11)	1020 (5)	3321 (9)	2623 (10)
C(12)	501 (5)	2276 (11)	2010 (11)
C(13)	−159 (5)	1981 (14)	2799 (12)
C(14)	−299 (5)	2823 (14)	4197 (13)
C(15)	215 (6)	3873 (12)	4842 (22)
C(16)	889 (5)	4130 (11)	4055 (11)
C(21)	2304 (5)	−388 (10)	−1348 (11)
C(22)	2841 (4)	440 (10)	−519 (10)
C(23)	3568 (5)	−81 (12)	−519 (12)
C(24)	3734 (7)	−1438 (13)	−1425 (16)
C(25)	3192 (7)	−2325 (14)	−2268 (15)
C(26)	2447 (9)	−1782 (9)	−2228 (13)
C(31)	1525 (6)	3738 (19)	−1687 (16)

Table 2. *Positional parameters* (×10³) *of the H atoms bonded to* C *atoms of identical labelling*

During the refinement the temperature factor was fixed at $B = 5 \cdot 0$ Å².

	x	y	z
H(13)	−36 (6)	148 (12)	226 (14)
H(14)	−82 (5)	284 (9)	459 (12)
H(15)	15 (6)	445 (11)	543 (15)
H(16)	120 (5)	486 (10)	444 (12)
H(23)	387 (5)	58 (10)	5 (18)
H(24)	420 (6)	−201 (11)	−122 (13)
H(25)	329 (5)	−353 (12)	−303 (13)
H(26)	205 (6)	−244 (13)	−297 (16)

Discussion. During a structural investigation of penta-coordinate oxyphosphoranes (Wunderlich, 1978) with different fifth ligands of varying electronegativity and size, a comparison of a phosphorane (Wunderlich, 1974) and an analogous arsorane (this paper) was of interest. Because of the larger size of the As atom the influence of the steric hindrance should be reduced, although it still might determine the geometry of the pentacoordination. From a simple point-charge-model consideration of AB_5 complexes (Zemann, 1963) there is only a small energetic difference between the alternative of a trigonal bipyramid (t.b.p., symmetry D_{3h}) and a tetragonal pyramid (t.p., symmetry C_{4v}) which has to be replaced in this kind of spiro system by a rectangular pyramid (r.p., symmetry C_{2v}).

Fig. 1 shows the molecule with all the bond lengths, except those of the H atoms, which lie in the range 0·7
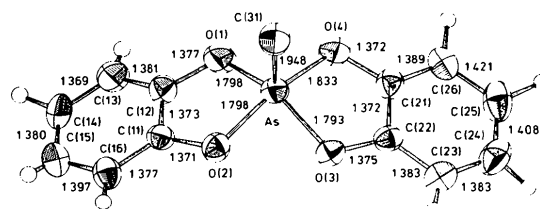

Fig. 1. $(C_6H_4O_2)_2AsCH_3$ in an arbitrary orientation with bond lengths in Å. The atoms are represented by thermal ellipsoids of 50% probability (Johnson, 1976). The e.s.d.'s are: As—O 0·005–0·009, As—C 0·013, C—O 0·010–0·011, and C—C 0·012–0·019 Å.

Table 3. *Bond angles* (°) *of* $(C_6H_4O_2)_2AsCH_3$ *except those involving* H *atoms*

(i) Angles at the As atom

The e.s.d.'s are 0·3–0·5°.

	O(1)	O(2)	O(3)	O(4)
O(2)	89·1			
O(3)	143·1	85·3		
O(4)	84·2	158·6	87·9	
C(31)	108·6	100·2	108·3	101·1

(ii) Other angles in the five-membered rings

The e.s.d.'s are 0·5–0·9°.

As—O(1)—C(12)	110·5	As—O(3)—C(22)	111·9
O(1)—C(12)—C(11)	114·8	O(3)—C(22)—C(21)	114·5
C(12)—C(11)—O(2)	114·7	C(22)—C(21)—O(4)	114·7
C(11)—O(2)—As	110·8	C(21)—O(4)—As	110·7

(iii) Angles in the benzene rings

The e.s.d.'s are 0·8–1·1°.

	$n = 1$	$n = 2$
C(n1)—C(n2)—C(n3)	122·0	121·1
C(n2)—C(n3)—C(n4)	117·8	117·4
C(n3)—C(n4)—C(n5)	121·3	122·7
C(n4)—C(n5)—C(n6)	120·4	118·9
C(n5)—C(n6)—C(n1)	118·2	117·0
C(n6)—C(n1)—C(n2)	120·3	122·9

(iv) Exocyclic angles

The e.s.d.'s are 0·7–0·8°.

O(1)—C(12)—C(13)	123·1	O(3)—C(22)—C(23)	124·3
O(2)—C(11)—C(16)	124·8	O(4)—C(21)—C(26)	122·3

to 1·2 Å. Table 3 contains the bond angles; those involving H atoms are in the range 105 to 137°. The two *trans*-basal angles O(1)—As—O(3) and O(2)—As—O(4) of 143·1 and 158·6° show remarkable deviations from the values for an ideal t.b.p. (120 and 180° respectively) and give preference for a description in terms of an r.p. with the methyl group at the apex. This is supported by the similarity of the apical-basal angles which are in the range 100·2 to 108·6°. The As—O lengths differ slightly but cannot be classified

into pairs of long axial and short equatorial bonds of a t.b.p. (1·798 and 1·833 *versus* 1·798 and 1·793 Å). The average deviation of the four O atoms from coplanarity divided by $\frac{1}{4}$ of the 'equatorial' bond lengths is a sensitive criterion for classifying every geometry between t.b.p. and r.p. (Wunderlich, 1978). The average distance of the four O atoms from their least-squares plane is 0·116 Å; thus the geometry is 0·116/0·449 = 0·26 away from the ideal r.p. and can be called a 74% r.p. Because of enlarged bond lengths (average difference 0·15 Å) at the As atom, the steric hindrance of the methyl group in this arsorane is reduced in comparison with the analogous phosphorane which was described as an 86% r.p. (Wunderlich, 1976). A similar spiroarsorane (Goldwhite, Grey & Teller, 1976) containing a phenyl group as the fifth ligand is described as intermediate between t.b.p. and r.p. This could not be evaluated by the above criterion, since atomic parameters were not reported. However, by consideration of the central angles (axial 169·8, equatorial 117·4, 118·0, 124·6°) the geometry is 75% t.b.p. [angle criterion according to Holmes (1974)].

Compared with spirocyclic oxyphosphoranes the organic moiety of the molecule shows no unusual features although several deviations from standard basic geometries do occur. The six-membered rings are squeezed toward the centre of the molecule and are planar within 0·017 Å. The five-membered rings are planar within 0·033 Å and are coplanar with the benzene rings within 2·5°.

References

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71–98. Birmingham: Kynoch Press.
GOLDWHITE, H., GREY, J. & TELLER, R. (1976). *J. Organomet. Chem.* 113, C1–C3.
HOLMES, R. R. (1974). *J. Am. Chem. Soc.* 96, 4143–4149.
JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
WIEBER, M., EICHHORN, B. & GÖTZ, J. (1973). *Chem. Ber.* 106, 2738–2741.
WUNDERLICH, H. (1974). *Acta Cryst.* B30, 939–945.
WUNDERLICH, H. (1976). 3rd Eur. Crystallogr. Meet. Zurich, Switzerland. Abstr. 054D.
WUNDERLICH, H. (1978). *Acta Cryst.* B34, 342–344.
ZEMANN, J. (1963). *Z. Anorg. Allg. Chem.* 324, 241–249.

2-Formyl-4-morpholinopyridine Thiosemicarbazone

BY JOE N. BROWN

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, USA

AND KRISHNA C. AGRAWAL

Department of Pharmacology, Tulane University School of Medicine, New Orleans, Louisiana 70112, USA

Abstract. $C_{11}H_{15}N_5OS$, $P2_1/c$, monoclinic, $a = 7·458(1)$, $b = 11·653(1)$, $c = 15·732(1)$ Å, $\beta = 109·51(1)°$, $D_x = 1·37$ g cm^{-3}, $Z = 4$. The conformation of the molecule is similar to that observed in related thiosemicarbazone derivatives and suggests that the overall conformation of the thiosemicarbazone moiety is not responsible for increased or decreased biological activity.

Introduction. Several studies, which have been reviewed recently (Agrawal & Sartorelli, 1975) have shown that α-(*N*)-heterocyclic carboxaldehyde thiosemicarbazones possess significant antineoplastic activity against a wide variety of transplanted tumors. It is believed that these compounds inhibit the biosynthesis of DNA by blocking the conversion of ribonucleotides to deoxyribonucleotides. Kinetic data support an inhibitory mechanism in which either a preformed Fe chelate of the molecule interacts with the target enzyme, ribonucleoside-diphosphate reductase, or the ligand itself coordinates to the Fe-charged enzyme (Sartorelli, Agrawal & Moore, 1971). Among the initial