Fig. 1. The conformation of the molecule ($2R,3R$ enantiomer depicted) showing the atom numbering.
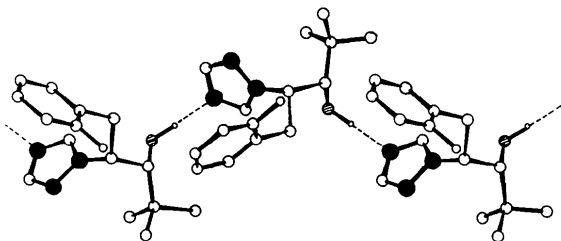
significantly larger than C(5)—N(1)—N(2), which, as previously noted (Branch & Nowell, 1985), appears to be a characteristic of the triazolyl ring itself rather than the influence of any intra- or intermolecular interactions.

Fig. 2. Linking of molecules of $2R,3R$ and $2S,3S$ configurations by hydrogen bonding into chains running parallel to the c axis.

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All four C—N and the N—N bond distances in the triazolyl ring are intermediate between the expected single- and double-bond lengths. The three atoms bonded to N(1) are coplanar with it and, taken together, these data indicate extensive delocalization in the heterocyclic ring. The exocyclic angles at N(1) show considerable asymmetry, C(5)—N(1)—C(1) being

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The Structure of Triphenyl[α-(phenylseleno)phenacylidene]phosphorane

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Abstract. $C_{32}H_{25}OPSe$, $M_r = 535.48$, monoclinic, $P2_1/c$, $a = 10.943$ (5), $b = 13.576$ (6), $c = 17.494$ (6) Å, $\beta = 96.63$ (3)°, $V = 2581.6$ Å^3, $Z = 4$, $D_x = 1.378$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.521$ mm^{-1}, $F(000) = 1096$, $T = 296$ K, final $R = 0.053$ for 3038 unique observed reflections. The molecule is essentially a phosphorus ylide with a phenacylidene and a phenylseleno substituent at the ylide carbon atom, C(1). The central P(1)=C(1)—C(2)=O group is nearly planar and *cis* relative to C(1)—C(2). Corresponding bond lengths are P—C(1) = 1.746 (4), C(1)—C(2) = 1.406 (6) and

C(2)—O = 1·252 (5) Å, all intermediate between single and double bonds. This implies a mesomeric shift of electron density from phosphorus to oxygen. As expected, both C(1) and C(2) are essentially sp^2 hybridized. Bond lengths involving selenium are Se—C(1) = 1·898 (4) and Se—C(11) = 1·927 (4) Å. The shorter ylide carbon-to-selenium bond may indicate a slight delocalization of charge from the ylide to the selenium atoms. All other bond lengths and the bond angles are normal.

Introduction. It has previously been suggested that selenophosphoranes of the type

$$Ph_3P = \underset{\underset{R}{|}}{C}-SePh \longleftrightarrow Ph_3\overset{+}{P}-\underset{\underset{R}{|}}{\overset{-}{C}}-SePh$$
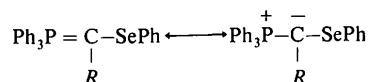
are stabilized partly because of delocalization of negative charge into the d orbitals of selenium. Further stabilization is obtained when R is a carboxylic ester group so that a carbonyl group is conjugated to the P=C bond. In the latter case, stabilization is great enough to prevent a Wittig reaction between these phosphoranes and aldehydes (Petragnani, Rodriguez & Comasseto, 1976). A corresponding stabilization should then be expected for α-acyl-α-(arylseleno)-phosphoranes.

$$Ph_3P = \overset{\alpha}{\underset{\underset{O = C-R}{|}}{C}}-SeAr$$
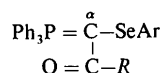
However, these compounds have been shown to undergo intramolecular Wittig reactions upon pyrolysis in vacuum, producing arylselenoacetylenes and triphenylphosphine oxide (Braga, Comasetto & Petragnani, 1984). This implies that resonance forms of the type

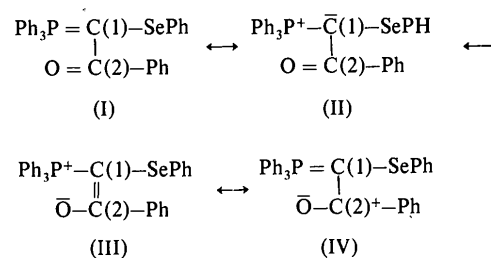$$Ph_3\overset{+}{P}-\underset{\underset{O-C-R}{\|}}{\overset{-}{C}}-SeAr$$
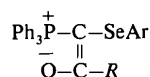
contribute significantly to the structure of such phosphoranes. Structures of other acylphosphoranes support this theory (Speziale & Ratts, 1965). The present structural investigation was undertaken in order to examine the bonding and charge delocalization both in the P—C—C—O and the arylseleno group in a representative α-acyl-α-(arylseleno)phosphorane.

Experimental. The preparation has been reported (Braga, Comasseto & Petragnani, 1984). Enraf–Nonius CAD-4 automated diffractometer, data collected by Molecular Structure Corporation, College Station, Texas. Yellow prismatic crystal 0·30 × 0·20 × 0·20 mm mounted on glass fiber. Graphite monochromatized Mo $K\alpha$ radiation. 25 reflections used to determine cell parameters. Systematic absences, $k = 2n+1$ for 0k0 and $l = 2n+1$ for h0l, compatible with

space group $P2_1/c$. Intensities of 4527 unique reflections with $2\theta < 50°$ measured by scanning in 2θ; $-12 \le h \le 12$, $0 \le k \le 16$, $0 \le l \le 20$. 1021 had $I < 0·5\sigma(I)$, an additional 468 had $F < \sigma(F)$, all these rejected. No significant decline in intensities of three standard reflections. Corrections applied for Lorentz, polarization and absorption (ψ scan, min. transmission coefficient = 0·930, av. = 0·972). Programs from SHELX76 (Sheldrick, 1976) modified for PDP 1144 computer. Structure solved by Patterson and Fourier methods, refined by successive experimentally weighted least-squares iterations. Positions of hydrogen atoms calculated for C—H = 1·08 Å, assigned same isotropic temperature factors as C atoms to which they belong. All H atoms kept constant, in final least-squares iterations anisotropic temperature factors assigned to all non-hydrogen atoms. Refinement terminated when all parameter shifts less than $0·06\sigma$. $\sum w(|F_o| - |F_c|)^2$ minimized; $R = 0·053$, $wR = 0·051$, $S = 1·14$, $w = 1/\sigma^2(F)$, $\sigma(I) = |\sigma^2 + (0·05I)^2|^{1/2}$, σ calculated from counting statistics. Final difference electron density map showed no maxima above $0·35$ e Å^{-3}. Scattering factors (including anomalous dispersion) taken from Cromer & Liberman (1970), Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion. Final atomic parameters are given in Table 1.* An ORTEP plot of the molecule is shown in Fig. 1, and bond lengths and angles are listed in Table 2. The compound is best described as a phosphorus ylide where the P=C bond is conjugated to a C=O bond, as described by the following resonance forms:

$$Ph_3P = \underset{\underset{O = C(2)-Ph}{|}}{C(1)}-SePh \longleftrightarrow Ph_3P^+-\underset{\underset{O = C(2)-Ph}{|}}{\overset{-}{C}(1)}-SePH \longleftrightarrow$$

$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

$$Ph_3P^+-\underset{\underset{\overset{-}{O}-C(2)-Ph}{\|}}{C(1)}-SePh \longleftrightarrow Ph_3P = \underset{\underset{\overset{-}{O}-C(2)^+-Ph}{|}}{C(1)}-SePh$$

$$\text{(III)} \qquad\qquad\qquad \text{(IV)}$$

Of these, (III) is probably the most important. Examination of the final difference electron density map revealed a small minimum near P and a small maximum near O in agreement with this. The bond lengths in the P—C(1)—C(2)—O sequence are successively: 1·746 (4), 1·406 (6) and 1·252 (5) Å. They may be compared to normal P—C(phenyl) single-bond lengths of ca 1·80
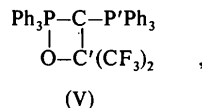

Table 1. *Final atomic parameters for non-H atoms with e.s.d.'s in parentheses*

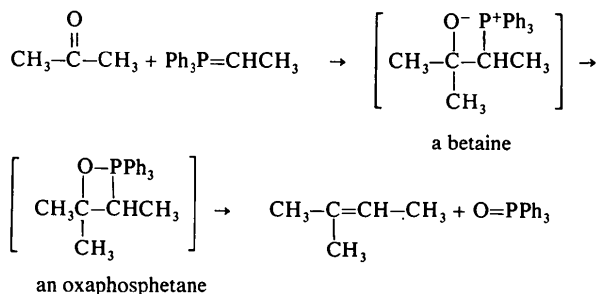$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Se	0·63900 (4)	0·44427 (3)	0·39609 (3)	0·03706 (2)
P	0·77540 (10)	0·25077 (9)	0·45157 (6)	0·03073 (4)
O	0·9231 (3)	0·2857 (2)	0·3300 (2)	0·0448 (1)
C(1)	0·7474 (4)	0·3393 (3)	0·3793 (2)	0·0330 (2)
C(2)	0·8322 (4)	0·3422 (3)	0·3247 (2)	0·0346 (2)
C(11)	0·4789 (4)	0·3866 (3)	0·3690 (2)	0·0357 (2)
C(12)	0·3822 (4)	0·4275 (4)	0·4031 (3)	0·0486 (2)
C(13)	0·2650 (5)	0·3891 (5)	0·3855 (3)	0·0654 (2)
C(14)	0·2430 (5)	0·3096 (5)	0·3374 (3)	0·0621 (2)
C(15)	0·3393 (5)	0·2693 (4)	0·3050 (3)	0·0543 (2)
C(16)	0·4569 (4)	0·3072 (4)	0·3201 (3)	0·0443 (2)
C(21)	0·8181 (4)	0·4150 (3)	0·2589 (2)	0·0370 (2)
C(22)	0·9205 (4)	0·4675 (4)	0·2433 (3)	0·0481 (2)
C(23)	0·9137 (6)	0·5360 (4)	0·1844 (3)	0·0622 (2)
C(24)	0·8033 (6)	0·5496 (4)	0·1395 (3)	0·0659 (2)
C(25)	0·7010 (5)	0·4946 (4)	0·1515 (3)	0·0666 (2)
C(26)	0·7085 (5)	0·4287 (4)	0·2124 (3)	0·0503 (2)
C(31)	0·6458 (4)	0·2428 (3)	0·5072 (2)	0·0368 (2)
C(32)	0·6360 (4)	0·3071 (4)	0·5681 (3)	0·0469 (2)
C(33)	0·5330 (5)	0·3040 (4)	0·6080 (3)	0·0584 (2)
C(34)	0·4417 (5)	0·2353 (5)	0·5874 (3)	0·0707 (2)
C(35)	0·4508 (5)	0·1717 (5)	0·5276 (3)	0·0701 (2)
C(36)	0·5530 (4)	0·1745 (4)	0·4878 (3)	0·0506 (2)
C(41)	0·7888 (4)	0·1292 (3)	0·4116 (2)	0·0329 (2)
C(42)	0·8431 (4)	0·0521 (3)	0·4559 (2)	0·0382 (2)
C(43)	0·8423 (4)	−0·0420 (4)	0·4259 (3)	0·0496 (2)
C(44)	0·7901 (5)	−0·0609 (4)	0·3526 (3)	0·0542 (2)
C(45)	0·7361 (5)	0·0149 (5)	0·3082 (3)	0·0620 (2)
C(46)	0·7363 (5)	0·1105 (4)	0·3368 (3)	0·0520 (2)
C(51)	0·9059 (4)	0·2776 (3)	0·5223 (2)	0·0327 (1)
C(52)	0·9139 (4)	0·2392 (4)	0·5961 (3)	0·0405 (2)
C(53)	1·0084 (5)	0·2688 (4)	0·6514 (3)	0·0483 (2)
C(54)	1·0961 (5)	0·3336 (4)	0·6329 (3)	0·0561 (2)
C(55)	1·0887 (5)	0·3712 (5)	0·5593 (3)	0·0722 (2)
C(56)	0·9937 (5)	0·3437 (4)	0·5038 (3)	0·0583 (2)

(Bjørnevåg, Husebye & Maartmann-Moe, 1982) and 1·48 Å (Bastiansen & Trætteberg, 1962) for the first two; the last is significantly longer than a C=O double bond of ca 1·20 Å (Bozak, Husebye, Maartmann-Moe & Rinehart, 1985). In the analogous ylides where SePh is replaced by halogens (Speziale & Ratts, 1965), the corresponding bond lengths are 1·736 (14), 1·361 (20) and 1·301 (19) Å for the Cl compound, and the Br and I compounds are quite similar. In these ylides, as well as in the present compound, the P—C—C—O group is *cis* with respect to the C—C bond. This will align P⁺ and O⁻(III, P—O = 2·856 Å) and the result may be considered as an intermediate in the intramolecular Wittig reaction that leads to the formation of tri-phenylphosphine oxide and phenyl(phenylseleno)-acetylene (Braga, Comasseto & Petragnani, 1984). A *trans* orientation of the P—C(1)—C(2)—O group is difficult owing to steric interactions of phenyl bonded to C(2) and the triphenylphosphine group. According to the resonance shown, C(1) and C(2) should be sp^2 hybridized and the central P—C(1)—C(2)—O—Se—C(21) group should be planar. While C(2) is sp^2, C(1) is slightly pyramidal (angle sum = 357·5°). Thus, only the P—C(1)—C(2)—O part of the central group is really planar. The effect is probably due to steric interactions between the phenylseleno group and other phenyl

groups [Se—C(36) = 3·393, Se—C(32) = 3·542, Se—C(26) = 3·393, C(16)—C(36) = 3·499 and C(11)—C(31) = 3·460 Å]. With phenylseleno replaced by Cl, the P—C—C—O—Cl group is, as expected, found to be more planar (Speziale & Ratts, 1965). Chicciola & Daly (1968) have solved the structure of another Wittig-reaction intermediate containing a four-membered planar ring, namely

$$\begin{array}{c} \text{Ph}_3\text{P}-\text{C}-\text{P}'\text{Ph}_3 \\ \quad |\quad\; | \\ \quad \text{O}-\text{C}'(\text{CF}_3)_2 \end{array} \quad,$$

(V)

where P—C = 1·760 (20), P—O = 2·012 (14), O—C' = 1·390 (22), C'—C = 1·572 (26) Å and ring angles vary from 71·3 to 98·5°. P—O is significantly longer than a single bond, while P—C and C—O have some double-bond character. Thus, there is some contribution from an ionic form analogous to (III). There is considerable double-bond character in C—P' [=1·745 (20) Å] and Chicciola & Daly propose that the ring structure is stabilized by P⋯C⋯P' bonding.

The Wittig reaction as outlined in recent textbooks is a three-step reaction. For example (Streitwieser & Heathcock, 1981):

$$\begin{array}{c}\quad\;\;\text{O}\\ \quad\;\;\|\\ \text{CH}_3-\text{C}-\text{CH}_3 + \text{Ph}_3\text{P}=\text{CHCH}_3\end{array} \rightarrow \left[\begin{array}{c}\quad\text{O}^-\;\text{P}^+\text{Ph}_3\\ \quad\;\;|\quad\;|\\ \text{CH}_3-\text{C}-\text{CHCH}_3\\ \quad\;\;|\\ \quad\;\;\text{CH}_3\end{array}\right] \rightarrow$$

a betaine

$$\left[\begin{array}{c}\quad\text{O}-\text{PPh}_3\\ \quad\;|\\ \text{CH}_3\text{C}-\text{CHCH}_3\\ \quad\;|\\ \quad\;\text{CH}_3\end{array}\right] \rightarrow \begin{array}{c}\text{CH}_3-\text{C}=\text{CH}-\text{CH}_3 + \text{O}=\text{PPh}_3\\ \quad\;|\\ \quad\;\text{CH}_3\end{array}$$

an oxaphosphetane

From the above, we see that in the present investigation we have a betaine-type intermediate, whereas (V) represents an oxaphosphetane-type intermediate. Both
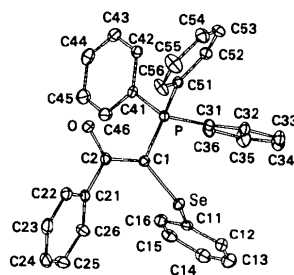

Fig. 1. *ORTEP* (Johnson, 1965) drawing of $C_{32}H_{25}OPSe$. (H atoms not shown.)

intermediates upon heating yield O—PPh₃ and unsaturated hydrocarbons (Birum & Matthews, 1967). It is possible that an oxaphosphetane-ring-type structure is less stable than the betaine-type structure for the triphenyl[α-(phenylseleno)phenacylidene]phosphorane because of the extra strain imposed on a four-membered ring by the C=C double bond. At 2·856 Å, P and O are fairly close when compared to a van der Waals contact of 3·30 Å (Pauling, 1960), but it is doubtful that this indicates the existence of bonding interaction between the two atoms.

Bond lengths involving Se are Se—C(11) = 1·927 (4) and Se—C(1) = 1·898 (4) Å. These distances both agree well with average Se—C(sp^2) single bonds of 1·915 Å found in diaryl diselenides (Van den Bossche, Spirlet, Dideberg & Dupont, 1984). Recently, the structure of triphenyl[(phenylseleno)(phenylthio)-methylene]phosphorane, an ylide with both a phenyl-seleno and a phenylthio group bonded to the ylide C

atom, was solved (Schmidbaur, Zybill, Kruger & von Kraus, 1983). Here the Se—C bonds to phenyl and ylide C are nearly equal, 1·924 (8) and 1·919 (7) Å, respectively. The corresponding S—C bond lengths are 1·732 (4) and 1·800 (7) Å, and this highly significant difference in the S—C bonds was taken as an indication of possible multiple bonding in the S—C ylide bond [the S—C(phenyl) bond corresponds to a normal single bond]. P—C(ylide) in this compound was found to be 1·707 (Å), shorter than that found in the present investigation, but longer than that found in the ylide Ph₃P=CH₂, 1·66 Å (Bart, 1969). This is probably due to delocalization of negative charge into the d orbitals of S. The difference in the Se—C bonds in triphenyl[α-(phenylseleno)phenacylidene]phosphorane is perhaps not significant but, if it is, it may indicate a weak tendency to double bonding analogous to that for S—C(ylide) mentioned above. The stability of ylides of the type Ph₃P=C(R)SePh has been attributed to delocalization of negative charge into d orbitals on selenium (Petragnani, Rodriguez & Comasseto, 1976). The interatomic angles have normal values, but angle P—C(1)—C(2) is only 115·9°, while Se—C(1)—C(2) is 123·9°. This is probably due to the repulsion between Se and the phenyl group bonded to C(2) mentioned above. Average C—C bond lengths and C—C—C angles in the phenyl groups are 1·383 Å and 120·0°, respectively. The endocyclic angles at substituted carbons are systematically smaller than 120°. For P, Se and C substitution, they are 119·4 (2), 119·4 (4) and 118·9 (4)°, respectively, in reasonable agreement with the predictions of Domenicano, Vaciago & Coulson (1975). Average C—H bond lengths and C—C—H angles are 1·08 Å and 119·9°. Stereoviews of the unit cell and its contents are given in Fig. 2.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Se—C(11)	1·927 (4)	C(31)—C(32)	1·391 (7)
Se—C(1)	1·898 (4)	C(32)—C(33)	1·394 (7)
P—C(1)	1·746 (4)	C(33)—C(34)	1·385 (8)
P—C(31)	1·814 (4)	C(34)—C(35)	1·369 (9)
P—C(41)	1·804 (4)	C(35)—C(36)	1·385 (7)
P—C(51)	1·815 (4)	C(36)—C(31)	1·387 (6)
C(1)—C(2)	1·406 (6)	C(41)—C(42)	1·395 (6)
C(2)—O	1·252 (5)	C(42)—C(43)	1·381 (7)
C(2)—C(21)	1·512 (6)	C(43)—C(44)	1·367 (7)
C(11)—C(12)	1·390 (6)	C(44)—C(45)	1·380 (8)
C(12)—C(13)	1·386 (7)	C(45)—C(46)	1·391 (8)
C(13)—C(14)	1·373 (9)	C(46)—C(41)	1·391 (6)
C(14)—C(15)	1·367 (8)	C(51)—C(52)	1·385 (6)
C(15)—C(16)	1·383 (7)	C(52)—C(53)	1·391 (6)
C(16)—C(11)	1·379 (6)	C(53)—C(54)	1·368 (8)
C(21)—C(22)	1·381 (7)	C(54)—C(55)	1·380 (8)
C(22)—C(23)	1·384 (7)	C(55)—C(56)	1·390 (7)
C(23)—C(24)	1·376 (8)	C(56)—C(51)	1·380 (7)
C(24)—C(25)	1·382 (9)		
C(25)—C(26)	1·386 (7)		
C(26)—C(21)	1·382 (6)		

C(11)—Se—C(1)	102·9 (2)	C(23)—C(24)—C(25)	120·9 (5)
Se—C(1)—P	117·7 (2)	C(24)—C(25)—C(26)	119·3 (5)
Se—C(1)—C(2)	123·9 (3)	C(25)—C(26)—C(21)	120·6 (5)
P—C(1)—C(2)	115·9 (3)	P—C(31)—C(32)	120·5 (3)
C(1)—P—C(31)	110·3 (2)	P—C(31)—C(36)	120·3 (3)
C(1)—P—C(41)	111·4 (2)	C(32)—C(31)—C(36)	119·2 (4)
C(1)—P—C(51)	114·5 (2)	C(31)—C(32)—C(33)	120·2 (4)
C(31)—P—C(41)	104·9 (2)	C(32)—C(33)—C(34)	119·4 (5)
C(31)—P—C(51)	104·4 (2)	C(33)—C(34)—C(35)	120·6 (5)
C(41)—P—C(51)	110·8 (2)	C(34)—C(35)—C(36)	120·1 (5)
C(1)—C(2)—O	121·0 (4)	C(35)—C(36)—C(31)	120·4 (5)
C(1)—C(2)—C(21)	121·2 (4)	P—C(41)—C(42)	121·3 (3)
O—C(2)—C(21)	117·8 (4)	P—C(41)—C(46)	119·2 (3)
Se—C(11)—C(12)	116·6 (3)	C(42)—C(41)—C(46)	119·3 (4)
Se—C(11)—C(16)	124·0 (3)	C(41)—C(42)—C(43)	119·9 (4)
C(12)—C(11)—C(16)	119·4 (4)	C(42)—C(43)—C(44)	121·0 (4)
C(11)—C(12)—C(13)	119·0 (5)	C(43)—C(44)—C(45)	119·5 (5)
C(12)—C(13)—C(14)	121·6 (5)	C(44)—C(45)—C(46)	120·7 (5)
C(13)—C(14)—C(15)	118·6 (5)	C(45)—C(46)—C(41)	119·5 (4)
C(14)—C(15)—C(16)	121·1 (5)	P—C(51)—C(52)	121·3 (3)
C(15)—C(16)—C(11)	120·1 (4)	P—C(51)—C(56)	118·9 (3)
C(2)—C(21)—C(22)	118·2 (4)	C(52)—C(51)—C(56)	119·6 (4)
C(2)—C(21)—C(26)	122·8 (4)	C(51)—C(52)—C(53)	120·0 (4)
C(22)—C(21)—C(26)	118·9 (4)	C(52)—C(53)—C(54)	120·5 (4)
C(21)—C(22)—C(23)	121·2 (4)	C(53)—C(54)—C(55)	119·4 (5)
C(22)—C(23) C(24)	119·0 (5)	C(54)—C(55)—C(56)	120·8 (5)
		C(55)—C(56)—C(51)	119·7 (4)

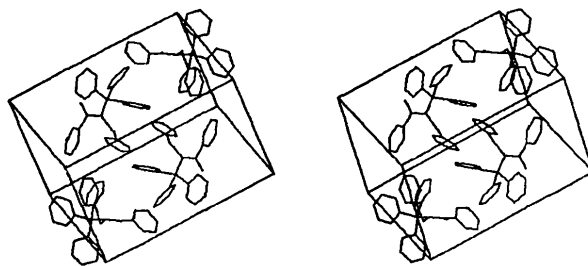

Fig. 2. Packing diagram for C₃₂H₂₅OPSe.

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Molecular Geometry of 3-Bromo-λ⁶-thietane 1,1-Dioxide in the Gas Phase and Comparison with the Crystal Molecular Structure

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Abstract. The molecular geometry of 3-bromo-λ⁶-thietane 1,1-dioxide, $C_3H_5BrO_2S$ ($M_r = 185$), was determined in the gas phase by electron diffraction. The overall structure of the free molecule is in agreement with that determined in the crystal [Chiang (1983). *Acta Cryst.* C**39**, 737–738]. The most important differences are as follows: the ring is more puckered, the C—C bond is longer and the SO_2 group is more open in the gas phase than were found in the crystal.

Introduction. The purpose of this study is to determine the molecular geometry of 3-bromo-λ⁶-thietane 1,1-

dioxide in the gas phase by electron diffraction, to compare it to other organosulfone structures (Hargittai, 1985a) and, in particular, to the crystal molecular structure of the same compound (Chiang, 1983).

Experimental. The sample was supplied by Professor D. C. Dittmer of Syracuse University. The electron diffraction patterns were recorded in Budapest with a modified EG-100A apparatus (Hargittai, Tremmel & Kolonits, 1980; Tremmel, Kolonits & Hargittai, 1977). A so-called membrane nozzle system was used (Hargittai, Hernádi, Kolonits & Schultz, 1971) with a nozzle temperature of 453 K and nozzle-to-plate distance of 50 and 19 cm. The treatment of the experimental data and the procedure of analysis followed the usual techniques of the Budapest group (see, for example, Domenicano, Schultz, Kolonits & Hargittai, 1979). The total range of

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