Eight-membered Heterocycles Containing Two Phosphorus Atoms. *X*-Ray Diffraction† and Nuclear Magnetic Resonance Studies of 2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane 2,6-Disulphides and 2,6-Diselenides

Carla Piccinni-Leopardi * and Jacques Reisse
Laboratoire de Chimie Organique E.P. (C.P. 165), Université Libre de Bruxelles, 50 Av. F. D. Roosevelt, B-1050 Bruxelles, Belgium
Gabriel Germain, Jean Paul Declercq, and Maurice Van Meerssche
Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, 1 Pl. L. Pasteur, B-1348 Louvain-la-Neuve, Belgium
Klaus Jurkschat, Clemens Mügge, and Adolf Zschunke
Sektion Chemie der Martin-Luther-Universität, 4020 Halle/S. Weinbergweg 16, German Democratic Republic
Jean-Pierre Dutasta
L.E.D.S.S. II, Université Scientifique et Médicale de Grenoble, B.P.68, 38402 Saint Martin d'Hères Cedex, France
Jean-Bernard Robert
C.N.R.S.–S.N.C.I., Avenue des Martyrs, 166X, 38048 Grenoble Cedex, France

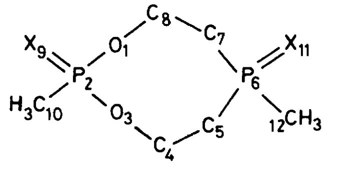
trans- and *cis*-2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane 2,6-disulphides (**1**) and (**2**), and *trans*- and *cis*-2,6-diselenides (**3**) and (**4**), have been investigated by means of ^{1}H (2D, *J*-resolved), ^{13}C, and ^{31}P n.m.r. spectroscopy and *X*-ray diffraction. In the solid state the *cis*-isomers adopt a crown conformation and the *trans*-isomers a boat-chair conformation. The orientations of P–X (X = S or Se) and P–Me bonds are quasi-axial and quasi-equatorial, respectively. Room-temperature n.m.r. data can be interpreted on the basis of the *X*-ray data. A fast enantiomerization between two boat-chair conformations of opposite chirality characterizes the *trans*-isomers, whereas the *cis*-isomers exist mainly in a crown conformation similar to that observed in the crystal.

We have investigated the title compounds (**1**)—(**4**) by means of n.m.r. spectroscopy and *X*-ray diffraction. The molecular and crystal structure of (**1**) has been previously described,[1] but is included in the present study for comparison.

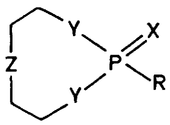
Eight-membered phosphorus heterocycles with heteroatoms located in positions 1, 2, 3, and 6 have been extensively studied in recent years;[2–8] some of them provide attractive models in co-ordination chemistry.[9] Solid-state molecular structures of compounds (**5**)—(**8**)[2,5,8,10] have been determined. The preferred conformation in the solid state depends on ring shape and substituent orientations.

Spontaneous dimerization in solution has been observed for five-, six-, seven-, and eight-membered-ring phosphonites. In the case of 1,3-dioxa-2-phosphacyclo-octane derivatives, this process leads to the formation of sixteen-membered-ring compounds.[11]

2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclo-octanes and their dimeric forms have been described earlier.[12] These molecules possess two kinds of phosphorus atom corresponding to the phosphane and phosphonite moieties, and are of potential interest in co-ordination chemistry. Moreover, the existence of two different phosphorus atoms might be expected to give rise to conformational effects associated with transannular interactions.



	trans	cis
X = S	(**1**)	(**2**)
X = Se	(**3**)	(**4**)



	R	X	Y	Z	Ref.
(**5**)	Me	S	O	O	8
(**6**)	Me	S	O	NMe	10
(**7**)	Me	O	O	NPh	2
(**8**)	Bu^t	S	S	S	5

Results and Discussion

2,6-Dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane 2,6-disulphide and 2,6-diselenide exist as *cis*- and *trans*-diastereoisomers depending on the relative orientation of the *P*-substituents. The *trans* (**1**) and *cis* (**2**) P–S derivatives as well as the *trans* (**3**) and *cis* (**4**) P–Se derivatives were isolated and characterized by the usual methods.[12] Here, we discuss the structural study only.

X-Ray Crystal Structures.—Table 1 contains physical and crystallographic data together with the experimental conditions for data collection and refinement procedure. The fractional

---

† *Supplementary data available* (SUP 56384, 4 pp.): H-co-ordinates and thermal parameters for compounds (**2**)—(**4**). For details of Supplementary Publications see Instructions for Authors, Issue No. 1, 1986. Structure factor tables are available from the editorial office.

Table 1. Physical and crystallographic data, data collection, and refinement conditions for compound (**1**)—(**4**)

Compound	*trans*-PS (**1**)[1]	*cis*-PS (**2**)	*trans*-PSe (**3**)	*cis*-PSe (**4**)
Formula unit	$C_6H_{14}O_2P_2S_2$	$C_6H_{14}O_2P_2S_2$	$C_6H_{14}O_2P_2Se_2$	$C_6H_{14}O_2P_2Se_2$
M	244.24	244.24	338.05	338.05
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Unit cell a/Å	9.954(2)	7.140(2)	10.109(1)	6.844(3)
b	9.632(1)	8.566(2)	9.819(1)	10.726(5)
c	12.165(1)	10.984(3)	12.456(1)	8.364(5)
β/°	102.31(1)	121.32(2)	104.51(1)	97.76(4)
V/Å^3	1 139.5(3)	573.9(3)	1 197.0(2)	608.4(5)
Space group	$P2_1/n$	$P2_1/m$	$P2_1/n$	$P2_1$
D_x/g cm^{-3}	1.42	1.41	1.88	1.85
Z	4	2	4	2
Instrument	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$	Siemens AED
Radiation	Mo-K_α	Cu-K_α	Mo-K_α	Cu-K_α
λ/Å	0.710 69	1.541 78	0.710 69	1.541 78
Monochromator	Graphite	Graphite	Graphite	Graphite
$2\theta_{max.}$/°	50	114	50	140
Independent reflections				
Measured	2 012	830	2 104	1 311
Observed [$I > 2.5\sigma(I)$]	1 770	800	1 726	1 243
Resolution	MULTAN 78[a]	MULTAN 80[b]	MULTAN 78[a]	MULTAN 80[b]
Refinement	SHELX 76[c]	SHELX 76[c]	SHELX 76[c]	SHELX 76[c]
R final	0.037	0.079	0.064	0.068

[a] P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN 78, a System of Computer Programmes for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data,' Universities of York and Louvain, 1978. [b] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN 80, A System of Computer Programmes for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data,' Universities of York (England) and Louvain-la-Neuve (Belgium), 1980. [c] G. M. Sheldrick, 'SHELX 76, Program for Crystal Structure Determination,' University of Cambridge, England, 1976.

Table 2. Fractional atomic co-ordinates (× 10^4) and B_{eq} values for the non-hydrogen atoms of compounds (**1**)—(**4**); standard deviations in parentheses

	trans-PS (**1**)[1]				*cis*-PS (**2**)			
	x/a	y/b	z/c	B_{eq}/Å^2	x/a	y/b	z/c	B_{eq}/Å^2
O(1)	8 793(2)	3 798(2)	5 147(2)	3.29				
P(2)	7 691(1)	3 931(1)	3 991(1)	3.06	3 290(2)	2 500(0)	37(1)	1.71
O(3)	6 295(2)	2 474(2)	3 841(1)	3.41	2 240(3)	3 958(3)	337(2)	2.70
C(4)	5 830(2)	2 140(3)	4 410(2)	3.47	3 193(5)	4 755(4)	1 670(3)	2.32
C(5)	6 277(2)	2 116(2)	5 684(2)	3.05	2 206(5)	4 247(4)	2 523(3)	2.20
P(6)	7 680(1)	943(1)	6 277(1)	2.90	3 295(2)	2 500(0)	3 599(1)	1.86
C(7)	9 310(3)	1 876(3)	6 438(2)	3.96				
C(8)	9 620(3)	2 539(3)	5 392(3)	3.98				
S(9)	6 564(1)	5 541(1)	4 018(1)	4.53	6 427(2)	2 500(0)	1 013(2)	3.41
C(10)	8 611(4)	3 863(3)	2 875(3)	5.32	1 835(10)	2 500(0)	−1 855(6)	3.38
S(11)	7 612(1)	−806(1)	5 453(1)	4.30	6 500(2)	2 500(0)	4 738(1)	2.79
C(12)	7 536(4)	746(3)	7 719(3)	4.63	2 059(12)	2 500(0)	4 650(7)	4.10

	trans-PSe (**3**)				*cis*-PSe (**4**)			
	x/a	y/b	z/c	B_{eq}/Å^2	x/a	y/b	z/c	B_{eq}/Å^2
O(1)	3 851(4)	8 734(4)	5 263(4)	3.31	6 737(13)	1 513(0)	3 382(11)	4.61
P(2)	2 784(2)	8 876(2)	4 086(1)	3.09	5 294(3)	2 620(10)	2 987(3)	3.37
O(3)	1 989(5)	7 469(5)	3 908(4)	3.34	4 197(12)	2 879(16)	4 506(10)	5.13
C(4)	874(6)	7 170(7)	4 416(6)	3.62	5 017(16)	3 544(16)	5 933(14)	3.83
C(5)	1 295(6)	7 124(7)	5 674(5)	3.19	5 671(14)	2 667(17)	7 309(13)	4.00
P(6)	2 661(2)	5 948(2)	6 298(1)	2.88	8 238(3)	2 134(10)	7 558(3)	2.63
C(7)	4 279(7)	6 854(7)	6 539(6)	4.09	8 658(18)	1 072(15)	5 982(14)	4.19
C(8)	4 631(6)	7 464(7)	5 546(6)	4.02	8 677(17)	1 594(16)	4 302(14)	4.03
Se(9)	1 622(1)	10 616(1)	4 051(1)	4.33	6 595(2)	4 189(10)	2 137(2)	4.60
C(10)	3 746(11)	8 756(10)	3 057(8)	5.93	3 303(19)	1 941(22)	1 617(15)	5.96
Se(11)	2 594(1)	4 107(1)	5 420(1)	4.07	10 208(2)	3 643(10)	7 734(2)	4.20
C(12)	2 481(9)	5 725(8)	7 684(6)	4.83	8 472(18)	1 174(17)	9 308(15)	4.49

atomic co-ordinates of the non-hydrogen atoms are listed in Table 2. Bond lengths and angles are given in Table 3. Table 4 contains the torsion angles.

The crystallographic data of compounds (**1**) and (**3**) show an isostructural relationship, *i.e.* the same space group, the same Z value, and similar unit-cell dimensions. Moreover the two products exhibit similar crystal packing. Different behaviour is observed for (**2**) and (**4**): they do not belong to the same space

Table 3. Molecular dimensions for compounds (**1**)—(**4**); standard deviations in parentheses

	trans-PS (**1**)[1]	*cis*-PS (**2**)	*trans*-PSe (**3**)	*cis*-PSe (**4**)
Bond lengths (Å)				
O(1)–P(2)	1.594(2)		1.594(4)	1.551(10)
O(1)–C(8)	1.460(3)		1.471(8)	1.445(14)
P(2)–O(3)	1.589(2)	1.577(2)	1.585(5)	1.585(9)
P(2)–X(9)	1.918(1)	1.916(1)	2.068(2)	2.074(3)
P(2)–C(10)	1.793(3)	1.776(6)	1.796(7)	1.810(13)
O(3)–C(4)	1.446(3)	1.427(4)	1.454(8)	1.438(15)
C(4)–C(5)	1.519(3)	1.500(4)	1.518(9)	1.507(17)
C(5)–P(6)	1.821(2)	1.813(3)	1.819(6)	1.832(10)
P(6)–C(7)	1.828(2)		1.820(7)	1.795(11)
P(6)–X(11)	1.954(1)	1.956(2)	2.105(2)	2.099(2)
P(6)–C(12)	1.800(3)	1.781(5)	1.794(7)	1.779(13)
C(7)–C(8)	1.513(4)		1.495(10)	1.515(17)
Bond angles (°)				
P(2)–O(1)–C(8)	119.9(2)		119.5(4)	125.5(9)
O(1)–P(2)–O(3)	104.7(1)	104.7(2)	104.8(2)	108.7(6)
O(1)–P(2)–X(9)	110.2(1)		109.9(2)	113.8(4)
O(1)–P(2)–C(10)	107.4(1)		106.8(4)	103.3(7)
O(3)–P(2)–X(9)	116.6(1)	115.3(1)	116.8(2)	113.8(5)
O(3)–P(2)–C(10)	101.0(1)	101.1(1)	100.9(4)	100.4(6)
X(9)–P(2)–C(10)	115.9(1)	117.2(2)	116.5(4)	115.5(5)
P(2)–O(3)–C(4)	122.3(2)	124.7(2)	122.4(4)	125.3(7)
O(3)–C(4)–C(5)	113.9(2)	112.0(2)	114.1(5)	111.5(11)
C(4)–C(5)–P(6)	116.5(2)	117.7(2)	116.5(4)	117.6(7)
C(5)–P(6)–C(7)	109.0(1)	111.3(2)	108.4(3)	111.1(5)
C(5)–P(6)–X(11)	113.1(1)	112.3(1)	113.7(2)	111.4(4)
C(5)–P(6)–C(12)	103.8(1)	103.5(2)	103.8(3)	104.6(6)
C(7)–P(6)–X(11)	114.3(1)		114.6(3)	112.1(5)
C(7)–P(6)–C(12)	101.6(1)		101.8(4)	103.4(7)
X(11)–P(6)–C(12)	114.1(1)	113.3(3)	113.4(3)	113.8(4)
P(6)–C(7)–C(8)	116.9(2)		116.7(5)	118.0(8)
O(1)–C(8)–C(7)	108.4(2)		108.3(5)	110.4(10)

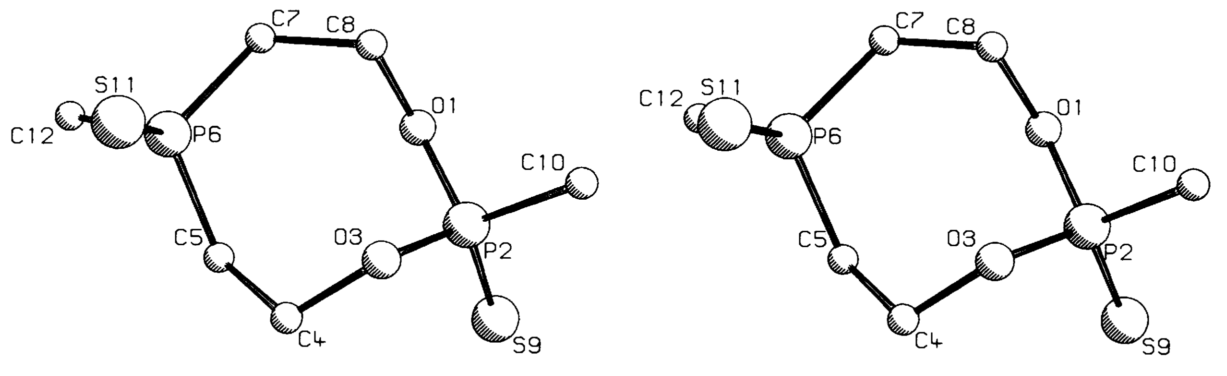
Table 4. Torsion angles (°) in compounds (**1**)—(**4**), [$\langle\sigma\rangle < 0.5°$ for (**1**) and (**2**), $\leqslant 1°$ for (**3**), and $\leqslant 2°$ for (**4**)]

Compound	*trans*-PS (**1**)[1]	*cis*-PS (**2**)	*trans*-PSe (**3**)	*cis*-PSe (**4**)
C(8)–O(1)–P(2)–O(3)	44.2		44	−81
C(8)–O(1)–P(2)–X(9)	170.3		170	47
C(8)–O(1)–P(2)–C(10)	−62.6		−63	173
P(2)–O(1)–C(8)–C(7)	−118.5		−119	105
O(1)–P(2)–O(3)–C(4)	81.0	93.2	80	79
X(9)–P(2)–O(3)–C(4)	−41.0	−34.6	−41	−49
C(10)–P(2)–O(3)–C(4)	−167.6	−162.1	−169	−173
P(2)–O(3)–C(4)–C(5)	−63.2	−98.8	−64	−103
O(3)–C(4)–C(5)–P(6)	−57.0	84.0	−56	92
C(4)–C(5)–P(6)–C(7)	91.1	−79.2	92	−71
C(4)–C(5)–P(6)–X(11)	−37.2	47.7	−37	55
C(4)–C(5)–P(6)–C(12)	−161.3	170.3	−161	178
C(5)–P(6)–C(7)–C(8)	−56.4		−59	71
X(11)–P(6)–C(7)–C(8)	71.1		69	−54
C(12)–P(6)–C(7)–C(8)	−165.6		−168	−177
P(6)–C(7)–C(8)–O(1)	75.9		78	−93

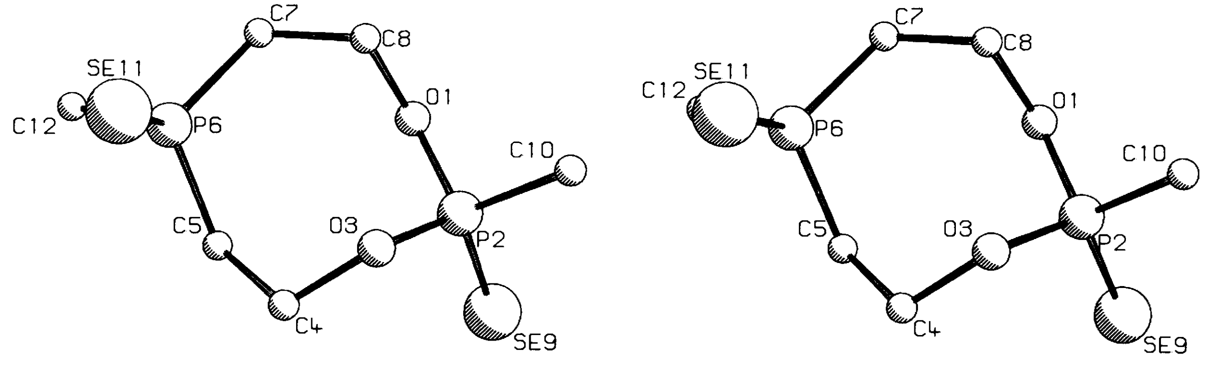
group, although the system is the same (monoclinic). The asymmetric unit is half a molecule in the case of (**2**), and one molecule in the cases of (**1**), (**3**), and (**4**).

The shape of a cyclic molecule is easily described in terms of the torsion angles around the intracyclic bonds. In the case of the eight-membered-ring molecules under study, the stereochemical nomenclature used is that adopted for the cyclo-octane itself.[13] In the case of the *trans*-isomers (**1**) and (**3**), the torsion angles (Table 4) and the bond lengths and angles (Table 3) lead to the conclusion that the two molecules adopt a very similar asymmetric boat-chair (BC) conformation with the pseudo-mirror plane passing through O(3) and C(7) (see Figure 1). This conformation implies a corner position for the O–P–O moiety [in (**1**) and (**3**)], which satisfies not only the steric requirements of the P(2) substituents, but also the approximate *gauche*(±), *gauche*(±) local conformation around the P–O bonds.[14] This isoclinal arrangement is observed in unstrained molecules containing the C–O–X–O–C fragment (X = C or P),[15] and also in *cis*-2,5,5,8,11,11-hexamethyl-1,3,7,9-tetraoxa-2,8-diphosphacyclododecane 2,8-disulphide.[16] Regarding the ring conformation of (**1**) and (**3**), we note the difference between the O(1)–C(8)–C(7) and O(3)–C(4)–C(5) angles [5.5° and 5.8° for (**1**) and (**3**), respectively]. Similarly, the O(1)–P(2)–X(9) and O(3)–P(2)–X(9) (X = S or Se) angles differ significantly [6.4° and 6.9° for (**1**) and (**3**), respectively] and the same comment applies to the O(1)–P(2)–C(10) and O(3)–P(2)–C(10) angles. These differences are reflected both in the intracyclic torsion angles [for example O(1)–P(2)–O(3)–C(4) is +81.0°, while C(8)–O(1)–P(2)–O(3) is +44.2° in (**1**)] and in the torsion angles involving the P(2) substituents. The relationship between the torsion and the bond angles has already been discussed relative to other phosphorus-containing compounds.[17] The methyl substituent on P(2) can be described as pseudo-equatorial while the X atom (X = S or Se) is pseudo-axial. A similar situation is observed at P(6). It seems that the preference of the methyl group for the equatorial position in tetra-co-ordinate phosphorus cyclic molecules is normal, since it has been observed not only in other eight-membered-ring molecules,[2,8–10] but also for 2,5,5-trimethyl-1,3,2-dioxaphosphorinane 2-sulphide.[18] In terms of a traditional but certainly oversimplified description, it seems that the steric requirement of sulphur or selenium is less than that of a methyl group. This fact is probably related to the bond length difference between P–C and P–X on the one hand, and to the higher polarizability of S (or Se) with respect to CH$_3$ on the other.

cis-Isomers (**2**) and (**4**) adopt a crown or a chair-chair (CC) conformation (see Figure 2). Structure (**2**) possesses a crystallographic symmetry plane passing through P(2), P(6), S(9), C(10), S(11), and C(12), while (**4**) is slightly distorted and does not possess a true C_s symmetry. The local intracyclic conformations around the P–O bonds are approximately (±)*gauche*, (∓)*gauche*. This structural unit is characteristic both of the chair conformation of the six-membered 1,3,2-dioxaphosphorinane,[19] and of the conformation of the twelve-membered ring in *trans*-2,5,5,8,11,11-hexamethyl-1,3,7,9,-tetraoxa-2,8-diphosphacyclododecane 2,8-disulphide,[20] and the CC conformations of 1,3-dioxa-2-phosphacyclo-octanes.[2,8–10] It is interesting that the O(1)–P(2)–O(3) angles in (**2**) and (**4**) are significantly different (104.7° and 108.7°, respectively) while in the *trans* series these angles are identical. More generally, the geometrical differences between the two *cis*-isomers are more important than those observed between the two *trans*-isomers. This fact is difficult to interpret because it is not clear whether it is related to intramolecular or to intermolecular factors. As in the case of the *trans*-isomers, the methyl groups on P(2) and P(6) are equatorial. This observation substantiates our previous comments concerning the relative steric requirements of the CH$_3$ group on the one hand and the S or Se atoms on the other. The equatorial orientation of the CH$_3$ group can be regarded as the driving force which determines the preferred conformation of the ring (crown or CC for the *cis*-isomers; BC for the *trans*). In the case of the *cis*-isomers, a BC conformation similar to that observed for the *trans* would imply the axial orientation of one CH$_3$ group, or strong steric interactions in the other conformations of the BC series.



(1)



(3)

Figure 1. Stereoscopic views of the *trans*-isomers of 2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane 2,6-disulphide (**1**) and 2,6-diselenide (**3**)

It is difficult to predict what the ring conformation would be if it were independent of substituent effects: the BC conformation is observed for 1,3-dioxocane and 1,3,6-trioxocane[21] whereas the 1,3,6-trithia-2-phosphacyclo-octane derivative (**8**) adopts a twist-boat-chair conformation with an axial extracyclic P–S bond.[5]

Finally we point out that neither the *cis*- nor the *trans*-isomers exhibit transannular interactions (P . . . P, P . . . S, or P . . . Se). This observation is in contrast to observations for compounds (**5**) and (**6**), for which P . . . O and P . . . N distances[8,10] are shorter than the sum of the van der Waals radii.[22] As expected P–X (X = S or Se) bonds are shorter for P(2) than for P(6). This observation is discussed in a previous paper.[1]

N.m.r. Results.—Table 5 contains the δ(^{13}C) and δ(^{31}P) values[23] together with the absolute values of the coupling constants $J_{P,C}$ and $J_{P,Se}$.

The ^{1}H n.m.r. spectra of (**1**)—(**4**), recorded at room temperature, were analysed by means of a 2D *J*-resolved technique.[24] The δ and *J* values are given in Table 6. The a,b nomenclature used in Table 6 is introduced to discriminate between diastereotopic H atoms. In the following discussion we will also use an A,B nomenclature to label the two diastereotopic H atoms located on the same carbon atom in the solid-state conformation.

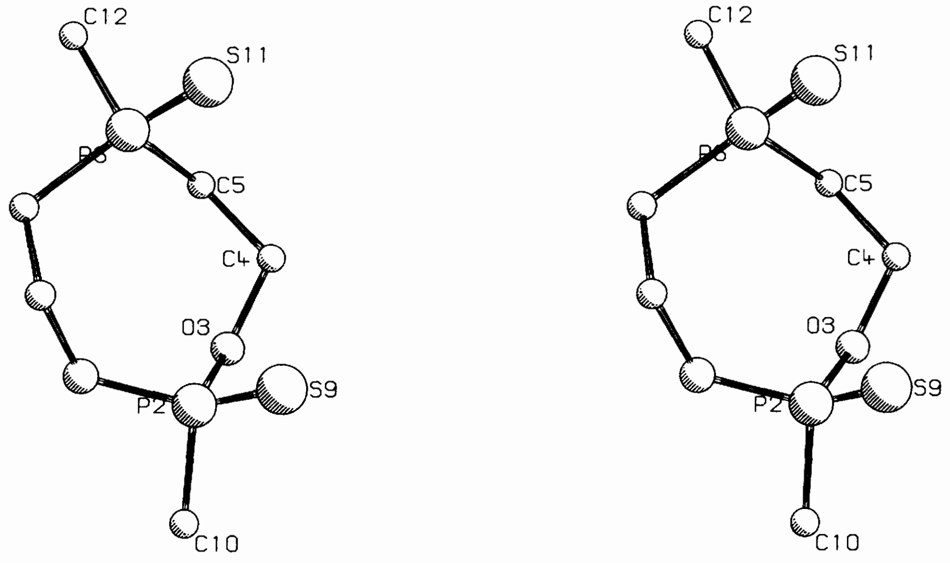
For the molecules under study, the number of signals characterized by different chemical shifts in the ^{13}C-decoupled n.m.r. spectra is compatible with C_s symmetry. Of course, the number of signals observed for each derivative is also compatible with fast equilibration between asymmetric conformations leading to an average C_s symmetry.

Table 5. N.m.r. parameters (^{31}P and ^{13}C) for compounds (**1**)—(**4**)

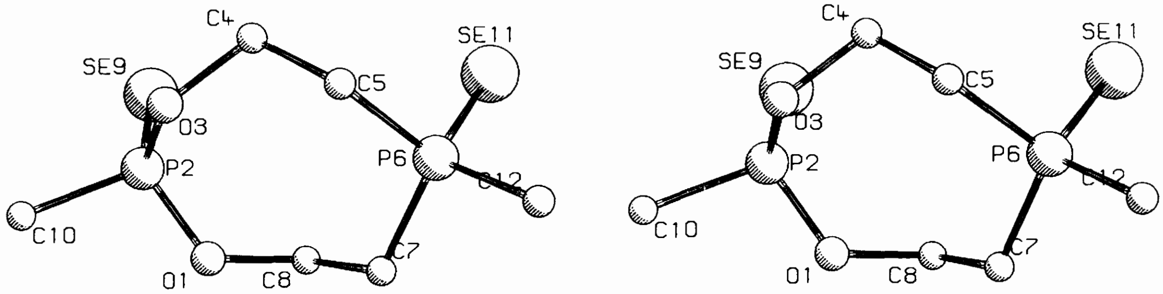
		trans-PS (**1**)^{a,c}	*cis*-PS (**2**)^a	*trans*-PSe (**3**)^a	*cis*-PSe (**4**)^b
δ_P (p.p.m.)	2-P	93.05	93.61	95.46	97.30
	6-P	36.02	35.93	21.66	21.30
$J_{P,Se}$/Hz	$J_{2,9}$			927.3	890.6
	$J_{6,11}$			734.1	737.6
δ_C (p.p.m.)	4,8-C	60.65	59.26	61.88	60.91
	5,7-C	35.30	36.03	34.97	35.93
	10-C	19.63	20.54	22.80	23.75
	12-C	21.56	20.75	21.64	20.78
$J_{P,C}$/Hz	$J_{2,4-8}$	8.9	7.6	9.4	7.4
	$J_{2,5-7}$	2.5	1.1	2.2	0.5
	$J_{6,4-8}$	6.7	5.6	6.7	5.5
	$J_{6,5-7}$	50.5	49.6	43.3	42.3
	$J_{6,12}$	57.7	58.0	66.0	51.9
	$J_{2,10}$	109.9	119.8	108.8	105.4

^{a} In C_6D_6. ^{b} In $CDCl_3$. ^{c} $^4J_{P,P}$ = 1.1 Hz.

Coupling constants may shed considerable light on stereochemical problems, and ^3J values play a unique role in this context. It is important to remember that the Karplus-type dependence of ^3J on torsion angles is observed not only for H–C–C–H[25] but also for P–O–C–H[26] and P–C–C–H.[27]



(2)



(4)

Figure 2. Stereoscopic view of the *cis*-isomers of 2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane 2,6-disulphide (**2**) and 2,6-diselenide (**4**)

The *cis*-selenide (**4**) is very similar to the sulphide (**2**): the solid-state conformations are nearly identical and the coupling constant values in solution are almost the same. The angular values determined by *X*-ray diffraction and involving H-atoms are only approximately known since the H atoms are either badly localized on the Fourier difference map [for (**2**)] or are not localized at all [for (**4**)]; under the latter circumstances the H atoms were positioned on the basis of an ideal geometry. The torsion angle values used here are the values calculated for (**4**), but these values are also valid for (**2**) if we take an uncertainty of the order of $\pm 5°$ into account.

The various torsion angles of interest for the conformational study of the *cis*-derivatives are indicated in Table 7. They come from the *X*-ray diffraction study of (**4**). Knowledge of the two H(4)–C(4)–C(5)–P(6) torsion angles allows estimation of the corresponding $^3J_{\mathrm{P,H}}$ values on the basis of the published Karplus-type curve.[27] The nature of this curve is such that an important error affects the $^3J_{\mathrm{P,H}}$ values (an error which we put at ± 5 Hz). The predicted $^3J_{\mathrm{P,H}}$ values, *i.e.* 15 ± 5 Hz and 32 ± 5 Hz, are in qualitative agreement with the experimental values [20.4 Hz and 29.8 Hz for (**4**); 20.1 Hz and 28.9 Hz for (**2**)]. This means that H(4a) ≡ H(4A) and H(4b) ≡ H(4B) if the conformation present in the solution is the same as that in the crystal.

The Karplus-type dependence is not as well known in the case of J_{POCH} as in the case of J_{PCCH}.[26–28] Nevertheless, it is possible to predict that $^3J_{\mathrm{P(2),H(4A)}} < {}^3J_{\mathrm{P(2),H(4B)}}$. In the case of (**4**), $^3J_{\mathrm{P(2),H(4a)}}$ is 14.5 Hz and $^3J_{\mathrm{P(2),H(4b)}}$ is 21.4 Hz, and this agrees with the conclusion arrived at previously.

The $^3J_{\mathrm{H,H}}$ values are very sensitive to conformational changes and we have a better knowledge of the shape of the Karplus curve in this case. Two torsion angles involving H(4) and H(5) are nearly equal to 90° (see Figure 3). In Table 6, it is easy to see that no $^3J_{\mathrm{H,H}}$ values are close to zero, and this observation forces us to conclude that the conformational situation in the solution is not identical to that observed in the crystal. A slight distortion of the molecular skeleton must be taken into account, at least. Qualitatively, the $^3J_{\mathrm{H,H}}$ coupling pattern is consistent with H(5A) ≡ H(5b) and H(5B) ≡ H(5a). The previously performed assignment of H(4) [H(4A) ≡ H(4a) and H(4B) ≡ H(4b)] leads to the conclusion that $J_{4a,5a}$ corresponds to a torsion angle of approximately 150°, while $J_{4b,5b}$ corresponds to an angle of approximately 25°. The experimental values (9.1 and 7.2 Hz) fit this description well.

In the case of the *trans*-sulphide (**1**) and the *trans*-selenide (**3**), two enantiomeric conformations are present in the solid state. Any attempt to interpret the n.m.r. spectra of these derivatives in the solution requires that account should be taken of a fast enantiomerization process or of the presence of a symmetrical conformation different from the one found in the crystal.

However, the spectra of (**1**) and (**3**) can be interpreted as spectra corresponding to a fast exchange between the two

Table 6. ^{1}H N.m.r. chemical shifts (δ) and coupling constants (J) for compounds (**1**)—(**4**), as determined from 2D J-resolved spectra at 200 MHz†

		trans-PS (**1**)		*cis*-PS (**2**)		*trans*-PSe (**3**)		*cis*-PSe (**4**)	
Compound		*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
δ_H (p.p.m.)	H(4a)	4.25	4.51	5.18	5.15	4.26	4.57	5.15	5.18
	H(4b)	3.93	4.43	3.39	4.05	3.89	4.43	3.36	4.06
	H(5a)	2.03	2.70	1.48	2.43	2.11	2.92	1.69	2.64
	H(5b)	1.16	2.01	1.37	2.22	1.09	2.08	1.46	2.31
	H(10)	1.35	1.85	1.42	1.81	1.46	2.04	1.57	1.99
	H(12)	0.96	1.75	0.91	1.74	1.05	1.96	1.08	1.95
$J_{H,H}$/Hz	$J_{4a,4b}$	−11.5	−11.4	−12.3	−12.4	−11.5	−11.6	−12.6	−12.5
	$J_{4a,5a}$	11.7	11.8	9.1	9.1	11.8	11.7	9.1	8.9
	$J_{4a,5b}$	2.0	2.0	2.0	2.1	2.0	2.0	2.1	2.1
	$J_{4b,5a}$	4.0	4.1	2.3	2.2	3.8	3.9	2.1	2.2
	$J_{4b,5b}$	3.7	3.6	7.1	7.0	3.8	3.7	7.2	7.2
	$J_{5a,5b}$	−15.1	−15.3	−15.4	−15.4	−15.1	−15.1	−15.3	−15.1
$J_{P,H}$/Hz	$J_{2,4a}$	22.3	22.4	14.4	14.5	23.3	23.3	14.5	14.8
	$J_{2,4b}$	9.8	9.9	20.9	21.1	10.1	9.9	21.4	21.6
	$J_{2,5a}$	0.5	0.5	0.4	0.4	0.5	0.5	0.5	0.5
	$J_{2,5b}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	$J_{6,4a}$	13.4	13.2	20.1	20.2	13.6	13.6	20.4	20.6
	$J_{6,4b}$	34.1	34.3	28.9	29.1	35.5	35.5	29.8	30.1
	$J_{6,5a}$	4.1	4.2	6.4	6.4	5.8	5.9	7.9	7.9
	$J_{6,5b}$	14.9	15.1	15.4	15.4	14.7	15.1	14.4	15.0
	$J_{2,10}$	15.0		15.8		14.3		15.1	
	$J_{6,12}$	12.5		12.7		12.8		12.7	

[a] In C_6D_6. [b] In $CDCl_3$. † Owing to the apparent symmetry of the molecules appearing in the n.m.r. spectra at room temperature, averaged signals were observed for atoms 5 and 7, 4 and 8, and the attached H atoms. In this table, H(4a) signifies an averaged value between H(4a) and H(8a), and similarly for the other H atoms.

Table 7. Torsion angles (°) of the *cis*-selenide (**4**) relevant for the n.m.r. study (*qv.* Figure 3)

H(4A)–C(4)–C(5)–P(6)	29	H(4A)–C(4)–C(5)–H(5A)	92
H(4B)–C(4)–C(5)–P(6)	148	H(4A)–C(4)–C(5)–H(5B)	149
H(4A)–C(4)–O(3)–P(2)	17	H(4B)–C(4)–C(5)–H(5A)	26
H(4B)–C(4)–O(3)–P(2)	137	H(4B)–C(4)–C(5)–H(5B)	91

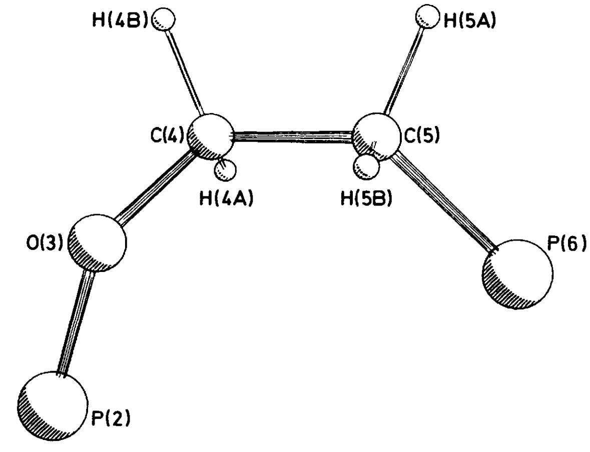


Figure 3. Solid-state conformation of the *cis*-selenide (**4**) used for the interpretation of the n.m.r. spectra

conformations existing in the solid state. The pathway for the interconversion could be similar to that described for the tetrasubstituted 1,3-dioxocanes.[29]

Table 8. Torsion angles (°) of the *trans*-selenide (**3**) relevant for the n.m.r. study (*qv.* Figure 4)

H(4A)–C(4)–C(5)–P(6)	177	H(4A)–C(4)–O(3)–P(2)	57
H(4B)–C(4)–C(5)–P(6)	64	H(4B)–C(4)–O(3)–P(2)	175
H(8A)–C(8)–C(7)–P(6)	42	H(8A)–C(8)–O(1)–P(2)	2
H(8B)–C(8)–C(7)–P(6)	162	H(8B)–C(8)–O(1)–P(2)	122
H(4A)–C(4)–C(5)–H(5A)	56	H(8A)–C(8)–C(7)–H(7A)	79
H(4A)–C(4)–C(5)–H(5B)	61	H(8A)–C(8)–C(7)–H(7B)	162
H(4B)–C(4)–C(5)–H(5A)	175	H(8B)–C(8)–C(7)–H(7A)	41
H(4B)–C(4)–C(5)–H(5B)	57	H(8B)–C(8)–C(7)–H(7B)	77

As in the case of the *cis*-derivatives, the similarities between (**1**) and (**3**) (the n.m.r. spectra and the solid-state conformation) lead us to discuss the two systems together. The angular values given in Table 8 correspond to the *trans*-selenide (**3**). The enantiomerization process leads to the exchanges H(4A) ↔ H(8B), H(4B) ↔ H(8A), H(5A) ↔ H(7B), and H(5B) ↔ H(7A). The coupling constants ^3J between P(6) and H are given by the equations (1) and (2). This means that one $^3J_{P(6),H}$ coupling

$$^3J_{P(6),H} = 0.5\,J_{177^\circ} + 0.5\,J_{162^\circ} \qquad (1)$$

$$^3J_{P(6),H} = 0.5\,J_{64^\circ} + 0.5\,J_{42^\circ} \qquad (2)$$

constant must be characterized by a high value, and the other must be smaller.[27] In Table 6 the higher value (35.5 Hz) is labelled $J_{6,4b}$ and the other (13.6 Hz) $J_{6,4a}$. If the n.m.r. spectra of (**1**) and (**3**) in fact correspond to a fast exchange between the two conformations existing in the crystal, then H(4b) is an average between H(4A) and H(8B), and H(4a) an average between H(4B) and H(8A). Starting out from the torsion angles given in Table 8 and taking into account a fast exchange between the two enantiomeric conformations, we can write equations (3) and (4).

$$^3J_{P(2),H} = 0.5\,J_{57^\circ} + 0.5\,J_{122^\circ} \qquad (3)$$

$$^3J_{P(2),H} = 0.5\,J_{175^\circ} + 0.5\,J_{2^\circ} \qquad (4)$$

The average value yielded by equation (4) will be higher than that yielded by (3). In other words, H(4b) [the average between

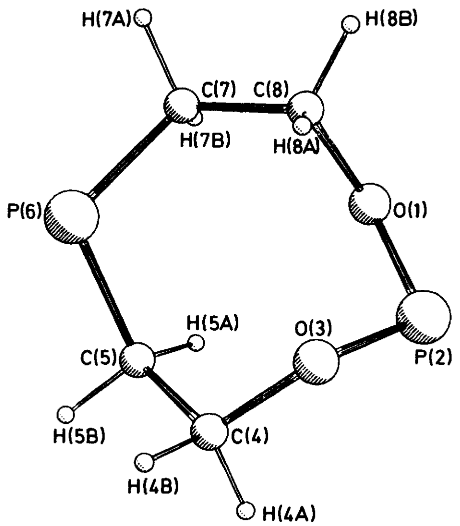


Figure 4. Solid-state conformation of the *trans*-selenide (**3**) used for the interpretation of the n.m.r. spectra

H(4A) and H(8B) in our scheme] is predicted to be less coupled to P(2) than H(4a) [the average between H(4B) and H(8A)]. The experimental values are the following: $J_{2.4a} = 23.3$ Hz, $J_{2.4b} = 10.1$ Hz; the agreement is satisfactory if we accept a $^3J_{P.H}$ value of 45—50 Hz when the P–O–C–H angle is 180° in such types of molecule.

The four $^3J_{H.H}$ values are yielded by equations (5)—(8)

$$^3J^{\alpha}_{H.H} = 0.5\,J_{56^\circ} + 0.5\,J_{77^\circ} \tag{5}$$

$$^3J^{\beta}_{H.H} = 0.5\,J_{61^\circ} + 0.5\,J_{41^\circ} \tag{6}$$

$$^3J^{\gamma}_{H.H} = 0.5\,J_{175^\circ} + 0.5\,J_{162^\circ} \tag{7}$$

$$^3J^{\delta}_{H.H} = 0.5\,J_{57^\circ} + 0.5\,J_{79^\circ} \tag{8}$$

(where the superscripts α—δ is introduced in order to differentiate the four average values).

$^3J^{\gamma}_{H.H}$ is predicted to be higher than all the others. Moreover, this constant implies the coupling H(4B) $\leftrightarrow$ H(8A) on the one hand, and the coupling H(5A) $\leftrightarrow$ H(7B) on the other. On the basis of the assignment previously made, this high coupling constant must therefore involve H(4a). In Table 6 all the coupling constants are small but one: $J_{4a.5a}$ is 11.8 Hz, a value which corresponds to a torsion angle close to 180°. Therefore, in our scheme, 5a corresponds to the average between 5A and 7B and this means that 5b corresponds to the average between 5B and 7A.

The three other coupling constants $^3J_{H.H}$ predicted from the equations giving $^3J^{\alpha}_{H.H}$, $^3J^{\beta}_{H.H}$, and $^3J^{\delta}_{H.H}$ are too similar to be used to test our conclusions again. A small distortion of the molecular skeleton may easily modify the sequence of these three $^3J_{H.H}$ values. The smallest experimental value corresponds to $^3J_{4a.5b}$ and in this scheme may therefore be assigned to the couplings 4B $\leftrightarrow$ 8A and 5B $\leftrightarrow$ 7A, *i.e.* to $^3J^{\delta}_{H.H}$.

We can therefore conclude that the proton n.m.r. spectra of the *trans*-derivatives (**1**) and (**3**) can be interpreted on the basis of a fast equilibration between the two enantiomeric conformations existing in the crystal. The room-temperature ^{1}H n.m.r. spectra of the derivatives (**1**)—(**4**), recorded in solution, are therefore compatible with the structural data obtained by *X*-ray diffraction of the crystals. It is important to emphasize that this conclusion does not exclude the presence in solution of other minor conformations in fast exchange with those considered in our analysis. More precisely, in the case of the *cis*-derivatives, we were obliged to concede a distortion of the skeleton in order to be able to interpret the $^3J_{H.H}$ values. The presence of a minor conformation (either a BC conformation or even the inverted CC conformation with the two methyl groups on the P atoms in axial positions) is obviously another possible explanation.

In the case of (**2**) the coupling constant $^1J_{P(2).C(10)}$[30] is 119.8 Hz. This value is smaller than the 125.1 Hz value observed for (**5**), a derivative known to exist at room temperature in a fixed CC conformation.[4] This observation again is in favour of a skeletal distortion but can also be interpreted in terms of the presence of another minor conformation. In fact, it is known that in eight-membered heterocycles the CC and BC conformations are generally very close in energy.[22,31]

We conclude that the *X*-ray diffraction study and the complete n.m.r. study provide a good overview of the structural characteristics of four new heterocycles, which can be compared to the series of compounds recently described by Dräger.[32]

Experimental

1,3-Dioxa-2,6-diphosphacyclo-octane disulphides and diselenides (**1**)—(**4**) were obtained by the addition of elemental sulphur or selenium to a solution containing *cis*- and *trans*-2,6-dimethyl-1,3-dioxa-2,6-diphosphacyclo-octane. The *cis*- and *trans*-disulphide and diselenide isomers were separated by successive crystallizations from benzene. The starting dioxa-diphosphacyclo-octane was obtained by treating dichloro-(methyl)phosphane with bis-(2-hydroxyethyl)methylphosphane,[12] and was separated from dimeric and oligomeric by-products by vacuum distillation (b.p. 65—68 °C at 0.05 Torr) (**CAUTION:** bath temperatures higher than 120 °C lead to explosion); the *cis*- and *trans*-isomers could not be separated. Single crystals of (**1**)—(**4**) were grown from benzene solution [m.p.s 116 °C (**1**), 174 °C (**2**), 152 °C (**3**), 184 °C (**4**)].

N.m.r. Studies.—Fourier transform ^{1}H (200.1 MHz), ^{13}C (50.3 MHz), and ^{31}P (81 MHz) n.m.r. spectra were obtained with a Bruker WP 200 spectrometer. ^{1}H{^{31}P} Spectra were obtained with a Cameca 250 instrument. Chemical shifts are given in p.p.m. downfield from 85% H_3PO_4(^{31}P) or tetramethylsilane (^{1}H,^{13}C). The 2D *J*-resolved spectra were obtained with a Bruker WM200 instrument, with a standard Aspect 2000 software program, FTNMR2D Vers.810515.1. 2D *J*-Resolved spectra were recorded under the following conditions: SW $F_1 = 40.6$ Hz; SW $F_2 = 1\,298.7$ Hz. The data storage of the FIDs on a DRE 30 disc took place at 128 × 1 024 words; after a double Fourier transformation at 256 × 2 048 words the 2D spectra resulted in digital resolutions of 0.317 and 1.268 Hz along F_1 and F_2 directions respectively. The ^{1}H n.m.r. spectra were simulated with the PANIC program (Bruker software for the Aspect 2000 computer).

References

1 C. Piccinni-Leopardi, G. Germain, J. P. Declercq, M. Van Meerssche, J. B. Robert, and K. Jurkschat, *Acta Crystallogr., Sect. B*, 1982, **38**, 2197.
2 A. E. Kalinin, V. G. Andrianov, and Y. T. Stroutchkov, *Zh. Strukt. Khim.*, 1975, **16**, 1041.
3 O. A. Koulikova, L. T. Razvodovskaia, and N. N. Melnikov, *Zh. Vses. Khim. Ova. in D.I. Mendeleeva*, 1978, **23**, 355.
4 J. P. Dutasta and J. B. Robert, *J. Am. Chem. Soc.*, 1978, **100**, 1925.
5 J. Martin and J. B. Robert, *Acta Crystallogr., Sect. B*, 1979, **35**, 1623.
6 J. Devillers, D. Houalla, J. J. Bonnet, and R. Wolf, *Nouv. J. Chim.*, 1980, **4**, 179.

7 R. K. Sharma, K. Sampath, and R. Vaidyanathaswamy, *J. Chem. Res. (S)*, 1980, 12.

8 A. Grand, *Cryst. Struct. Commun.*, 1982, **11**, 569.

9 C. Pradat, J. G. Riess, D. Bondoux, B. F. Mentzen, I. Tkatchenko, and D. Houalla, *J. Am. Chem. Soc.*, 1979, **101**, 2234.

10 J. P. Dutasta, Thesis, University of Grenoble, 1980.

11 J. P. Dutasta, J. Martin, and J. B. Robert, *Heterocycles*, 1980, **14**, 1631.

12 J. P. Dutasta, K. Jurkschat, and J. B. Robert, *Tetrahedron Lett.*, 1981, **22**, 2549.

13 J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Am. Chem. Soc.*, 1969, **91**, 1386.

14 B. J. Van Der Veken and M. A. Herman, *J. Mol. Struct.*, 1977, **42**, 161.

15 D. G. Gorenstein and D. Kar, *J. Am. Chem. Soc.*, 1977, **99**, 672; S. Vishveshwara, *Chem. Phys. Lett.*, 1978, **59**, 30.

16 J. P. Dutasta, A. Grand, and J. B. Robert, *Acta Crystallogr., Sect. B*, 1978, **34**, 3820.

17 D. Perahia and B. Pullman, *Biochim. Biophys. Acta*, 1976, **435**, 282; D. G. Gorenstein, B. A. Luxon, and J. B. Findlay, *ibid.*, 1977, **475**, 184.

18 J. P. Dutasta, A. Grand, and J. B. Robert, *Tetrahedron Lett.*, 1974, 2655.

19 R. W. Warrent, C. N. Caughlan, J. H. Hargis, K. C. Yee, and W. G. Bentrude, *J. Org. Chem.*, 1978, **43**, 4266.

20 A. Grand, unpublished work.

21 F. A. L. Anet, *Top. Curr. Chem.*, 1974, **45**, 169.

22 L. Pauling, 'The Nature of the Chemical Bond,' Cornell Univ. Press, Ithaca, 1960.

23 V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, 1967, **5**, 227.

24 W. P. Aue, J. Karhan, and R. R. Ernst, *J. Chem. Phys.*, 1976, **64**, 4226; A. Kumar, *J. Magn. Reson.*, 1978, **30**, 227; L. D. Hall and S. Sukumar, *J. Am. Chem. Soc.*, 1979, **101**, 3120; L. D. Hall and J. K. M. Saunders, *ibid.*, 1980, **102**, 5703.

25 M. Karplus, *J. Am. Chem. Soc.*, 1963, **85**, 2870; M. Barfield and D. M. Grant, *Adv. Magn. Reson.*, 1965, **1**, 149.

26 W. G. Bentrude, H. W. Tan, and K. C. Yee, *J. Am. Chem. Soc.*, 1975, **97**, 573; J. P. Dutasta, A. Grand, J. B. Robert, and M. Taieb, *Tetrahedron Lett.*, 1974, 2659; A. J. Dale, *Acta Chem. Scand., Ser. B*, 1976, **30**, 255.

27 C. Benezra, *J. Am. Chem. Soc.*, 1973, **95**, 6890; K. M. Pietrusiewicz, *Org. Magn. Reson.*, 1983, **21**, 345.

28 W. G. Bentrude, R. O. Day, J. M. Holmes, G. S. Quin, W. N. Setzer, A. E. Sopchik, and R. R. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 106.

29 F. A. L. Anet, P. J. Degen, and J. Krane, *J. Am. Chem. Soc.*, 1976, **98**, 2059.

30 W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Am. Chem. Soc.*, 1971, **93**, 797; W. G. Stec, K. Lesiak, D. Mielczarek, and B. Stec, *Z. Naturforsch., Teil B*, 1975, **30**, 710.

31 U. Burkert, *Z. Naturforsch., Teil B*, 1980, **35**, 1479.

32 M. Dräger, *Z. Anorg. Allg. Chem.*, 1981, **482**, 7; *J. Organomet. Chem.*, 1983, **251**, 209.

Received 24*th October* 1984; *Paper* 4/1820