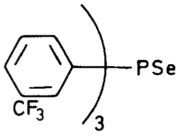
The Chemistry of Heteroarylphosphorus Compounds. Part 16.[1] Unusual Substituent Effects on Selenium-77 Nuclear Magnetic Resonance Chemical Shifts of Heteroaryl- and Aryl-phosphine Selenides. *X*-Ray Crystal Structure of Tri(2-furyl)phosphine Selenide†

David W. Allen* and I. W. Nowell
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB
Brian F. Taylor
Department of Chemistry, The University, Brook Hill, Sheffield S3 7HF

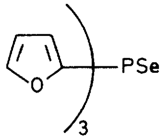
Crystals of PR_3Se (R = 2-furyl) are monoclinic, space group *Cc*, with $a = 11.720(6)$, $b = 12.527(9)$, $c = 8.569(5)$ Å, and $Z = 4$. The structure was solved using multisolution direct methods and refined by least squares to *R* 0.038 (*R'* 0.041) for 1 030 observed diffractometer data. Phosphorus adopts a distorted tetrahedral geometry with mean Se–P–C and C–P–C angles of 114.9 and 103.4°, respectively. The molecule has almost ideal C_3 symmetry. The C–P–C angle is the smallest reported for a tertiary phosphine selenide. The average P–C bond length [1.778(6) Å] and the P–Se bond length (2.094 Å) are both considerably shorter than found in other arylphosphine selenides. The oxygen atoms of the 2-furyl groups are arranged about the selenium atom, with an average Se • • • O distance of 3.577 Å. ^{77}Se N.m.r. studies show that the selenium atom is shielded by 86 p.p.m. compared with that in triphenylphosphine selenide, implying a 'through-space' interaction involving the 2-furyl oxygen atoms. Selenium-77 chemical shifts have also been determined for a range of heteroaryl- and substituted phenyl-phosphine selenides. Whereas the 2-furyl group causes the selenium to become shielded, the related 2-thienyl group causes it to become deshielded. Deshielding of selenium is also experienced on introduction of *ortho* substituents in arylphosphine selenides. Thus, for example, the selenium atom of tris(2,4,6-trimethoxyphenyl)phosphine selenide is deshielded by 240 p.p.m. compared with that in triphenylphosphine selenide. Possible origins of these effects are considered.

We have recently reported a study of the donor properties of a series of heteroaryl- and substituted aryl-phosphines towards selenium and platinum(II) acceptors, as indicated by the ^{31}P n.m.r. one-bond coupling constants $^1J(^{77}Se-^{31}P)$ and $^1J(^{195}Pt-^{31}P)$.[1] The respective coupling constants increase as the groups attached to phosphorus become more electron-withdrawing, indicating an increased *s* character for the phosphorus orbital involved in bonding to selenium or platinum, in accordance with Bent's rule.[2] Consequently, for such electron-withdrawing substituents, the bonds from phosphorus to the acceptor atom would be expected to be shorter than in related molecules bearing less electron-withdrawing substituents. Support for this view has been gained from an *X*-ray study of tris(*m*-trifluoromethylphenyl)phosphine selenide (**1**) in which the phosphorus–selenium bond shows significant shortening compared with that in triphenylphosphine selenide.[3]

In this paper, we present a structural study of tri(2-furyl)-phosphine selenide (**2**) and show that a similar shortening of the phosphorus–selenium bond is observed, consistent with the increased value of the coupling constant $^1J(^{77}Se-^{31}P)$ compared with that for triphenylphosphine selenide. In addition, we also present ^{77}Se n.m.r. chemical shift data for a range of aryl- and heteroaryl-phosphine selenides, and draw attention to some unusual 'through-space' effects on the magnitude of the selenium chemical shift.



(**1**)



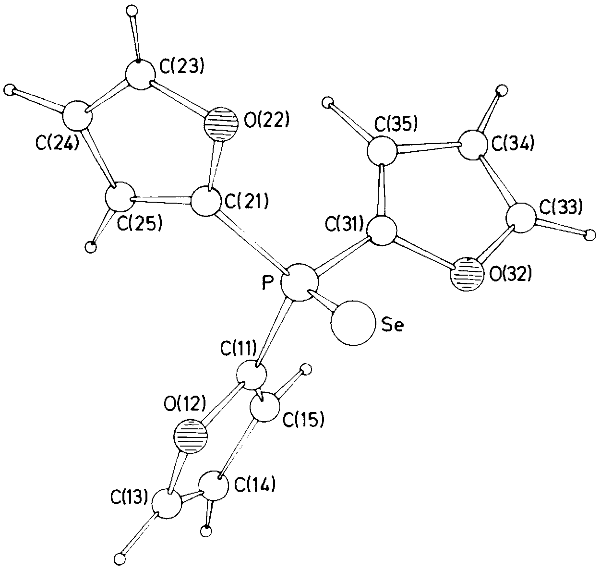
(**2**)

Results and Discussion

Tri(2-furyl)phosphine selenide (**2**) is found to be a distorted tetrahedral molecule (Figure), but although the general structural features are similar to those found in other triarylphosphine selenides (Table 1) there are a number of differences worthy of note. Thus, of the five selenides listed, the 2-furyl derivative is unique in having almost ideal C_3 symmetry. The inclination of each 2-furyl group to the respective Se–P–C(*n*1) plane is almost identical for the three rings, the Se–P–C(*n*1)–O(*n*2) torsion angles being 48.2(5), 46.3(6), and 46.7(5)° (*n* = 1, 2, and 3). The lower steric requirements of the 2-furyl group compared with the phenyl and *o*-, *m*-substituted aryl groupings would appear to be a major factor in enabling compound (**2**) to adopt such a symmetrical arrangement. The low steric demand of the heterocyclic groups may also facilitate their close approach to phosphorus and certainly the average phosphorus–carbon bond length in (**2**) is considerably shorter [1.778(6) Å] than those found in the other triarylphosphine selenides, $R_3P=Se$ [R = *o*-tolyl, 1.834(14); *m*-tolyl, 1.82(2); Ph, 1.826(13); and *m*-$CF_3C_6H_4$, 1.815(7) Å]. Alternatively, the shortening of the

---

† *Supplementary data available* (No. SUP 56336, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.



Molecular structure of tri(2-furyl)phosphine selenide

phosphorus–carbon bonds in (**2**) could be attributed to an increased degree of $P_{3d\pi}$–$C_{2p\pi}$ interaction between phosphorus and the ring π system as a result of the σ-electron-withdrawing properties of the 2-furyl group, which become apparent when the π system of the ring is unable to interact in a p_π–p_π manner with a substituent atom or group.[1]

The phosphorus–selenium bond length is identical to that found in tris(*m*-trifluoromethylphenyl)phosphine selenide (**1**), the value of 2.094 Å being the shortest yet reported for a tertiary phosphine selenide. The shortness of this bond in both (**1**) and (**2**) may be attributed to the σ-electron-withdrawing effects of the substituent groups and the accompanying increase in *s* character of the phosphorus orbital involved in bonding to selenium. However, from the higher value of $^1J(^{77}Se–^{31}P)$ observed for compound (**2**) (Table 1), one might have anticipated that the phosphorus–selenium bond would have been detectably shorter than that in (**1**). This apparent anomaly may either reflect our inability to detect such a shortening from the crystallographic data or it may be that the increased value of $^1J(^{77}Se–^{31}P)$ is not solely due to the electron-withdrawing effects of the 2-furyl groups. One possible contributing factor is associated with the positions adopted by the three heteroaryl rings. Not only are they all oriented such that the lone pairs of electrons on the oxygen atoms form a sheath of electron density parallel to the phosphorus–selenium direction, but the extreme asymmetry of the exocyclic angles at the C(*n*1) atoms (Table 2) enhances the effect by decreasing the Se • • • O(*n*2) distances to an average of 3.577 Å. It is noteworthy that the ^{77}Se chemical shift of compound (**2**) shows a marked shielding compared to that of (**1**) and triphenylphosphine selenide (see below) and this may also influence the value of $^1J(^{77}Se–^{31}P)$. The asymmetry at C(*n*1), with average bond angles for P–C(*n*1)–O(*n*2) and P–C(*n*1)–C(*n*5) of 117.4 and 133.2° respectively, appears to be a feature of the 2-furyl bond, and similar asymmetry has been reported in di(2-furyl)mercury.[4] The furyl rings in (**2**) are all effectively planar and their geometry is in good agreement with that reported for other 2-substituted derivatives.[4,5]

Finally, it should be noted that the C–P–C intervalence angles at phosphorus (Table 2) are the smallest recorded for a tertiary phosphine selenide. This is consistent with the assumption of a greater degree of *p* character in the orbitals used by phosphorus to bond to the 2-furyl groups, again a consequence of the electron-withdrawing effects of these substituents, in accordance with Bent's rule.[2] Alternatively, it may simply reflect the reduced steric bulk of the 2-furyl groups.

Table 1. Phosphorus–selenium bond distances in tertiary phosphine selenides, together with ^{77}Se–^{31}P coupling constants

R in PR_3Se	Bond distance (Å)	$^1J(^{77}Se–^{31}P)$/Hz
C_6H_4Me-*o*	2.116 (5)[a]	708[b]
C_6H_4Me-*m*	2.109(5)[c]	726[b]
Ph	2.106(1)[d]	732[e]
$C_6H_4CF_3$-*m*	2.094(2)[f]	766[e]
2-Furyl	2.094	793[e]

[a] Ref. 14. [b] R. P. Pinnell, C. A. Megerle, S. L. Manatt, and P. A. Kroon, *J. Am. Chem. Soc.*, 1973, **95**, 977. [c] T. S. Cameron, K. D. Howlet, and K. Miller, *Acta Crystallogr., Sect. B*, 1978, **34**, 1639. [d] P. W. Codding and K. A. Kerr, *Acta Crystallogr., Sect. B*, 1979, **35**, 1261. [e] Ref. 1. [f] Ref. 3.

The effect of substituents at phosphorus on the ^{77}Se chemical shifts of tertiary phosphine selenides have been considered by McFarlane and Rycroft.[6] From studies of a wide range of organoselenium compounds, it is known that the selenium chemical shift moves to lower field as the extent of withdrawal of electronic charge from selenium increases.[7] Since phosphine selenides usually have very high-field selenium chemical shifts, it has been assumed[6] that the dipolar form (**3**) is the major contributor to the resonance hybrid of the canonical forms (**3**) and (**4**). However, it has been pointed out that the contribution of form (**4**) to the resonance hybrid depends on the ability of the substituents at phosphorus to become involved in p_π–d_π interactions with phosphorus. The presence of substituents capable of π bonding to phosphorus means that the phosphorus 3*d* orbitals will be less readily available for overlap with a selenium 4*p* orbital, and consequently the contribution of form (**4**) will diminish, and that of (**3**) will increase, the selenium atom becoming more shielded.[6]

$$R_3\overset{+}{P}–\overset{-}{Se} \longleftrightarrow R_3P{=}Se$$

(**3**) (**4**)

Selenium chemical shift data, together with $^1J(^{77}Se–^{31}P)$ [and $\delta(^{31}P)$], for a series of heteroaryl- and substituted arylphosphine selenides are presented in Table 3. A number of interesting trends are apparent. First, progressive replacement of phenyl by 2-furyl causes a shielding of the selenium atom, the coupling constant also increasing steadily; the latter reflects the electron-withdrawing properties of the 2-furyl group as discussed previously.[1] If it is assumed that the 2-furyl groups promote $C_{2p\pi}$–$P_{3d\pi}$ interactions between the ring π system and phosphorus (as might be inferred from the observed shortening of the phosphorus–carbon bond), then as argued above the contribution of the dipolar form (**3**) will increase with concomitant shielding of selenium, as is observed. Alternatively, the observed shielding may be a reflection of 'through-space' interactions involving the oxygen lone pairs, as revealed by the above crystallographic study. It is noteworthy that the ^{77}Se shift of tri(3-furyl)phosphine selenide, in which the oxygen atoms cannot interact with the selenium in this way, is very similar to that of triphenylphosphine selenide.

Secondly, *in contrast*, progressive replacement of phenyl by 2-thienyl results in a deshielding of the selenium atom, whereas the coupling constant $^1J(^{77}Se–^{31}P)$ increases. From studies of the reactivity of a wide range of heteroarylphosphorus compounds[8] we have concluded that the following order of substituent electron-withdrawing ability applies: 2-furyl > 2-thienyl > 3-furyl > 3-thienyl > phenyl. Thus, the progressive

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses* for compound (**2**)

	$n = 1$	$n = 2$	$n = 3$		$n = 1$	$n = 2$	$n = 3$
P–C(n1)	1.782(6)	1.776(6)	1.776(7)	Se–P–C(n1)	114.6	115.2	115.1
C(n1)–O(n2)	1.368(8)	1.378(8)	1.390(7)	P–C(n1)–O(n2)	117.6(4)	117.3(5)	117.2(5)
O(n2)–C(n3)	1.349(10)	1.356(10)	1.372(10)	P–C(n1)–C(n5)	132.9(6)	133.1(6)	133.5(6)
C(n3)–C(n4)	1.350(12)	1.326(13)	1.318(11)	O(n2)–C(n1)–C(n5)	109.4(6)	109.3(6)	109.1(6)
C(n4)–C(n5)	1.434(12)	1.449(11)	1.448(13)	C(n1)–O(n2)–C(n3)	107.4(6)	106.3(6)	106.8(5)
C(n5)–C(n1)	1.350(9)	1.352(10)	1.336(10)	O(n2)–C(n3)–C(n4)	110.7(7)	112.3(8)	110.3(7)
Se–P	2.094			C(n3)–C(n4)–C(n5)	105.7(7)	105.3(7)	107.0(7)
				C(n4)–C(n5)–C(n1)	106.8(7)	106.7(7)	106.7(7)

C(11)–P–C(21) 103.9(3) C(11)–P–C(31) 103.4(3) C(21)–P–C(31) 103.1(3)

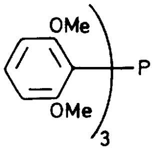
* No errors are given for bond distances and angles associated with Se, for which the *x* and *z* co-ordinates have been fixed.

Table 3. Selenium-77 and phosphorus-31 data for tertiary phosphine selenides $PR^1{}_2R^2Se$ in $CDCl_3$

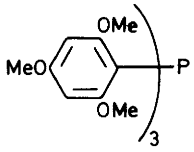
Phosphine selenide	$\delta(^{77}Se)$/ p.p.m.	$\delta(^{31}P)$/ p.p.m.	$^1J(^{77}Se-^{31}P)$/ Hz
$R^1 = R^2 = Ph$	−268	35.9	732
$R^1 = Ph, R^2 =$ 2-furyl	−300	16.9	754
$R^1 =$ 2-furyl, $R^2 = Ph$	−334	−2.0	774
$R^1 = R^2 =$ 2-furyl	−354	−22.1	793
$R^1 = R^2 =$ 3-furyl	−270	−20.3	745
$R^1 = Ph, R^2 =$ 2-thienyl	−234	20.6	743
$R^1 =$ 2-thienyl, $R^2 = Ph$	−199	9.3	752
$R^1 = R^2 =$ 2-thienyl	−168	−4.2	757
$R^1 = R^2 =$ 3-thienyl	−234	−1.4	740
$R^1 = R^2 = m\text{-}CF_3C_6H_4$	−268	35.5	766
$R^1 = Ph, R^2 = o\text{-}MeOC_6H_4$	−242	32.8	718
$R^1 = Ph, R^2 = p\text{-}MeOC_6H_4$	−263	34.7	722
$R^1 = R^2 = o\text{-}MeOC_6H_4$	−226	−20.2	720
$R^1 = R^2 = p\text{-}MeOC_6H_4$	−252	−39.7	710
$R^1 = R^2 = 2,6\text{-}(MeO)_2C_6H_3$	−46.2	−15.2	717
$R^1 = R^2 = 2,4,6\text{-}(MeO)_3C_6H_2$	−28.4	−16.8	703
$R^1 = Ph, R^2 = o$-tolyl	−278	32.6	730
$R^1 = R^2 = o$-tolyl	−204	28.7	703
$R^1 = R^2 = p$-tolyl	−264	34.4	715

increase in $^1J(^{77}Se-^{31}P)$ with introduction of 2-thienyl substituents can be understood as previously argued, whereas the progressive deshielding of the selenium atom is more difficult to explain. If π interactions are assumed for the 2-furyl group, then it would also seem reasonable to assume a similar involvement in the case of the 2-thienyl group, and one would therefore expect an increase in shielding at selenium. That this is not so suggests that in this series the π-bonding postulate may not be correct, and that the observed shielding in the case of the 2-furyl derivatives is indeed a consequence of some 'through-space' effect involving the oxygen atoms, which does not occur in the case of sulphur. It is of interest that tri(3-thienyl)phosphine selenide also exhibits a significant deshielding of selenium compared with that in triphenylphosphine selenide. It is also significant that the selenium chemical shift of tris(*m*-trifluoromethylphenyl)phosphine selenide is effectively the same as that of triphenylphosphine selenide, although the greater electron-withdrawing properties of the *m*-trifluoromethylphenyl substituent are reflected in the magnitude of $^1J(^{77}Se-^{31}P)$.

In order to explore the possibility of specific 'through-space' effects we have also studied some *o*-methoxyphenylphosphine selenides. There is some evidence in the literature that the oxygen atoms of *o*-methoxyphenylphosphines are involved in weak co-ordinative interactions with the metal atoms of their transition-metal complexes.[9] In addition, such interactions have been shown to have an effect on the subsequent reactivity of the metal atom of such complexes, *e.g.* in oxidative-addition processes.[10] Furthermore, interactions between the oxygen atom of *o*-methoxyphenyl substituents and a developing phosphonium centre have been noted in kinetic studies of the quaternization of *o*-methoxyphenylphosphines[11] and structural studies of such salts indicate a $\overset{+}{P}\cdots OMe$ interaction.[12] It was therefore of considerable interest to consider the possibility of similar interactions between oxygen and *either* phosphorus *or* selenium in a series of *o*-methoxyphenylphosphine selenides.



(**5**)



(**6**)

It is apparent from Table 3 that the introduction of only one *o*-methoxy-group into a triarylphosphine selenide causes the selenium atom to be deshielded by an amount similar to the shielding experienced on replacement of phenyl by a 2-furyl group. Introduction of an additional two *o*-methoxy-groups, as in tri(*o*-methoxyphenyl)phosphine selenide, results in further deshielding. Deshielding of selenium is also caused by the introduction of *p*-methoxyphenyl groups, but to a smaller degree than for the *o*-methoxy-systems. However, especially noteworthy is the massive deshielding of selenium observed in the poly-*o*-methoxylated phosphine selenides derived from the phosphines (**5**) and (**6**). These phosphines have attracted some interest, recently, in view of their enhanced basicity. Thus, for example, compound (**6**) is reported to be as basic as piperidine, *i.e.* an order of magnitude more basic than a typical triarylphosphine.[13] However, it is interesting that whereas the effects on selenium chemical shifts are large, these 2,6-dimethoxyphenyl substituents have little further effect on the values of $^1J(^{77}Se-^{31}P)$ compared with the less heavily substituted systems. It is also evident that introduction of methoxy-substituents causes the phosphorus nucleus to become shielded. However, the increase in shielding at phosphorus is not regular, and the greatest degree of shielding is observed in tri(*p*-methoxyphenyl)phosphine selenide.

In order to explore the possibility of a general *ortho* effect on selenium chemical shifts, we have also studied the effects of introducing *o*-tolyl substituents. Introduction of one *o*-tolyl group causes a slight shielding of selenium, which is significantly reversed on introduction of a further two *o*-tolyl groups. Thus the selenium atom of tri(*o*-tolyl)phosphine selenide is deshielded by 64 p.p.m. compared with triphenylphosphine selenide. This effect is not observed in the related tri(*p*-tolyl)phosphine

Table 4. Final fractional co-ordinates for non-hydrogen atoms ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Se	0	2 500(1)	2 500
P	1 514(1)	2 501(1)	4 014(2)
C(11)	2 691(5)	1 836(4)	3 268(7)
O(12)	2 926(5)	2 080(5)	1 776(6)
C(13)	3 797(6)	1 446(6)	1 430(9)
C(14)	4 122(6)	788(7)	2 640(10)
C(15)	3 413(6)	1 063(6)	3 854(10)
C(21)	2 065(6)	3 785(5)	4 547(8)
O(22)	1 300(4)	4 534(3)	4 997(7)
C(23)	1 900(8)	5 454(7)	5 240(10)
C(24)	2 981(8)	5 354(7)	4 931(11)
C(25)	3 104(6)	4 245(6)	4 495(10)
C(31)	1 414(5)	1 873(5)	5 854(8)
O(32)	882(4)	881(4)	5 840(6)
C(33)	824(7)	595(7)	7 376(9)
C(34)	1 282(7)	1 344(7)	8 319(10)
C(35)	1 685(8)	2 177(8)	7 338(10)

selenide. It would seem therefore that there are some specific 'through-space' effects in these systems which are quite different from those in the above 2-furyl derivatives. An *X*-ray study of tri(*o*-tolyl)phosphine selenide reveals that two of the *ortho* substituents are in close proximity to the selenium atom, the third group having rotated away about the phosphorus–aryl bond. In the related phosphine oxide, all three *o*-methyl groups are in close proximity to the oxygen atom.[14]

We are currently carrying out further structural studies in order to shed some light on this problem. In the absence of such structural data, it is difficult to account for the above results in terms of the usual electronic effects of substituents.

Experimental

Selenium-77 n.m.r. spectra were recorded on a Bruker AM-250 instrument at 21 °C in 10-mm tubes, at 47.7 MHz. Chemical shifts are reported on the δ scale with respect to external dimethyl selenide. Phosphorus-31 n.m.r. spectra were also recorded on the above instrument under the same conditions, at 101.2 MHz, and ^{31}P chemical shifts are reported with respect to external 85% H_3PO_4. Shifts to high field are negative in sign. Coupling constants are reported in Hz and are accurate to ± 1.5 Hz. Proton n.m.r. spectra were recorded on a Bruker WP80SY instrument at 80 MHz, using $SiMe_4$ as internal standard.

Preparation of Phosphine Selenides.—These were prepared by the reaction of the phosphine (10^{-3} mol) with selenium (0.3 g, excess) under reflux for 5 h in chloroform (2.5 cm^3), as previously described.[1] The following compounds are new: *tris*(2,6-*dimethoxyphenyl*)*phosphine selenide*, m.p. 148 °C (from EtOH) (Found: C, 55.45; H, 5.20. $C_{24}H_{27}O_6PSe$ requires C, 55.25; H, 5.20%); ^1H n.m.r. ($CDCl_3$) δ 7.2 (m, 3 H), 6.5 (m, 6 H), and 3.55 p.p.m. (s, 18 H); *tris*(2,4,6-*trimethoxyphenyl*)*phosphine selenide*, m.p. 199—200 °C (from EtOH) (Found: C, 52.55; H, 5.95. $C_{27}H_{33}O_9PSe$ requires C, 53.00; H, 5.45%); ^1H n.m.r. ($CDCl_3$) δ 6.3 (d, 6 H), 4.8 (s, 9 H), and 4.57 p.p.m. (s, 18 H).

X-*Ray Study of Tri*(2-*furyl*)*phosphine Selenide.*—Crystals of this compound were prepared as described previously.[1]

Crystal data. $C_{12}H_9O_3PSe$, $M = 239.1$, monoclinic, space group *Cc*, $a = 11.720(6)$, $b = 12.527(9)$, $c = 8.569(5)$ Å, $\beta = 95.56(5)°$, $U = 1\,252.2$ Å^3, $D_m = 1.29$, $Z = 4$, $D_c = 1.27$ Mg m^{-3}, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 3.01$ mm^{-1}, $F(000) = 616$.

Intensity measurements. A crystal of approximate dimensions 0.25 × 0.30 × 0.40 mm was mounted with the *c* axis coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using the background–ω scan–background technique. Corrections for Lorentz and polarization effects were applied, but not for absorption. Of 1 397 unique reflections collected, 1 030 had $I \geqslant 3.0\sigma(I)$ and were used in the subsequent structure analysis.

Structure determination and refinement. The observed extinctions: hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, do not distinguish between the space groups $C2/c$ and Cc. The presence of four molecules in the unit cell allows the selenide molecule to occupy a general position in Cc, but requires it to be on a two-fold axis in $C2/c$ (a situation possible only if the molecule is statistically disordered). A trial solution was initially attempted in the non-centrosymmetric Cc and subsequent analysis confirmed this to be the correct space group. The x and z co-ordinates of the selenium atom were fixed at 0.0 and 0.25 respectively and the y co-ordinate was determined from a Patterson synthesis. Successive electron-density difference maps revealed the remaining atoms and full-matrix refinement with anisotropic thermal parameters for all non-hydrogen atoms gave the final $R = 0.038$ and $R' = 0.041$. Hydrogen atoms were included in positions calculated from the geometry of the molecule (C–H 1.08 Å) and the common isotropic thermal parameters applied to all hydrogens refined to a final value of $U = 0.129(25)$ Å^2. Scattering factors were calculated[15] using an analytical approximation and the final weighting scheme adopted was $w = 0.7714/[\sigma^2(F_o) + 0.0032\,(F_o)^2]$.

Final atomic parameters are given in Table 4. All calculations were carried out on an IBM 4341 computer using the SHELX computing package.[16]

References

1 Part 15, D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51.

2 H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

3 D. W. Allen, L. A. March, and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 1984, 483.

4 M. Sikirica, D. Grdenić, and S. Cimas, *Acta Crystallogr., Sect. B*, 1982, **38**, 926.

5 M. Soriano-Garcia and R. Parthasarathy, *Acta Crystallogr., Sect. B*, 1977, **33**, 2674.

6 W. McFarlane and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 1973, 2162.

7 W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, 1972, 1397.

8 See, for example, D. W. Allen and B. G. Hutley, *J. Chem. Soc., Perkin Trans. 1*, 1978, 675 and refs. therein.

9 J. C. Jeffery and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658.

10 A. G. Constable, C. R. Langrick, B. Shabanzadeh, and B. L. Shaw, *Inorg. Chim. Acta*, 1982, **65**, L151.

11 See, for example, W. E. McEwen, A. B. Jones, J. W. Knapczyk, V. L. Kyllingstad, W-I. Shiau, S. Shore, and J. H. Smith, *J. Am. Chem. Soc.*, 1978, **100**, 7304.

12 J. S. Wood, R. J. Wilkholm, and W. E. McEwen, *Phosphorus Sulfur*, 1977, **3**, 163.

13 M. Wada and S. Higashizaki, *J. Chem. Soc., Chem. Commun.*, 1984, 482.

14 T. S. Cameron and E. Dahlen, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1737.

15 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

16 G. M. Sheldrick, SHELX program for crystal structure determination, University of Cambridge, 1976.

Received 27th February 1985; *Paper* 5/332