

[mean values 124.3 (1) and 121.8 (1)°, respectively] and in 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane, the angle is 133.1 (2)° (Ferguson *et al.*, 1990). The dihedral angle Si—O2—B—O1 is 26.9 (5)° and the Si atom is 0.334 (1) Å from the plane defined by B, O1 and O2.

The Si—O bond length [1.585 (2) Å] is at the lower end of the known range of Si—O distances (1.55 to 1.80 Å; James & Oldfield, 1986). The B—O distances are slightly different being 1.439 (4) Å for B—O(Si) and 1.461 (3) Å for B—O(ring), respectively.

Typical values of B—O distances for tetrahedrally coordinated boron in complexes which also contain B—N bonds lie within the range 1.43 (1) Å [in N(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>B (Taira & Osaki, 1971)] to 1.484 (3) Å [in Ph<sub>2</sub>BOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (Rettig & Trotter, 1973)]. The corresponding Si—O and B—O(Si) distances in 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane are 1.634 (2) and 1.363 (5) Å.

At first sight it is tempting to ascribe the shorter Si—O distance and the larger B—O—Si angle in the title compound compared with those in 2-(triphenylsiloxy)-4,4,6-trimethyl-1,3,2-dioxaborinane to an increase in the Si—O  $\pi$ -bonding component in the former compound. However, extensive studies of Si—O—Si-bonded compounds have shown that attempted correlations of Si—O distances, Si—O—Si angles, and theoretically calculated  $\sigma$ - and  $\pi$ -bonding components have produced controversial results (James & Oldfield, 1986). Hence we are reluctant to suggest that an increase in Si—O  $\pi$ -bonding is solely responsible for the effects mentioned above and we are continuing our studies of B—O—Si compounds to try to elucidate the structure—bonding relationships.

The BOC<sub>3</sub>N ring adopts a chair conformation with the 2-phenyl substituent equatorial (Fig. 1), with atoms N, C2, O1 and C4 coplanar; atoms B and

C3 are respectively 0.678 and -0.675 Å above and below this plane. The B—N distance is 1.639 (4) Å; in the comparable compound Ph<sub>2</sub>BO(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>, the BOC<sub>3</sub>N ring is also in a chair conformation and the B—N distance is 1.643 (3) Å (Rettig & Trotter, 1983). The remaining Si—C, C—C, C—N and C—O bond lengths are all as anticipated.

In the crystal structure the molecules are linked to form infinite chains extending in the *a* direction by hydrogen bonding between one N—H moiety and an adjacent O(ring) atom of a molecule related by a 2<sub>1</sub> screw axis; the N...O distance is 2.971 (3) Å (Fig. 2). The other N—H group and the bridging oxygen (O2) do not take part in any hydrogen bonding.

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## Structure of Phenoxathiin (Phenothioxin), C<sub>12</sub>H<sub>8</sub>OS, at 223 K

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**Abstract.**  $M_r = 200.25$ , orthorhombic,  $P2_12_12_1$ ,  $a = 7.758$  (2),  $b = 20.506$  (3),  $c = 5.896$  (2) Å,  $V =$

$938.0$  (4) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.42$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 2.88$  cm<sup>-1</sup>,  $F(000) = 416$ ,  $T = 223$  K,  $R = 0.044$  for 1414 unique reflections having  $I > 3\sigma_I$ . The phenoxathiin molecule is constituted of two very

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nearly regular planar hexagonal carbocyclic (benzenoid) rings joined to a non-planar heterocyclic ring. The heterocyclic ring geometry is described in terms of two intersecting planes between which the dihedral angle, the molecular fold angle, is  $142.3^\circ$ . The angle at S (C—S—C) is  $97.7(1)^\circ$ , while the angle at O (C—O—C) is  $117.4(2)^\circ$ . The overall mean C—C distance in the carbocyclic rings is  $1.387(7) \text{ \AA}$ . The absence in this structure of the type of disorder previously found in the dibenzofuran structure is readily understandable since eight sets of close approaches involving each molecule were found in the present structure. These close approaches involve S and O atoms as well as H atoms.

**Introduction.** The structure of crystalline phenoxathiin was first discussed by Wood, McCale & Williams (1941) on the basis of morphological, optical and X-ray data. They concluded that the molecule should be folded about a line joining the O and S atoms and have a fold angle of  $150\text{--}160^\circ$ . Subsequently, Hosoya (1966) used photographically recorded X-ray data to obtain isotropically refined carbon, sulfur and oxygen coordinates. No hydrogen coordinate assignment was attempted, and the final *R* value for 352 unique reflections was 0.134.

Our interest in the structure of phenoxathiin arose because the molecular shape appeared to allow the possibility of the type of disorder elucidated for the dibenzofuran structure by Reppart, Gallucci, Lundstedt & Gerkin (1984). Although the results of the Hosoya study did not necessarily indicate disorder, neither did they rule disorder out. The goals of the present investigation were thus a definitive analysis of the structure with respect to disorder and, secondarily, a more definitive determination of the atomic and molecular parameters, including those for the H atoms.

Since phenoxathiin melts just above room temperature, it appeared advantageous to obtain our diffraction data from a cooled crystal, particularly since the presence of disorder was considered.

**Experimental.** Phenoxathiin obtained from Pfaltz and Bauer, Inc. was twice recrystallized from ethanol by slow evaporation at room temperature to provide the experimental sample, a clear platy crystal with approximate principal dimensions  $0.15 \times 0.30 \times 0.42 \text{ mm}$ . This was mounted with epoxy cement on a glass rod and cooled to 223 K on a Rigaku AFC5S diffractometer utilizing a Molecular Structure Corporation low-temperature apparatus. The stated temperature was measured continuously during data collection in the cold gas flow just upstream of the crystal; the estimated uncertainty of the crystal temperature is  $\pm 2 \text{ K}$ .

Unit-cell parameters were obtained from a symmetry-restricted least-squares fit of the setting angles for 25 centered reflections with  $20 < 2\theta < 28^\circ$ . Intensity data were measured for 2859 reflections (exclusive of standards) with  $+h$ ,  $+k$ ,  $+l$  indices ( $h_{\max} = 13$ ;  $k_{\max} = 33$ ;  $l_{\max} = 10$ ) and  $2\theta$  values in the range  $4 \leq 2\theta \leq 75^\circ$ . The  $\omega$  scan technique was employed with scan widths  $(1.10 + 0.35 \tan \theta)^\circ$  in  $\omega$ , and a background/scan time ratio of 0.5. An uncertainty was assigned to each reflection using the formula  $\sigma_I^2 = \sigma_{cs}^2(I) + (0.03I)^2$  where  $\sigma_{cs}$  is based on counting statistics and *I* is the integrated intensity. Six standard reflections ( $\bar{1}\bar{1}\bar{1}$ , 220, 02 $\bar{1}$ , 3 $\bar{4}$ 3, 421 and 371) were measured after every 150 reflections; they showed, on average, a maximum non-systematic relative intensity variation of  $\pm 2.4\%$ . Accordingly, no decay correction was applied. The data were corrected for Lorentz and polarization effects. A  $\psi$ -scan absorption correction was applied based on  $\psi$ -scan data obtained at the conclusion of intensity data collection; the range of transmission factors was 0.964–1.000, with an average value 0.985.

The observed systematic absences ( $h00$ ,  $h = \text{odd}$ ;  $0k0$ ,  $k = \text{odd}$ ;  $00l$ ,  $l = \text{odd}$ ) determined the allowed primitive orthorhombic space group uniquely as  $P2_12_12_1$  (No. 19). A Patterson map gave the initial location of the S atom, after which Fourier difference methods were used to locate the remaining non-H atoms and subsequently the H atoms. Full-matrix least-squares refinement was performed using the TEXSAN structure analysis package (Molecular Structure Corporation, 1988) to minimize the function  $\sum \sigma_F^{-2} (|F_o| - |F_c|)^2$  in which  $\sigma_F = \sigma_I/2FLp$ . Neutral-atom scattering factors and anomalous-dispersion factors were taken from Cromer & Waber (1974) for S, O and C; the scattering factor for H was taken from Stewart, Davidson & Simpson (1965).

Following refinement to the isotropic stage for all atoms except hydrogen using the data having  $I > 3\sigma_I$ , the  $\psi$ -scan absorption correction was applied. Then, using all the (unique) reflections with  $I > 3\sigma_I$ , least-squares refinement proceeded to the anisotropic stage for all atoms except hydrogen and to the isotropic stage for the hydrogens.

The results for the final refinement cycle were: 1414 independent observations having  $I > 3\sigma_I$ ; 159 variables;  $R = 0.044$ ;  $wR = 0.048$ ;  $w = \sigma_F^{-2}$ ;  $S = 1.43$ ;  $(\Delta/\sigma)_{\max} < 0.01$ . \* Maximum and minimum peaks on the final electron density difference map had values  $+0.27$  and  $-0.22 \text{ e \AA}^{-3}$ , respectively. The maximum

\* For the final refinement cycle for 1675 independent observations having  $I > \sigma_I$ :  $R = 0.055$ ;  $wR = 0.052$ ;  $S = 1.42$ ;  $(\Delta/\sigma)_{\max} < 0.01$ . Similarly, for the final refinement cycle for 2357 independent observations having  $I > 0$ :  $R = 0.069$ ;  $wR = 0.101$ ;  $S = 1.14$ ;  $(\Delta/\sigma)_{\max} < 0.01$ . These latter results are for comparison purposes only.

peak was located at  $x = 0.13$ ,  $y = -0.18$ ,  $z = -0.01$ , approximately halfway between S and C11; the minimum peak was located at  $x = 0.71$ ,  $y = -0.05$ ,  $z = 0.11$ , placing it at distances ranging from 2.0–2.9 Å from seven C atoms not all of which were in one molecule. The final electron density difference map provided no basis for an interpretation involving a second molecule in an alternative orientation.

A test of the enantiomer of this structure gave very slightly poorer indices of agreement, so the present structure was retained.

**Discussion.** The final coordinates and equivalent isotropic and isotropic displacement parameters with their uncertainties are given in Table 1.\* The molecule is shown in Fig. 1.

Since in this structure the asymmetric unit is an entire phenoxathiin molecule there are no symmetry constraints linking any sets of distances or angles in the molecule. Selected interatomic distances and angles within the molecule are given with their uncertainties in Table 2 and data regarding least-squares best-fit planes are given below.

The positions of the C atoms of each of the two benzenoid rings correspond closely to regular hexagonal geometry, as expected. The mean C—C distance for ring I (C1–C4, C11 and C12) is 1.386 (8) Å and for ring II (C6–C9, C13 and C14) is 1.388 (6) Å; the grand mean for the two rings is 1.387 (7) Å. The average magnitude of the deviations of the C—C—C ring angles from 120° is 0.6° for each ring and thus is twice the estimated standard deviation (e.s.d.) of the individual angles. The mean deviation of the C atoms in ring I from the least-squares best-fit plane is 0.007 Å, while for ring II, the mean deviation is 0.009 Å. Since the mean e.s.d. of the individual displacements is 0.004 Å, the mean deviations from planarity thus differ from zero by less than three times the mean e.s.d. of an individual displacement.

As reported earlier by Wood, McCale & Williams (1941) and Hosoya (1966), the heterocyclic ring is not planar. We have chosen to describe the geometry of this ring in terms of two least-squares best-fit planes: one including O, S, C11 and C12, the other including O, S, C13 and C14. The mean deviations of these sets of atoms from the least-squares best-fit planes are 0.008 Å for the first set and 0.001 Å for the second; the mean e.s.d. of the individual atomic deviations for both sets is 0.002 Å. The angle between these planes, which we take as the fold angle of the molecule, is 142.3°. As is apparent from the

Table 1. *Final positional parameters and displacement parameters (Å<sup>2</sup>) for phenoxathiin at 223 K, with their estimated standard deviations*

The form of the equivalent isotropic displacement parameter is:  
 $B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> / <i>B</i>
S	0.14096 (11)	-0.13904 (4)	0.04538 (14)	2.75 (3)
O	0.3388 (3)	-0.1355 (1)	-0.4004 (3)	2.63 (8)
C1	0.1578 (4)	-0.2697 (1)	-0.0595 (6)	2.7 (1)
C2	0.1980 (5)	-0.3217 (2)	-0.1978 (7)	3.2 (2)
C3	0.2823 (5)	-0.3117 (2)	-0.4024 (7)	3.1 (1)
C4	0.3296 (4)	-0.2491 (2)	-0.4651 (7)	2.6 (1)
C6	0.5236 (4)	-0.0486 (2)	-0.2964 (6)	2.3 (1)
C7	0.5706 (4)	0.0001 (2)	-0.1484 (6)	2.6 (1)
C8	0.4937 (4)	0.0054 (2)	0.0633 (6)	2.7 (1)
C9	0.3658 (5)	-0.0387 (1)	0.1243 (5)	2.2 (1)
C11	0.2016 (4)	-0.2061 (1)	-0.1244 (5)	2.1 (1)
C12	0.2891 (4)	-0.1971 (1)	-0.3271 (5)	2.2 (1)
C13	0.3915 (4)	-0.0914 (1)	-0.2372 (5)	2.0 (1)
C14	0.3132 (4)	-0.0871 (1)	-0.0258 (5)	2.0 (1)
H1	0.095 (4)	-0.276 (1)	0.080 (6)	2.0 (7)†
H2	0.161 (5)	-0.363 (2)	-0.166 (6)	3.6 (8)†
H3	0.309 (5)	-0.347 (2)	-0.506 (6)	4.4 (9)†
H4	0.387 (5)	-0.239 (1)	-0.595 (6)	2.6 (7)†
H6	0.571 (4)	-0.053 (1)	-0.441 (6)	2.2 (7)†
H7	0.658 (5)	0.027 (1)	-0.188 (6)	3.1 (8)†
H8	0.525 (4)	0.040 (1)	0.179 (6)	2.4 (7)†
H9	0.314 (4)	-0.037 (1)	0.270 (6)	2.1 (7)†

† Refined isotropically.

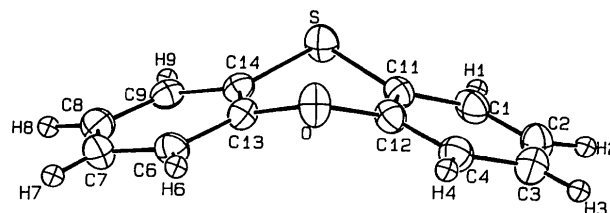


Fig. 1. A view of the phenoxathiin molecular structure as determined at 223 K in this research, prepared using ORTEPII (Johnson, 1971). The conventional labeling of atoms in this molecule is shown. Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

view of the molecule presented in Fig. 1, the angle between the best planes through the carbocyclic rings should be very similar to this fold angle and indeed it is found to be 147.8°. It is this latter angle that Hosoya (1966) identified as the fold angle, his value for it being given as 'about 138°'.\*

Although H atoms were not included in deriving least-squares best-fit planes for the carbocyclic rings, their deviations from these planes are given.†

\* It should be noted here that the angular standard deviations tabulated by Hosoya are approximately two orders of magnitude too small to be consistent with his stated standard deviations of distances (4 to  $8 \times 10^{-2}$  Å). Thus the actual angular uncertainties in that structure are of the order of a few degrees rather than a few hundredths of a degree as tabulated.

† See deposition footnote.

\* Lists of structure factors, anisotropic displacement parameters and data regarding least-squares best-fit planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53299 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) for phenoxathiin at 223 K, with their estimated standard deviations

Carbocyclic ring (benzene) I			
C1—C2	1.379 (5)	C1—H1	0.96 (3)
C2—C3	1.388 (5)	C2—H2	0.91 (3)
C3—C4	1.386 (4)	C3—H3	0.96 (4)
C4—C12	1.376 (4)	C4—H4	0.91 (3)
C12—C11	1.387 (4)		
C11—C1	1.402 (4)		
C11—C1—C2	120.3 (3)	H1—C1—C2	121 (2)
C1—C2—C3	120.4 (3)	H2—C2—C3	118 (2)
C2—C3—C4	119.6 (3)	H3—C3—C4	118 (2)
C3—C4—C12	120.0 (3)	H4—C4—C12	116 (2)
C4—C12—C11	121.2 (3)		
C12—C11—C1	118.5 (3)		
Mean C—C	1.386 (8)	Mean C—H	0.94 (3)
Mean C—C—C	120.0 (8)	Mean H—C—C	118 (2)
Carbocyclic ring (benzene) II			
C6—C7	1.375 (5)	C6—H6	0.93 (3)
C7—C8	1.388 (5)	C7—H7	0.90 (4)
C8—C9	1.390 (5)	C8—H8	1.02 (3)
C9—C14	1.390 (4)	C9—H9	0.95 (3)
C14—C13	1.390 (4)		
C13—C6	1.393 (4)		
C13—C6—C7	119.6 (3)	H6—C6—C7	123 (2)
C6—C7—C8	120.9 (3)	H7—C7—C8	120 (2)
C7—C8—C9	119.3 (3)	H8—C8—C9	117 (2)
C8—C9—C14	120.6 (3)	H9—C9—C14	118 (2)
C9—C14—C13	119.2 (3)		
C14—C13—C6	120.4 (3)		
Mean C—C	1.388 (6)	Mean C—H	0.95 (5)
Mean C—C—C	120.0 (7)	Mean H—C—C	120 (2)
Heterocyclic ring			
S—C11	1.764 (3)	S—C14	1.760 (3)
O—C12	1.390 (3)	O—C13	1.383 (3)
C11—C12	1.387 (4)		
C13—C14	1.390 (4)		
C11—S—C14	97.7 (1)	O—C13—C14	122.4 (3)
C12—O—C13	117.4 (2)	C13—C14—S	120.5 (2)
C11—C12—O	121.6 (3)	S—C11—C12	121.1 (2)

The closest intermolecular approaches (Table 3) involve O and S atoms as well as H atoms. The existence of eight close approaches involving six atoms of a given molecule makes straightforward an understanding of the absence of disorder in this structure: in particular, if one attempted to generate dibenzofuran-like disorder (Reppart, Gallucci, Lundstedt & Gerkin, 1984), the displaced S atom would be in very serious steric conflict with H9<sup>iii</sup>. A stereoview of the molecular arrangement in this structure is given in Fig. 2.

As indicated above, Hosoya's structural results for the non-H atoms were derived from limited photographic data, and though they are in qualitative agreement with the present results for the non-H atoms, they are entirely superseded by them quantitatively.

Following completion of this work, we learned that the crystal structures of C<sub>12</sub>H<sub>8</sub>XY, (X, Y) = (S, Se), (S, Te), (Se, Te) and (O, Se), have recently been

Table 3. Intermolecular closest approaches (Å) in the phenoxathiin structure at 223 K, with their estimated standard deviations

	van der Waals radius sum	Observed
H6—H7 <sup>i</sup>	2.4	2.61 (5)
H7—H6 <sup>ii</sup>	2.4	2.61 (5)
H6—H9 <sup>iii</sup>	2.4	2.64 (5)
H9—H6 <sup>iv</sup>	2.4	2.64 (5)
O—H9 <sup>iii</sup>	2.6	2.81 (3)
H9—O <sup>iv</sup>	2.6	2.81 (3)
S—H8 <sup>v</sup>	3.0	3.23 (3)
H8—S <sup>vi</sup>	3.0	3.23 (3)

Symmetry code: (i)  $\frac{1}{2}-x, -y, -\frac{1}{2}+z$ ; (ii)  $\frac{1}{2}-x, -y, \frac{1}{2}+z$ ; (iii)  $x, y, -1+z$ ; (iv)  $x, y, 1+z$ ; (v)  $\frac{1}{2}-x, -y, -\frac{1}{2}+z$ ; (vi)  $\frac{1}{2}-x, -y, \frac{1}{2}+z$ .

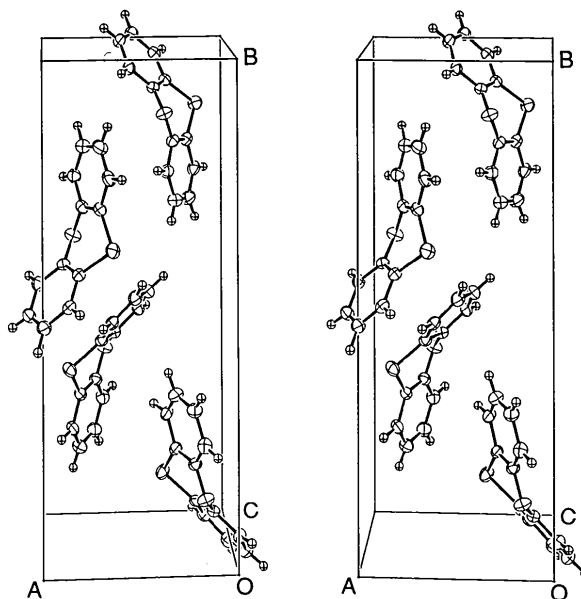


Fig. 2. Stereoview of a portion of the phenoxathiin structure at 223 K, prepared using ORTEPII (Johnson, 1971). Thermal ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

reported by Meyers, Irgolic, Zingaro, Junk, Chakravorty, Dereu, French & Pappalardo (1988). We had surmised that C<sub>12</sub>H<sub>8</sub>SSe might also have a P2<sub>1</sub>2<sub>1</sub>2 structure, but show disorder. Meyers *et al.* found that it is disordered (as also are C<sub>12</sub>H<sub>8</sub>STe and C<sub>12</sub>H<sub>8</sub>SeTe) but has a P2<sub>1</sub>/c structure isomorphous to that of C<sub>12</sub>H<sub>8</sub>S<sub>2</sub> and C<sub>12</sub>H<sub>8</sub>Se<sub>2</sub>. In various structural comparisons Meyers *et al.* used Hosoya's data for C<sub>12</sub>H<sub>8</sub>OS. Although (as stated above) the present data entirely supersede those of Hosoya, the magnitudes of the changes in the parameters considered by Meyers *et al.* were sufficiently small in view of the rather qualitative nature of many of their comparisons involving phenoxathiin that their conclusions in general need not be materially altered. A noteworthy exception, however, is that the present data for the

C—C bond lengths in phenoxathiin are in direct conflict with certain of their conclusions concerning C—C bond lengths in the series of ten  $C_{12}H_8XY$  structures for  $X, Y$  variously O, S, Se, Te. Specifically, while the range of differences in the present average C—C bond lengths (0.016 Å) is very similar to that given by Meyers *et al.* (0.019 Å), and is indeed less than the corresponding range for anthracene (0.071 Å) from the work of Lehmann & Pawley (1972), the pattern of lengths is quite different. Meyers *et al.* conclude that bonds C2—C3 and C7—C8 (our numbering; see Fig. 1) are of highest bond order and shortest at 1.374 (2) Å (weighted mean value for the ten structures), while C11—C12 and C13—C14 are of lowest bond order and longest at 1.393 (3) Å (weighted mean value); the present phenoxathiin data yield average values for these sets of 1.388 and 1.388 Å, respectively. For phenoxathiin, the minimum average bond length is for C3—C4 and C6—C7 at 1.380 Å while the maximum average bond length is for C11—C1 and C9—C14 at 1.396 Å. In view of the e.s.d.'s of the individual bond lengths, however, even this largest difference is of marginal significance.

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## Structure of 6 $\alpha$ -Methylprogesteron-17 $\alpha$ -yl Pivalate

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**Abstract.**  $C_{27}H_{40}O_4$ ,  $M_r = 428.6$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.821$  (3),  $b = 25.766$  (6),  $c = 9.802$  (3) Å,  $V = 2480$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.15$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.70$  cm<sup>-1</sup>,  $F(000) = 936$ ,  $T = 295$  K, final  $R = 0.063$  for 2778 observed reflections. The A ring assumes a normal 1 $\alpha$ ,2 $\beta$ -half-chair conformation. The progesterone

side chain has a conformation typical of 17 $\alpha$ -ester steroids; the C(16)—C(17)—C(20)—O(20) torsion angle is  $-17.9$  (5)°.

**Introduction.** Previous reviews of crystallographic data have shown that 17 $\alpha$ -ester substitution has a very restricting influence on the conformation of the