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Push–Pull Ethylenes: The Structures of 3-(2-Imidazolidinylidene)-2,4-pentanedione (I), $C_8H_{12}N_2O_2$, and 3-(1,3-Dimethyl-2-imidazolidinylidene)-2,4-pentanedione Trihydrate (II), $C_{10}H_{16}N_2O_2.3H_2O$

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Abstract. (I): $M_r = 168$, triclinic, $P\bar{1}$, $Z = 2$, $a = 5{\cdot}596$ (2), $b = 6{\cdot}938$ (3), $c = 10{\cdot}852$ (4) Å, $\alpha = 75{\cdot}64$ (3), $\beta = 93{\cdot}44$ (3), $\gamma = 95{\cdot}47$ (3)°, $V = 406{\cdot}0$ Å^3, $D_m = 1{\cdot}35$ (by flotation using carbon tetrachloride and *n*-hexane), $D_x = 1{\cdot}374$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) $= 1{\cdot}08$ cm^{-1}, $F(000) = 180$, $T = 293$ K. (II): $M_r = 250$, triclinic, $P\bar{1}$, $Z = 2$, $a = 7{\cdot}731$ (2), $b = 8{\cdot}580$ (2), $c = 11{\cdot}033$ (3) Å, $\alpha = 97{\cdot}66$ (2), $\beta = 98{\cdot}86$ (2), $\gamma = 101{\cdot}78$ (2)°, $V = 697{\cdot}5$ Å^3, $D_m = 1{\cdot}18$ (by flotation using KI solution), $D_x = 1{\cdot}190$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) $= 1{\cdot}02$ cm^{-1}, $F(000) = 272$, $T = 293$ K. Both structures were solved by direct methods and refined to $R = 4{\cdot}4\%$ for 901 reflexions for (I) and 5·7% for 2001 reflexions for (II). The C=C bond distances are 1·451 (3) Å in (I) and 1·468 (3) Å in (II), quite significantly longer than the C=C bond in ethylene [1·336 (2) Å; Bartell, Roth, Hollowell, Kuchitsu & Young (1965). *J. Chem. Phys.* **42**, 2683–2686]. The twist angle about the C=C bond in (II) is 72·9 (5)° but molecule (I) is essentially planar, the twist angle being only 4·9 (5)°.

Introduction. A large number of substituted ethylenes are known where the C=C bond is significantly longer than in ethylene and the deviation from planarity is quite appreciable (Abrahamsson, Rehnberg, Liljefors & Sandström, 1974; Ammon & Wheeler, 1975; Ammon, 1976; Adhikesavalu & Venkatesan, 1981, 1982). The two main factors which determine the geometry of a push–pull system are (i) conjugation (push–pull effect) and (ii) steric strain in the planar state. In this paper we report our findings on the molecular geometry of (I) and (II) as observed in their crystal structures. The conformation of (I) in the free state has also been determined by semi-empirical methods. The results are discussed along with the X-ray results. A sample of (II) was provided by Professor Jan Sandström, University of Lund, Sweden. Compound (I) was synthesized by us following the reported synthetic procedure (Ericksson, Sandström & Wennerbeck, 1970).

Experimental. Single crystals of (I) were obtained from a mixture of chloroform and benzene and of (II) from acetone by slow evaporation. Crystals of (I) and (II) with approximate dimensions 0·30 × 0·20 × 0·60 mm and 0·20 × 0·50 × 0·40 mm respectively were used for intensity-data collection; preliminary Weissenberg photographs indicated that the crystals are triclinic with two molecules in the unit cell; lattice parameters refined on a Nonius CAD-4 diffractometer using twenty reflexions in each case; intensity data collected using graphite-monochromated Mo $K\alpha$ radiation in the $\omega/2\theta$ mode with a scan speed of 1° min^{-1} up to $\theta < 23°$; two standard reflexions [014 and $\bar{1}12$ in (I) and 050 and 005 in (II)] monitored after every fifty reflexions showed only statistical fluctuations in both cases; 1100 reflexions for (I) and 2700 for (II) were measured, of which 901 and 2001, respectively, were judged significant ($|F_o| \geq 3\sigma|F_o|$).

The distribution of normalized structure factors was clearly centric for both structures and hence space group $P\bar{1}$ was chosen for structure solution and refinement. Structures solved by direct methods using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); full-matrix least-squares refinement of a scale factor, positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms, located from a difference map) converged at $R = 4{\cdot}4\%$ ($R_w = 4{\cdot}5\%$) for (I) and $R = 5{\cdot}7\%$ ($R_w = 6{\cdot}5\%$) for (II); function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1{\cdot}0/\sigma^2|F_o| + 0{\cdot}0004|F_o|^2$ for (I) and $w = 1{\cdot}0/(a + b|F_o| + c|F_o|^2)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) with $a = 6{\cdot}0$, $b = 1{\cdot}0$ and $c = 0{\cdot}06$ for (II); in final cycles of refinement, ratio of shift in parameters/e.s.d. about 0·02 for non-H atoms; final difference Fourier synthesis featureless; atomic scattering factors for C, N and O atoms from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965); *SHELX*76 (Sheldrick, 1976) and the full-matrix least-squares program of Gantzel, Sparks & Trueblood (1966) modified by T. N. Bhat used for the refinement of (I) and (II), respectively.*

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and hydrogen-bonding details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38457 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters* ($\times 10^4$) *for non-hydrogen atoms in* (I), *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq} (Å$^2\times 10^2$)
O(1)	5839 (3)	2962 (2)	756 (2)	399 (5)
O(2)	1623 (3)	−894 (2)	4266 (2)	422 (5)
N(1)	2512 (4)	4497 (3)	1657 (2)	331 (6)
N(2)	510 (3)	2713 (3)	3238 (2)	314 (6)
C(1)	7002 (6)	−269 (4)	1447 (3)	375 (9)
C(2)	5531 (4)	1370 (3)	1580 (2)	272 (6)
C(5)	5132 (5)	−2244 (4)	3984 (3)	381 (8)
C(4)	3405 (4)	−648 (3)	3593 (2)	273 (6)
C(3)	3789 (4)	1107 (3)	2555 (2)	242 (6)
C(6)	2293 (4)	2732 (3)	2479 (2)	245 (6)
C(7)	621 (5)	5753 (3)	1734 (2)	312 (7)
C(8)	−504 (5)	4633 (4)	2992 (2)	322 (7)

Table 2. *Final positional parameters* ($\times 10^4$) *for non-hydrogen atoms in* (II), *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq} (Å$^2\times 10^2$)
O(1)	9554 (3)	2066 (2)	−711 (2)	449 (6)
O(2)	12316 (2)	4134 (2)	2931 (2)	407 (5)
W(1)	12315 (3)	1902 (2)	4574 (2)	550 (7)
W(2)	14819 (3)	7110 (2)	3461 (2)	548 (6)
W(3)	7306 (4)	771 (3)	−3033 (2)	640 (8)
N(1)	8086 (3)	1578 (2)	2925 (2)	331 (6)
N(2)	8339 (3)	4162 (2)	3038 (2)	380 (6)
C(1)	6809 (4)	1665 (5)	−14 (3)	584 (10)
C(2)	8828 (3)	2202 (3)	209 (2)	315 (6)
C(5)	12825 (4)	3736 (5)	864 (3)	600 (10)
C(4)	11624 (3)	3586 (3)	1810 (2)	322 (6)
C(3)	9773 (3)	2870 (3)	1452 (2)	271 (6)
C(6)	8746 (3)	2869 (3)	2466 (2)	267 (6)
C(7)	8309 (4)	−56 (3)	2583 (3)	434 (8)
C(8)	7157 (4)	1977 (3)	3936 (3)	430 (8)
C(9)	7315 (4)	3776 (3)	4015 (2)	419 (8)
C(10)	8802 (5)	5796 (3)	2777 (3)	477 (9)

Table 3. *Bond lengths* (Å) *involving non-hydrogen atoms*

E.s.d.'s are given in parentheses.

	(I)	(II)
O(1)–C(2)	1·242 (3)	1·237 (3)
O(2)–C(4)	1·245 (3)	1·255 (3)
C(1)–C(2)	1·505 (4)	1·506 (4)
C(5)–C(4)	1·504 (4)	1·501 (4)
C(2)–C(3)	1·448 (3)	1·433 (3)
C(4)–C(3)	1·448 (3)	1·408 (4)
C(3)–C(6)	1·451 (3)	1·468 (3)
C(6)–N(1)	1·324 (3)	1·321 (3)
C(6)–N(2)	1·329 (3)	1·321 (3)
N(1)–C(7)	1·452 (3)	1·454 (3)
C(7)–C(8)	1·532 (3)	
C(8)–N(2)	1·455 (4)	
N(1)–C(8)		1·457 (4)
C(8)–C(9)		1·513 (4)
C(9)–N(2)		1·466 (4)
N(2)–C(10)		1·453 (3)

Table 4. *Bond angles* (°) *involving non-hydrogen atoms*

E.s.d.'s are of the order of 0·1 to 0·2°.

	(I)	(II)
O(1)–C(2)–C(1)	115·2	117·0
O(1)–C(2)–C(3)	121·6	124·4
C(1)–C(2)–C(3)	123·3	118·5
O(2)–C(4)–C(5)	115·0	118·0
O(2)–C(4)–C(3)	121·2	120·9
C(3)–C(4)–C(5)	123·8	121·1
C(2)–C(3)–C(4)	125·4	126·2
C(2)–C(3)–C(6)	117·2	118·5
C(4)–C(3)–C(6)	117·3	115·3
C(3)–C(6)–N(1)	125·6	124·9
C(3)–C(6)–N(2)	125·7	124·6
N(1)–C(6)–N(2)	108·7	110·5
C(6)–N(1)–C(7)	113·0	127·3
C(6)–N(1)–C(8)		111·7
C(7)–N(1)–C(8)		120·9
C(6)–N(2)–C(10)		126·6
C(6)–N(2)–C(9)		111·8
C(10)–N(2)–C(9)		121·6
C(6)–N(2)–C(8)	112·5	
N(1)–C(7)–C(8)	101·6	
N(1)–C(8)–C(9)		103·4
C(7)–C(8)–N(2)	102·1	
C(8)–C(9)–N(2)		102·6

Table 5. *Torsion angles* (°)

E.s.d.'s are of the order 0·2 to 0·4°.

	(I)	(II)
C(1)–C(2)–C(3)–C(4)	6·8	−172·8
C(1)–C(2)–C(3)–C(6)	−172·7	5·3
C(5)–C(4)–C(3)–C(2)	14·9	0·8
C(5)–C(4)–C(3)–C(6)	−165·6	−177·4
O(1)–C(2)–C(3)–C(4)	−176·3	5·4
O(1)–C(2)–C(3)–C(6)	4·2	−176·5
O(2)–C(4)–C(3)–C(2)	−168·1	−180·0
O(2)–C(4)–C(3)–C(6)	11·4	1·9
C(2)–C(3)–C(6)–N(1)	−5·8	73·4
C(2)–C(3)–C(6)–N(2)	175·7	−105·9
C(4)–C(3)–C(6)–N(1)	174·7	−108·2
C(4)–C(3)–C(6)–N(2)	−3·9	72·4
C(3)–C(6)–N(1)–C(7)	173·7	3·5
C(3)–C(6)–N(2)–C(8)	174·8	
C(3)–C(6)–N(1)–C(8)		179·2
C(3)–C(6)–N(2)–C(9)		−179·6
C(3)–C(6)–N(2)–C(10)		0·6
N(1)–C(6)–N(2)–C(10)		−178·9
N(2)–C(6)–N(1)–C(7)		−177·1
C(8)–C(9)–N(2)–C(10)		179·7
C(7)–N(1)–C(8)–C(9)		177·2

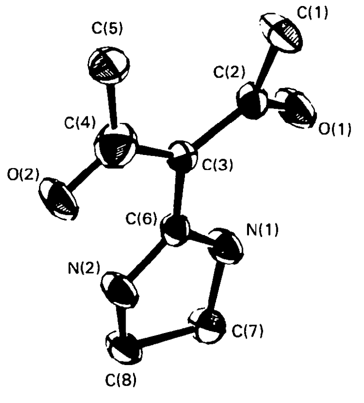

Fig. 1. Perspective view of a molecule of (I).

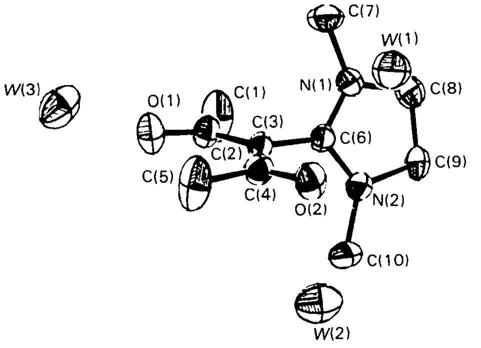

Fig. 2. Perspective view of a molecule of (II).

Discussion. Positional coordinates of the nonhydrogen atoms are recorded in Tables 1 and 2. Tables 3 and 4 give the bond lengths and angles, and torsion angles are given in Table 5. Figs. 1 and 2 give the numbering of the atoms for molecules (I) and (II). The combined effect of the powerful electron-donating imidazolidine ring and the electron-accepting acetyl groups in these structures is to produce a remarkable lengthening of the C=C bond. The C=C bond length is 1·451 (3) Å in (I) and 1·468 (3) Å in (II). These bond distances are indeed close to the C_{sp^2}—C_{sp^2} single-bond distance. The true C_{sp^2}—C_{sp^2} single-bond distance could be found in molecules where the π conjugation is negligible due to the twist about this bond. In dimethyl (dimethylaminoethylene)malonate (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973), one of the methoxycarbonyl groups is twisted by 68° from the molecular plane. The C_{sp^2}—C_{sp^2} single-bond distance in this case is 1·487 (5) Å. There would be severe steric interaction involving *N*-methyl groups at the donor end and the acetyl group at the acceptor end in (II). The molecule is twisted about the C=C bond to relieve this steric strain. The twist angle, defined as the angle between the plane through the atoms N(1), N(2) and C(6) and the plane through the atoms C(2), C(4) and C(3), is 72·9 (5)° in (II). The steric interactions in (I) would be expected to be less than in (II). However, the low twist angle of 4·9 (5)° in (I) is due to the strong intramolecular hydrogen bonding. Yet another consequence of the intramolecular hydrogen bonding is that the carbonyl groups are mutually *syn* in (I) whereas these groups are disposed in an *anti* conformation with respect to each other in (II). The small but significant increase in the C=C bond distance in (II) compared to that in (I) may be attributed to the difference in twist angles, which is 68°. Theoretical calculations have shown that the maximum twist of 90° leads to an increase in the C=C bond in ethylene of 0·03 Å (Dewar & Haselbach, 1970).

The conjugation has resulted in the shortening of the N—C(6), C(2)—C(3) and C(4)—C(3) bonds as expected. The N—C(6) distance, which takes an average value of 1·324 ± 0·004 Å in these structures, is much shorter than the value of 1·452 (2) Å reported for an $\ddot{N}$—C_{sp^2} bond (Ammon, Mazzocchi, Regan & Colicelli, 1979). On the acceptor side, the C(3)—C(2) and C(3)—C(4) bond lengths range from 1·408 (4) to 1·448 (3) Å, significantly shorter than the 1·487 (5) Å reported for a C_{sp^2}—C_{sp^2} single bond (Shmueli *et al.*, 1973). In (II), the two C=O bond lengths differ significantly: C(2)—O(1) is 1·237 (3) Å whereas C(4)—O(2) is 1·255 (3) Å. This difference could be attributed to the atom O(2) being hydrogen bonded to two water molecules whereas O(1) is bonded to one water molecule. Examples are known where the C=O bond is lengthened due to hydrogen bonding (Craven, Cusatis, Gartland & Vizzini, 1973; Ramani, Venkatesan & Marsh, 1978).

The imidazolidine ring is nonplanar in (I) with approximate C_2 symmetry. The twofold axis passes through the atom C(6) and bisects the C(7)—C(8) bond. This ring is planar in (II). The torsion angles within this ring about the bonds C(6)—N(1), N(1)—C(7), C(7)—C(8), C(8)—N(2) and N(2)—C(6) are −6·6 (3), 13·3 (3), −14·0 (2), 11·8 (3) and −3·9 (3)° in (I) whereas the corresponding angles in (II) are −1·4 (3), 1·2 (3), −0·6 (3), −0·2 (3) and 1·0 (3)°. The pyramidality at N(1) in (II) is appreciable, the deviation from the plane of the bonded atoms being 0·031 (2) Å, but there is no such feature at N(2). For (I), the pyramidality has not been calculated in view of the large inaccuracy associated with the H-atom positions.

Crystal packing and hydrogen bonding. The packing of the molecules of (I) in the unit cell is shown in Fig. 3. The crystal structure is stabilized by bifurcated hydrogen bonds of the N—H···O type. The proton associated with N(1) acts as a donor to O(1) within the molecule as well as to the symmetry-related O(1). Similarly, H(12) is shared by O(2) within the molecule as well as by the symmetry-related O(2). Spectral studies suggest the existence of intramolecular hydrogen bonding in solution also. The packing of molecules of (II) is shown in Fig. 4. There are three water molecules in the asymmetric unit and the crystal structure is stabilized

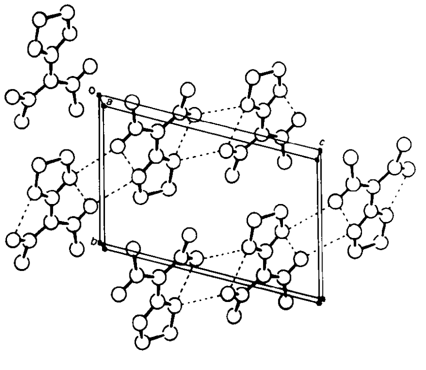

Fig. 3. Packing of the molecules viewed down **a** for (I).

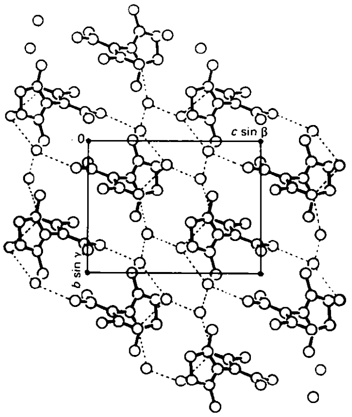

Fig. 4. Packing of the molecules viewed down **a** for (II).

by an extensive network of hydrogen bonding involving carbonyl O atoms and water molecules. Carbonyl atom O(1) is hydrogen bonded to one water molecule, whereas O(2) is hydrogen bonded to two water molecules.

Conformational-energy calculations. The twist about the C=C bond as observed in the crystalline state is as large as 72·9 (5)° in (II), whereas it is 4·9 (5)° in (I). As discussed earlier, the small twist angle in (I) could be partly due to less steric interaction in this case consequent upon the absence of methyl groups at the atoms N(1) and N(2). However, the predominant factor which would contribute towards the essentially planar conformation is the presence of intramolecular hydrogen bonds. It would be interesting, therefore, to ascertain the conformation of (I) in isolation. This would allow us to estimate the extent to which the absence of methyl groups would influence the conformation of the molecule (I).

The total energy (E_T) of the molecule was computed from the non-bonded interaction energy ($E_{\rm nb}$), the electrostatic interaction energy ($E_{\rm es}$), the torsional energy ($E_{\rm tor}$) and the hydrogen-bond energy ($E_{\rm hb}$). $E_{\rm nb}$ was computed using Kitaigorodsky's (1961) function. For the calculation of the electrostatic energy, the total charges ($\sigma+\pi$) obtained from the CNDO method were used. For computing the hydrogen-bond energy, the function proposed by Mcguire, Momany & Scheraga (1972) was used.

Since the barrier to rotation about the C=C bond was not available, an approximate barrier energy was assumed based upon the energies of similar molecules. For (I), excluding the contribution of intramolecular hydrogen bonds, the barrier energy was assumed to be 92·0 kJ mol^{-1} based upon the barriers of the following molecules: 3-methyl-2-(dimethoxycarbonylmethylene)-thiazolidine (39 kJ mol^{-1}), 2-(methoxycarbonylmethylene)thiazolidine (93·2 kJ mol^{-1}; Shvo & Belsky, 1969) and molecule (II) discussed in this paper (25 kJ mol^{-1}; Wennerbeck & Sandström, 1972).

In the first set of calculations for (I), the intramolecular hydrogen bonding was neglected and the N···O interaction was taken purely as a van der Waals interaction. The total energy was computed using the geometry of the molecule as found in the crystal structure, but varying only the rotation about the C=C bond. The total energy was computed for the rotation varying from −180 to 180° in 2° intervals. The minimum energy is found at the rotation angle of 22° and the energy difference between this state and the planar state is 13 kJ mol^{-1}. This suggests that on steric grounds alone this molecule should also be twisted to the extent of 22° in the free state. In the second set of potential-energy calculations, the two N—H···O intramolecular hydrogen bonds present were taken into account. The function proposed by Mcguire, Momany & Scheraga (1972) for calculating the hydrogen bond is a function of the distance between the H atom and the acceptor atom only, whereas it is well known that the hydrogen-bond energy depends upon the angles *D*—H···*A* and H—*D*···*A* also. This function was chosen owing to its simplicity. The minimum is at 8° which is close to the observed conformation of 5° in the crystal lattice. The conformation of the imidazolidine ring was not allowed to vary in the calculations.

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Structure of 2,2-Bis(1,1,1,3,3,3-hexafluoro-2-propyloxy)-2-phenyl-4,4,5,5-tetrakis(trifluoromethyl)-1,3,2λ^5-dioxaphospholane, $C_{18}H_7F_{24}O_4P$

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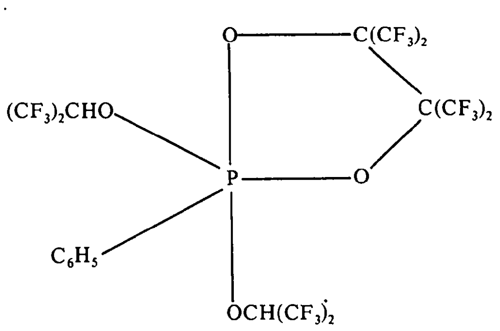
Abstract. $M_r = 774{\cdot}2$, triclinic, $P\bar{1}$, $a = 9{\cdot}828\,(5)$, $b = 10{\cdot}489\,(3)$, $c = 14{\cdot}530\,(3)$ Å, $\alpha = 74{\cdot}33\,(2)$, $\beta = 81{\cdot}36\,(2)$, $\gamma = 64{\cdot}54\,(3)°$, $U = 1301{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}98$ g cm^{-3}, $F(000) = 756$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}33$ mm^{-1}. The structure was solved by direct methods and refined to an R value of 0·049 for 3468 observed reflections. The geometry around the pentacoordinated P deviates 27·2% along the Berry coordinate from an ideal trigonal-bipyramidal arrangement. The O atoms of the five-membered ring span apical–equatorial sites on the P atom. The ring adopts an envelope conformation with unequal bond lengths and angles.

Introduction. The X-ray structures of a number of phosphoranes containing P bound to O in a five-membered hetero-ring have previously been determined (Holmes, 1980), mainly to establish the factors affecting the geometry around the P atom. Phosphoranes possessing a monocyclic five-membered ring and more electronegative ligands generally exhibit trigonal-bipyramidal geometry around the P atom (Holmes, 1975; Trippett, 1976). On the other hand, polycyclic/spirophosphoranes often adopt square- or rectangular-pyramidal arrangements, due to the steric and electronic demands of the ligands and the conformational requirements of the five-membered rings coordinated to P (Brown & Holmes 1977*a*,*b*; Wunderlich, 1978). In most of these compounds the skeletal geometry around P departs from the idealized trigonal-bipyramidal or square-pyramidal forms, and the distortions can be expressed in terms of a percentage deviation along the Berry (1960) coordinate.

The structure determination of compound (I) was undertaken in order to establish the stereochemistry of pentacoordination and the steric requirements of the ligands and the dioxaphospholane ring.



(I)

Experimental. A crystal of dimensions 0·55 × 0·65 × 1·00 mm was sealed in a Lindemann glass capillary; unit-cell dimensions and their standard deviations determined from a least-squares refinement of the angular settings of 25 accurately centred reflections ($\theta < 15°$); Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, take-off angle 5°, ω–2θ scan technique; intensities of all independent reflections to $\theta \leq 25°$ measured, with background counts being taken on both sides of each peak; range of hkl measured: $h = 0 \rightarrow 11$, $k = -12 \rightarrow 12$ and $l = -17 \rightarrow 17$; intensities of three standard reflections measured every 8000 showed no significant variation during data collection; 3468 out of 4717 reflections considered observed [$I > 3\sigma(I)$]; scattering factors for non-hydrogen atoms from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion terms for P from Cromer & Liberman (1970).

All calculations were carried out on the University of Petroleum and Minerals IBM 3033 computer, using *SHELX* (Sheldrick, 1976). An E map revealed the positions of all the non-hydrogen atoms of the molecule. Full-matrix least-squares refinement with isotropic temperature factors reduced R to 0·179. Anisotropic

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