Table 3. *Bond lengths* (Å)

N(1)–C(2)	1·381 (4)	O(2)–C(10)	1·456 (4)
C(2)–C(3)	1·354 (4)	C(5)–C(12)	1·458 (4)
C(2)–C(8)	1·505 (5)	O(3)–C(12)	1·213 (4)
C(3)–C(4)	1·524 (4)	O(4)–C(12)	1·330 (4)
C(3)–C(9)	1·473 (4)	C(13)–C(14)	1·489 (6)
C(4)–C(5)	1·517 (4)	O(4)–C(13)	1·450 (4)
C(4)–C(15)	1·516 (4)	C(4)–C(15)	1·516 (4)
C(5)–C(6)	1·355 (4)	C(15)–C(16)	1·389 (4)
C(5)–C(12)	1·458 (4)	C(15)–C(20)	1·384 (4)
N(1)–C(6)	1·377 (4)	C(16)–C(17)	1·405 (5)
C(6)–C(7)	1·507 (4)	C(17)–C(18)	1·369 (5)
O(1)–C(9)	1·204 (4)	C(18)–C(19)	1·362 (5)
O(2)–C(9)	1·352 (4)	C(20)–C(19)	1·410 (5)
C(10)–C(11)	1·493 (6)		

Table 4. *Bond angles* (°)

C(2)–N(1)–C(6)	123·6 (3)	O(2)–C(9)–C(3)	111·6 (3)
C(3)–C(2)–N(1)	118·2 (3)	O(2)–C(9)–O(1)	121·7 (3)
C(8)–C(2)–N(1)	113·5 (3)	O(2)–C(10)–C(9)	117·2 (3)
C(8)–C(2)–C(3)	128·2 (3)	O(2)–C(10)–C(11)	110·8 (3)
C(4)–C(3)–C(2)	119·1 (3)	O(3)–C(12)–C(5)	123·7 (3)
C(9)–C(3)–C(2)	120·8 (3)	O(4)–C(12)–C(5)	115·2 (2)
C(9)–C(3)–C(4)	119·9 (3)	O(4)–C(12)–O(3)	121·3 (3)
C(5)–C(4)–C(3)	109·7 (2)	O(4)–C(13)–C(14)	106·8 (3)
C(15)–C(4)–C(3)	109·8 (2)	C(16)–C(15)–C(4)	120·0 (3)
C(15)–C(4)–C(5)	112·4 (2)	C(20)–C(15)–C(4)	121·9 (3)
C(6)–C(5)–C(4)	119·4 (2)	C(20)–C(15)–C(16)	118·0 (3)
C(12)–C(5)–C(4)	115·0 (2)	C(17)–C(16)–C(15)	120·6 (3)
C(12)–C(5)–C(6)	125·5 (3)	C(18)–C(17)–C(16)	120·1 (3)
C(5)–C(6)–N(1)	118·3 (3)	C(19)–C(18)–C(17)	120·5 (3)
C(7)–C(6)–N(1)	112·9 (3)	C(20)–C(19)–C(18)	119·6 (3)
C(7)–C(6)–C(5)	128·8 (3)	C(19)–C(20)–C(15)	121·1 (3)
O(1)–C(9)–C(3)	126·7 (3)	C(13)–O(4)–C(12)	117·8 (3)

O(3)···H(10) 2·11 Å, O(3) being at x, $1 + y$, z] to form an infinite chain of the molecules along the b axis.

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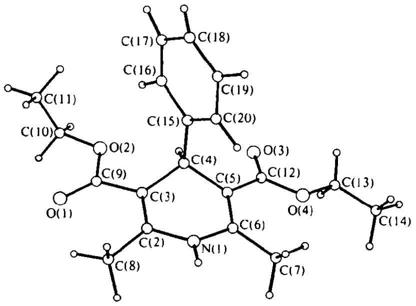

Fig. 1. The molecule and atom numbering.

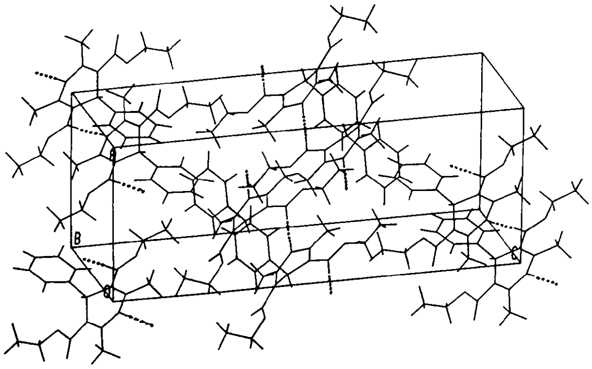

Fig. 2. Packing diagram.

References

Karle, I. L. (1961). *Acta Cryst.* **14**, 497–500.

Krajewski, J. W., Urbanczyk-Lipkowska, Z. & Gluzinski, P. (1977*a*). *Cryst. Struct. Commun.* **6**, 787–791.

Krajewski, J., Urbanczyk-Lipkowska, Z. & Gluzinski, P. (1977*b*). *Acta Cryst.* B**33**, 2967–2969.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1978). B**34**, 3817–3820

2,3-Dimethyl-2,3-butanediol (Pinacol)

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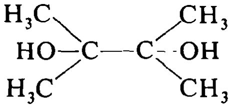
Abstract. $C_6H_{14}O_2$, $M_r = 118{\cdot}17$, m.p. 39–40°C, monoclinic, $C2/c$, $Z = 16$, $a = 16{\cdot}456\,(1)$, $b = 16{\cdot}320\,(2)$, $c = 11{\cdot}147\,(1)$ Å, $\beta = 91{\cdot}54\,(1)°$, $D_x = 1{\cdot}049$, $D_m = 1{\cdot}042$ g cm^{-3} (flotation in ether–bromobenzene at 20°C). The structure was solved with *MULTAN* and refined by full-matrix anisotropic least-squares calculations to $R = 0{\cdot}063$ for 2198 observed reflections. The structure contains three conformationally different molecules. One of the molecules has the *trans* centrosymmetrical conformation. The other two have the *gauche* conformation; one has twofold axial symmetry and the other is asymmetrical. The molecules on the center of symmetry are disordered, with one quarter in a different orientation. The molecules are linked by a closed loop of four hydrogen bonds.

Introduction. The primary interest in studying the crystal structure of pinacol (I) was to examine the conformation of the molecule in the absence of water molecules. A review of the hydration of diols by Hatt (1956) had suggested that only those diols with an even number of intervening carbon atoms and at least four methyl groups would form high hydrates. In addition, it was postulated that the hydrocarbon chain and the hydroxyl group must be *trans* extended in the hydrates. Pinacol hexahydrate was studied by Kim & Jeffrey (1970) and the molecule did in fact satisfy these criteria in the hydrate structure, which is a semi-clathrate (Jeffrey, 1969). Other diols which satisfy these criteria in hydrates which have been studied are 2,5-dimethyl-2,5-hexanediol tetrahydrate (Jeffrey & Shen, 1972) and 2,7-dimethyl-2,7-octanediol tetrahydrate (Jeffrey & Mastropaolo, 1978).



(I)

Pinacol sublimes at room temperature and good crystals are easily grown in a closed vessel. A crystal with dimensions $0{\cdot}16 \times 0{\cdot}20 \times 0{\cdot}32$ mm, sealed in a 0·3 mm thin-walled glass capillary with a plug of larger crystals, was used on a CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å) at 25 °C to measure 3083 independent intensities, of which 885 had $I < 2\sigma$.

The structure was solved using *MULTAN* (Germain, Main & Woolfson, 1971). The Fourier maps showed 16 peaks corresponding to the C and O atoms of the three symmetry-independent molecules: one on a center of symmetry, one on a twofold axis, and one asymmetrical. Initial refinement was by block-diagonal least-squares, and then by anisotropic full-matrix least-squares calculations. The function minimized was $\sum w(|F_o| - k|F_c|)^2$, with $w^{-1} = a + b|F_o| + c|F_o|^2$, where $a = 6{\cdot}0$, $b = 1{\cdot}0$, $c = 0{\cdot}01$. Difference syntheses showed that the molecule on the center of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$ was disordered in the ratio 3:1. All methyl H atoms were placed 1·0 Å from the C atoms with tetrahedral valence angles. The hydroxyl H atoms were located on the final difference Fourier map, but were not refined. The final R factor was 0·063 for all observed reflections. The atomic parameters for non-hydrogen atoms are given in Table 1.* The atomic notation and the molecular symmetry and dimensions are shown in Fig. 1. Additional dimensions have been deposited.* A stereo *ORTEP* view of the molecule is shown in Fig. 2.

Discussion. The most interesting feature of the crystal structure is that it consists of three symmetry-independent molecules, all with different conformations. Molecule 1 is ordered and has twofold axial symmetry about $\frac{1}{2},y,\frac{1}{4}$. Molecule 2 is asymmetrical and ordered. Molecule 3 is centrosymmetric about the center at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$ and is ordered, as shown in Fig. 3.

Two of the molecules, 1 and 2, have the hydroxyl groups in the *gauche* conformation, and the third, 3, is

Table 1. *Atomic coordinates* ($\times 10^4$) *in the crystal structure of pinacol*

Estimated standard deviations given in parentheses refer to the least significant digit. The hydrogen coordinates are less accurate, and have been deposited.

	x	y	z
Molecule 1 (on the twofold axis at $\frac{1}{2},y,\frac{1}{4}$)			
C(1)	4546 (1)	4024 (1)	2305 (2)
C(2)	4074 (2)	4728 (2)	2861 (3)
C(3)	4450 (2)	4026 (2)	951 (3)
O(1)	4187 (1)	3292 (1)	2771 (1)
Molecule 2			
C(4)	3564 (1)	1451 (2)	−883 (2)
C(5)	4266 (2)	1983 (3)	−1283 (3)
C(6)	3561 (2)	643 (2)	−1544 (3)
C(7)	3573 (1)	1354 (1)	493 (2)
C(8)	2820 (2)	892 (2)	908 (2)
C(9)	4339 (2)	935 (2)	978 (2)
O(2)	2822 (1)	1868 (1)	−1176 (1)
O(3)	3582 (1)	2149 (1)	1033 (1)
Molecule 3 (at the center of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$)			
C(10)	2482 (2)	2970 (2)	4926 (2)
C(11)	3083 (2)	3414 (2)	5752 (3)
C(12)	1608 (2)	3276 (3)	5197 (4)
O(4)	2605 (1)	3181 (1)	3684 (2)
C(10*a*)	2559 (5)	2295 (5)	4390 (7)
C(11*a*)	1736 (6)	1800 (6)	4122 (1)
C(12*a*)	3313 (6)	1751 (6)	4409 (9)
O(4*a*)	2624 (3)	2891 (4)	3517 (5)

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* Lists of observed and calculated structure factors, H atomic coordinates, all thermal parameters, additional valence angles not shown in Fig. 1, and torsion angles, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33841 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

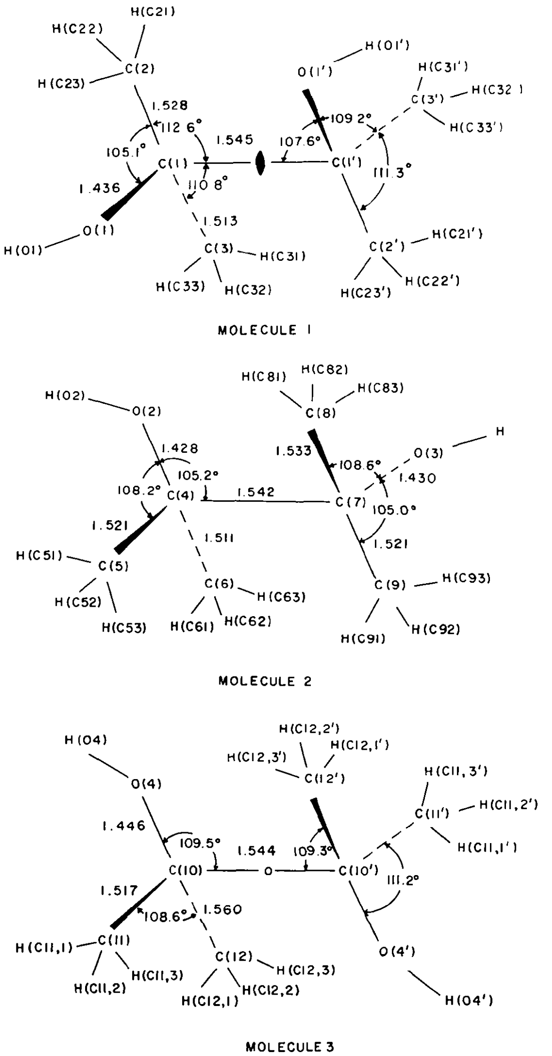

Fig. 1. Three symmetry-independent molecules in the crystal structure of pinacol, with bond lengths (Å) and valence angles (°). Only the high-occupancy form of molecule 3 is shown. Symmetry relationships: in molecule 1, primed atoms are related to unprimed by $-x, y, \frac{1}{2}-z$; in molecule 3, primed atoms are related to unprimed by $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

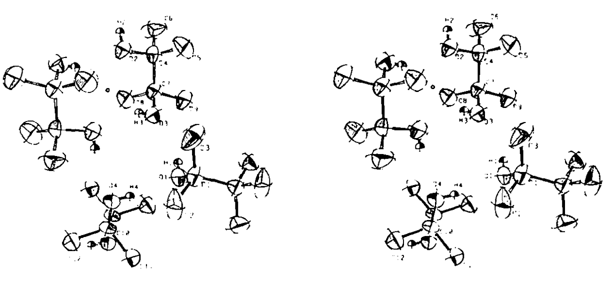

Fig. 2. *ORTEP* plot of thermal ellipsoids at 50% probability (Johnson, 1965) of molecules in the crystal structure of pinacol. Methyl H atoms are not shown, nor is the low-occupancy molecule at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$. The viewing direction is 20° from the twofold axis through C(1)—C(1′), thereby minimizing the overlap.

trans. The crystal structure, therefore, contains two racemic mixtures of *gauche* molecules and centrosymmetrical racemate, *trans*, molecules.

The standard deviations of the C—C and C—O bonds are 0·004 Å, and the observed values do not differ significantly from the mean values of C—C 1·5303, C—O 1·4351 Å. The standard deviations of the valence angles are 0·3°. The C—C—C angles, with a mean value of 111·2°, are significantly greater than the C—C—O angles, mean value 107·7°. The observed hydroxyl bond distances range from 0·65 to 0·75 Å. There is no evidence from the molecular dimensions of any subtle differences in the electronic bonding structure between the two *gauche* molecules and the *trans* molecule. In contrast, the *gauche* and *trans* molecules of ethanol, which also coexist in the same crystal structure, have possibly significant dimensional differences (Jönsson, 1976).

The position of the hydrogen H(4) is the same for both molecular orientations (Fig. 3). The hydrogen bonding forms closed loops of four bonds, as shown in Fig. 4. The covalent O—H bonds are all shorter than the standard neutron diffraction value (0·97 Å). When the H positions are corrected to this standard distance by moving along the direction of the bond, the H···O

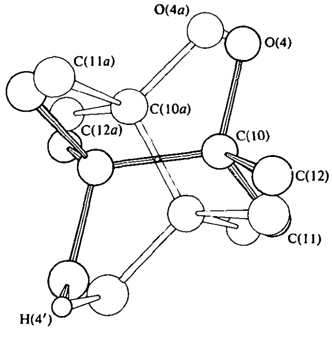

Fig. 3. Disordered molecule on the center of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{2}$. The molecule in heavy lines has an occupancy of 0·75. The H atoms are omitted for clarity.

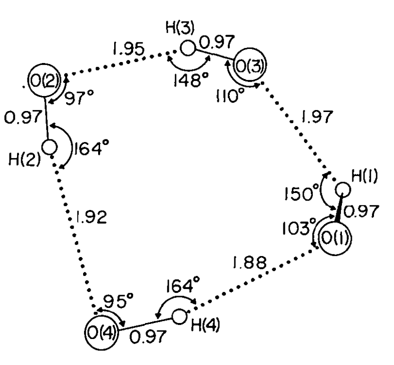

Fig. 4. Hydrogen bonds in the pinacol crystal structure. The O—H covalent bonds have been extended to 0·97 Å, the value obtained from neutron diffraction studies (Jeffrey & Takagi, 1978).

hydrogen-bond distances lie between 1·88 and 1·97 Å. These are longer than in the crystal structure of ethanol (Jönsson, 1976) where the hydrogen bonding forms infinite chains with corrected H···O distances of 1·75 Å. In order to form the closed loop, two of the four O—H···O angles are less than the theoretical value of 163° for the most probable temperature-dependent O—H···O angle (Newton, Jeffrey & Takagi, 1978).

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

HATT, H. H. (1956). *Rev. Pure Appl. Chem.* **6**, 154–189.

JEFFREY, G. A. (1969). *Acc. Chem. Res.* **2**, 344–352.

JEFFREY, G. A. & MASTROPAOLO, D. (1978). *Acta Cryst.* B**34**, 552–556.

JEFFREY, G. A. & SHEN, M. S. (1972). *J. Chem. Phys.* **57**, 56–61.

JEFFREY, G. A. & TAKAGI, S. (1978). *Acc. Chem. Res.* **11**, 264–270.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

JÖNSSON, P.-G. (1976). *Acta Cryst.* B**32**, 232–235.

KIM, H. S. & JEFFREY, G. A. (1970). *J. Chem. Phys.* **53**, 3610–3615.

NEWTON, M., JEFFREY, G. A. & TAKAGI, S. (1978). *J. Am. Chem. Soc.* Submitted for publication.

Acta Cryst. (1978). B**34**, 3820–3822

A Twelve-Membered-Ring Organophosphorus Compound: *cis*-2,8-Dithioxo-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane

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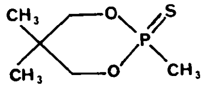
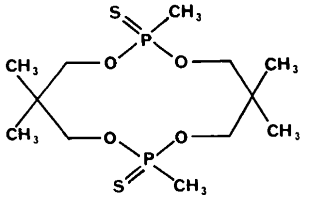
Abstract. $C_{12}H_{26}O_4P_2S_2$, $M_r = 360{\cdot}41$, triclinic $P\bar{1}$, $a = 6{\cdot}422\,(1)$, $b = 9{\cdot}155\,(1)$, $c = 16{\cdot}738\,(1)$ Å, $\alpha = 84{\cdot}64\,(2)$, $\beta = 89{\cdot}87\,(1)$, $\gamma = 70{\cdot}30\,(2)°$, $V = 922$ Å^3, $D_x = 1{\cdot}299$ Mg m^{-3}, $Z = 2$. The structure was refined to $R = 0{\cdot}073$ for 2227 observed data. The twelve-membered ring adopts a square conformation close to that found for cyclododecane. The substituted C and the P atoms are placed in the corner positions. The O—P—O and the P—O—C ring angles are larger than in the corresponding monomer.

Introduction. It has been established that cyclic phosphonite molecules of various ring sizes, *e.g.* five-membered 1,3,2-dioxaphospholanes, six-membered 1,3,2-dioxaphosphorinanes, seven-membered 1,3,2-dioxaphosphepanes and eight-membered 1,3,6,2-trioxaphosphocanes, can dimerize in solution to give ten- (Dutasta, Guimaraes, Martin & Robert, 1975), twelve- (Albrand, Dutasta & Robert, 1974), fourteen- (Dutasta, Guimaraes & Robert, 1977), and sixteen- (Dutasta & Robert, 1978) membered rings respectively. The structural study of these medium-ring compounds, which are stable when the P atom is tetracoordinate (thiophosphonate), offers several points of interest. By keeping the same substituents attached to the P atom, and by changing the ring size, one may follow the gradual modification of the chemical shift, δ, and hyperfine coupling constant, *J*, with the changes in bond angles and lengths. Also, knowledge of the solid-state conformation of these ring compounds when combined with NMR studies in solution (^{1}H, ^{13}C, ^{31}P) will help towards a better understanding of the ring conformation in solution.

The structure of the monomer (I) has already been reported (Dutasta, Grand & Robert, 1974; Grand & Robert, 1978). We now report the structure of the *cis* isomer (II) which is obtained from the dimerization and sulphurization of (I) (Albrand, Dutasta & Robert,



(I)
2-Thioxo-2,5,5-trimethyl-1,3,2-dioxaphosphorinane



(II)
2,8-Dithioxo-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane

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