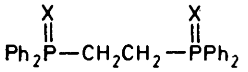
A Study of the Inclusion Properties of 1,2-Bis(diphenylphosphinoselenoyl)ethane and Related Host Molecules

By **Douglas H. Brown, Ronald J. Cross,* Paul R. Mallinson,*** and **David D. MacNicol,*** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

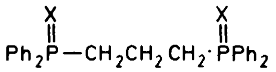
The title compound (I) has been found to form stable adducts when recrystallised from various pure solvents. Most significantly, host (I) exhibits a remarkably high selectivity for certain *para*-disubstituted aromatic molecules. For example, recrystallisation of (I) from an equimolar mixture of each of the xylenes, and ethylbenzene leads to incorporation of 97.5% of *p*-xylene. An *X*-ray investigation of the inclusion compound of (I) with *p*-xylene has been carried out. Crystals are triclinic, space group $P\bar{1}$, with $a = 8.958(1)$, $b = 14.822(2)$, $c = 15.496(2)$ Å, $\alpha = 81.20(1)°$, $\beta = 83.05(1)°$, $\gamma = 79.38(1)°$, with three host and a single guest molecule in the unit cell. The structure was refined by least-squares methods to a final R of 0.036 for 2 558 significant diffractometer data. The adduct is of the true clathrate type, the highly ordered *p*-xylene guest being accommodated in an effectively closed cage. Compounds (II)—(V) which are structurally related to (I) have also been prepared and found to exhibit inclusion behaviour, but to a lesser degree than (I).

In a preliminary communication[1] we briefly described the ability of the title compound (I) to act as host in the formation of molecular inclusion compounds.[2] The marked selective inclusion behaviour of (I) is of interest with respect to the separation of solvent mixtures,[3] and we now report results of a detailed study of the host (I). In the case of the inclusion compound with *p*-xylene we have performed a single-crystal *X*-ray diffraction analysis in order to determine the molecular architecture of (I) and also to elucidate accurately the geometry of the voids available for guest accommodation. We also report the discovery of significant inclusion behaviour for the structurally related compounds (II)—(V).



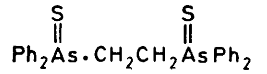
$$\mathrm{Ph_2}\overset{\overset{X}{\|}}{\mathrm{P}}\mathrm{-CH_2CH_2-}\overset{\overset{X}{\|}}{\mathrm{P}}\mathrm{Ph_2}$$

(I) X = Se
(II) X = S



$$\mathrm{Ph_2}\overset{\overset{X}{\|}}{\mathrm{P}}\mathrm{-CH_2CH_2CH_2\cdot}\overset{\overset{X}{\|}}{\mathrm{P}}\mathrm{Ph_2}$$

(III) X = S
(IV) X = Se



$$\mathrm{Ph_2}\overset{\overset{S}{\|}}{\mathrm{As}}\mathrm{\cdot CH_2CH_2}\overset{\overset{S}{\|}}{\mathrm{As}}\mathrm{Ph_2}$$

(V)

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian T-60, Varian HA-100, or JEOL C-60HL instruments, and i.r. spectra were obtained from Perkin-Elmer 225 or 580 spectrophotometers. Ditertiary phosphines and arsines were obtained from Strem Chemicals, Inc., Fluorochem Ltd., and Maybridge Chemical Co., and converted into the known sulphides and selenides (I)—(V) by refluxing in benzene with a small excess of sulphur or selenium, respectively.[4] Data for inclusion compounds formed by (I) on crystallisation from a number of single solvents are given in Table 1. Results for selective inclusion experiments are given in Table 2. In these experiments guest material was released from the clathrate compound by heating *in vacuo* at 400 K, and trapping the volatiles at 77 K. Quantitative analysis was by standard i.r. absorbance techniques[5] using the aromatic out-of-plane bending modes in the region 690—800 cm^{-1}.

The following experiments using host (I) and equimolar mixtures of the xylene isomers and ethylbenzene illustrate the methods used in the preparation of the inclusion compounds.

Example 1 (*No Co-solvent*).—Host (I) (3 g) was dissolved in an equimolar mixture of *o*-, *m*-, and *p*-xylene and ethylbenzene (25 ml) at 383 K. The solution was allowed to cool at *ca.* 1° min^{-1}, and crystallisation was initiated at 360 K by seeding the solution with crystal fragments of the *p*-xylene adduct of (I). The crystals (2.9 g) were purified by decantation, washing with n-pentane, and evacuation (*ca.* 0.01 Torr) at room temperature for 1 h. Multiple ^{1}H n.m.r. integration of a CDCl$_3$ solution established a host : guest molar ratio of 3 : 1. Hydrocarbon was recovered from a sample of the adduct by heating *in vacuo*, and shown (by i.r. analysis) to consist of predominantly *p*-xylene (see Table 2).

TABLE 1

Representative inclusion compounds of $Ph_2P(Se)C_2H_4P(Se)Ph_2$ (I)

Guest molecule	Mole ratio of host : guest	Conditions for guest release
Benzene	0.75 : 1 [a]	Slow loss at room temperature
Cyclohexane	4 : 1 [c]	*b*
Toluene	2.4 : 1 [c]	70 °C and 0.04 mmHg
o-Xylene	0.8 : 1 [c]	Slow loss at room temperature
Naphthalene [d]	2.5 : 1 [a]	160 °C and 0.08 mmHg
p-Xylene	2.9 : 1 [a,c]	155 °C and 0.08 mmHg
p-Chlorotoluene	3.0 : 1 [a,c]	135 °C and 0.08 mmHg
p-Dichlorobenzene	3.0 : 1 [a]	145 °C and 0.08 mmHg
p-Dibromobenzene	2.9 : 1 [a]	170 °C and 0.08 mmHg
sym-Tetrachloroethane	1.9 : 1 [c]	100 °C and 0.08 mmHg
p-Cresol [e]	2.5 : 1 [c]	*b*

[a] Determined by gravimetric analysis. [b] Not determined. [c] Found by multiple ^{1}H n.m.r. integration. [d] Chloroform was employed as co-solvent. [e] n-Hexane was employed as co-solvent.

Example 2 (CHCl$_3$ *Co-solvent*).—Host (I) (2 g) was dissolved in an equimolar mixture of the three xylene isomers, ethylbenzene, and chloroform (25 ml) at 363 K and the solution was allowed to cool at 1° min^{-1}. The crystalline inclusion compound (1.9 g) was obtained and purified as above. The hydrocarbon released on heating *in vacuo* was analysed by ^{1}H n.m.r. spectrometry and found to consist mainly of *p*-xylene (>95%), with detectable traces of ethylbenzene, *o*-xylene, and *m*-xylene.

Example 3 (*Sorption Method*).—Host (I) (1.9 g) was stirred for 20 h in an equimolar mixture of the xylene isomers and ethylbenzene (8 ml) at 295 K. The crystalline inclusion compound (1.85 g) was isolated and purified as before. Gravimetric analysis of a small sample gave a host : guest ratio of 3 : 1, and i.r. analysis of a sample of the recovered hydrocarbon guest gave the composition shown in Table 2.

TABLE 2

Guest-selectivity properties of hosts (I) and (III)

Host	Recrystallisation solvent mixture	Respective percentage of guest included [a]				Overall host : guest ratio [b]
(I)	*p*-Xylene–*m*-xylene–*o*-xylene–ethylbenzene (1 : 1 : 1 : 1)	97.5	0.6	0.4	1.5	3 : 1 [d]
		96.8 [c]	0.7 [c]	0.5 [c]	2.0 [c]	
(I)	*p*-Chlorotoluene–*m*-chlorotoluene–*o*-chlorotoluene (1 : 1 : 1)	98.3	1.5	0.2		3 : 1 [d]
(I)	*p*-Dichlorobenzene–*m*-dichlorobenzene–*o*-dichlorobenzene (1 : 1 : 1)	94.8	2.6	2.6		3 : 1 [d]
(III)	*p*-Xylene–*m*-xylene–*o*-xylene–ethylbenzene (1 : 1 : 1 : 1)	58	13	26	3	2 : 1 [d]
(III)	Benzene–cylohexane (1 : 1)	20 [d]	80 [d]			2 : 1 [d]
(III)	*p*-Xylene–*o*-xylene (1 : 1)	66 [d]	34 [d]			2 : 1 [d]

[a] Measured by i.r. absorption method.[5] [b] Given to nearest integral ratio. [c] Results from a sorption experiment (see Experimental section). [d] Determined by ^{1}H n.m.r. integration.

Crystal Structure Analysis of p-*Xylene Adduct of* (I).—*Crystal data.* $C_{78}H_{72}P_6Se_6[3\times(I)]\cdot C_8H_{10}$, $M = 1\,775.2$. Triclinic, $a = 8.958(1)$, $b = 14.822(2)$, $c = 15.496(2)$ Å, $\alpha = 81.20(1)°$, $\beta = 83.05(1)°$, $\gamma = 79.38(1)°$, $U = 1\,989.3$ Å^3, $Z = 1$, $D_c = 1.48$ g cm^{-3}. $F(000) = 892$. Space group $P\bar{1}$ (no. 2). $\mu = 28.2$ cm^{-1} for Mo-K_α radiation, $\lambda = 0.710\,7$ Å (1 Å $\equiv 10^{-10}$ m).

TABLE 3

Inclusion compounds of hosts (II)—(V)

Host	Guest	Mole ratio of Host : guest [a]
(II)	*p*-Xylene [d]	6 : 1
(III)	Benzene	2 : 1
(III)	Cyclohexane [e]	2 : 1
(III)	*p*-Xylene	2 : 1
(III)	*m*-Xylene	2 : 1
(III)	*p*-Diethylbenzene	1 : 1
(IV) [b]	Benzene	1 : 1
(IV)	Cyclohexane	2 : 1
(IV)	$CHCl_2CHCl_2$	1 : 1
(V)	Benzene	*c*

[a] Measured by multiple ^{1}H n.m.r. integration, and given to the nearest integral ratio. [b] All attempts to include *p*-xylene in host (IV) were unsuccessful. [c] Rapid loss of included benzene prevented accurate determination of the host : guest ratio. Toluene, *p*-xylene, and cyclohexane did not give adducts with (V). [d] (II) did not include any guest when crystallised from a 70 : 30 *o*-xylene–*p*-xylene mixture. [e] See also Table 2.

Colourless, tabular crystals, obtained by crystallisation of (I) from *p*-xylene, develop a slightly powdery surface after several days exposure to the atmosphere. An equidimensional fragment measuring 0.07 mm was used for the measurement at room temperature (20°) of 6 996 independent *X*-ray intensities by a θ—ω scan on a Nonius CAD-4 diffractometer, by use of graphite-monochromated Mo-K_α radiation. These comprised all possible reflections with $\sin\theta/\lambda < 0.59$ Å^{-1}. 2 558 Reflections having $F^2 > 2\sigma(F^2)$ were considered observed, where $\sigma(F^2) = [C + 4(B_1 + B_2) + 0.000\,9I^2]^{\frac{1}{2}}/(t_C Lp)$, where C is the total integrated count in time t_C, B_1 and B_2 are background counts, $I = C - 2(B_1 + B_2)$, and Lp is the correction factor for Lorentz and polarisation effects. Intensities were corrected for these but not for absorption. Counting-coincidence errors were avoided by use of an attenuator on high intensities. Unit-cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 reflections. Computations were carried out on an I.C.L. 2976 computer at Glasgow University; the principal computer programs used are listed in ref. 6. Atomic scattering factors were taken from ref. 7.

Structure Determination.—The formula contains two asymmetric units, requiring the guest molecule and at least one molecule of (I) to be centrosymmetric or disordered, with all atoms in general positions. The structure was solved by the heavy-atom method, the selenium positions having been deduced from the Patterson function. Two cycles of isotropic least-squares refinement of the non-hydrogen parameters brought R to 0.091. All the hydrogen atoms were located in difference-maps calculated during 10 cycles of anisotropic least-squares refinement, which reduced R to a final value of 0.036, with R' 0.037 [$R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. All isotropic hydrogen parameters were included in the refinement. The function minimised was $\Sigma w\Delta^2$, where $w = 1/\sigma^2(F_o)$, $\Delta = ||F_o| - |F_c||^2$. The three independent half-molecules of (I) were refined in separate, successive cycles, together with the guest molecule and hydrogen atoms. A difference-Fourier map computed from the final structure factors for the observed reflections showed no peaks or holes of magnitude >0.6 e Å^{-3}.

RESULTS

Atomic co-ordinates and their estimated standard deviations are in Table 4. Temperature factors, structure factors, and bond angles are in Supplementary Publication No. SUP 22741 (24 pp.).* Tables 5 and 6 show the bond lengths and selected angles. Selected torsion angles are in Table 7. The labelling of the atoms is shown on Figure 1.

DISCUSSION

Inclusion Properties of Compound (I).—Table 1 gives the host : guest ratios of adducts formed by (I). Notably, the *para*-disubstituted aromatic guests exhibit a ratio of close to 3 : 1, and these guest species are relatively tightly held in the adducts, requiring to be heated in

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* For details of Supplementary Publications see Notice to Authors No. 7, in *J.C.S. Perkin II*, 1979, Index issue.

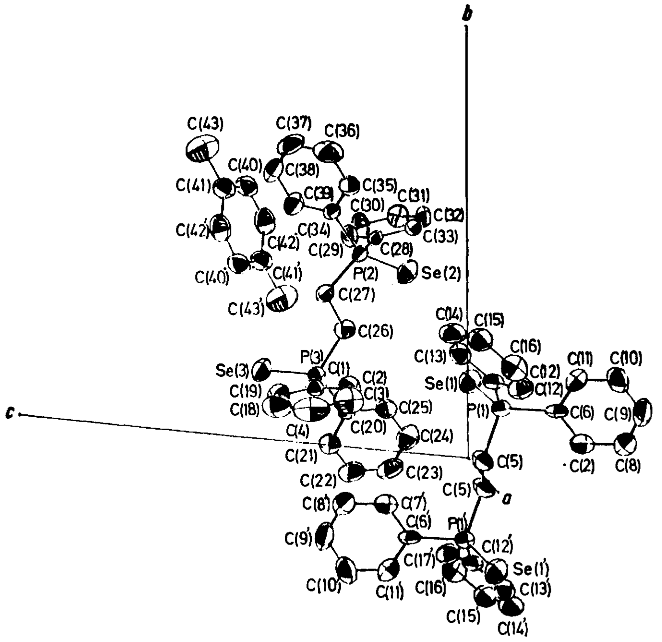

FIGURE 1 The two independent host molecules and the guest molecule. The primed symbols refer to the following equivalent positions with respect to the asymmetric unit at x, y, z: host atoms: $1 - x, -y, -z$; guest atoms: $1 - x, 1 - y, 1 - z$

TABLE 4

Fractional atomic co-ordinates ($\times 10^4$, hydrogen co-ordinates $\times 10^3$). Numbers in parentheses are the e.s.d. in the least significant digits. Hydrogen atoms have the numbers of the carbon atoms to which they are attached

	x/a	y/b	z/c
Se(1)	2 551(1)	11 956(1)	10 116(1)
Se(2)	−1 557(1)	5 713(1)	8 578(1)
Se(3)	1 586(1)	8 460(1)	5 379(1)
P(1)	4 788(2)	11 518(1)	9 594(1)
P(2)	225(2)	5 428(1)	7 600(1)
P(3)	279(2)	8 374(1)	6 599(1)
C(1)	−1 753(9)	8 581(5)	6 508(5)
C(2)	−2 756(11)	8 484(8)	7 249(9)
C(3)	−4 318(14)	8 667(10)	7 166(13)
C(4)	−4 870(14)	8 921(7)	6 354(11)
C(5)	5 518(12)	10 343(6)	10 044(7)
C(6)	4 991(9)	11 590(5)	8 411(5)
C(7)	6 030(12)	10 968(7)	7 955(7)
C(8)	6 209(14)	11 067(8)	7 049(8)
C(9)	5 362(15)	11 778(9)	6 597(8)
C(10)	4 313(14)	12 407(9)	7 025(7)
C(11)	4 167(12)	12 302(7)	7 912(7)
C(12)	6 168(9)	12 163(5)	9 850(5)
C(13)	5 868(12)	12 689(6)	10 531(6)
C(14)	6 911(16)	13 159(7)	10 750(8)
C(15)	8 305(15)	13 130(7)	10 263(7)
C(16)	8 626(12)	12 612(7)	9 585(7)
C(17)	7 583(12)	12 139(7)	9 382(7)
C(18)	−3 858(15)	8 987(7)	5 641(10)
C(19)	−2 309(12)	8 828(7)	5 702(7)
C(20)	611(8)	9 201(5)	7 281(5)
C(21)	945(12)	10 038(7)	6 880(7)
C(22)	1 255(12)	10 684(8)	7 382(9)
C(23)	1 139(12)	10 513(8)	8 260(9)
C(24)	806(14)	9 689(9)	8 662(8)
C(25)	526(12)	9 042(7)	8 165(7)
C(26)	648(11)	7 257(5)	7 255(6)
C(27)	393(11)	6 447(6)	6 814(5)
C(28)	2 053(8)	5 047(4)	8 020(5)
C(29)	3 396(10)	5 069(6)	7 475(6)
C(30)	4 799(11)	4 795(7)	7 785(6)
C(31)	4 880(11)	4 471(7)	8 659(7)
C(32)	3 578(11)	4 424(6)	9 196(7)
C(33)	2 160(10)	4 703(5)	8 886(5)
C(34)	−24(8)	4 528(5)	6 984(5)
C(35)	−938(11)	3 893(6)	7 348(7)
C(36)	−1 075(15)	3 184(7)	6 901(10)
C(37)	−311(15)	3 105(8)	6 097(9)
C(38)	551(12)	3 723(8)	5 723(7)
C(39)	723(11)	4 442(7)	6 161(6)
C(40)	4 091(13)	5 842(7)	4 899(6)
C(41)	5 292(12)	5 741(6)	5 367(6)
C(42)	6 217(11)	4 888(8)	5 465(6)
C(43)	5 631(18)	6 535(10)	5 785(11)
H(2)	−225(25)	828(14)	784(13)
H(3)	−487(15)	836(9)	762(9)
H(4)	−600(12)	892(6)	637(6)
H(5A)	555(5)	1 025(3)	1 072(3)
H(5B)	650(7)	1 019(4)	978(4)
H(7)	653(5)	1 052(3)	823(3)
H(8)	704(8)	1 060(5)	679(5)
H(9)	554(6)	1 185(4)	601(4)
H(10)	385(6)	1 289(4)	670(4)
H(11)	345(5)	1 258(3)	822(3)
H(13)	506(5)	1 265(3)	1 080(3)
H(14)	664(7)	1 348(4)	1 119(4)
H(15)	906(8)	1 346(5)	1 049(5)
H(16)	957(6)	1 265(4)	920(4)
H(17)	773(6)	1 186(4)	898(3)
H(18)	−415(9)	916(5)	508(5)
H(19)	−165(9)	894(6)	525(5)
H(21)	105(8)	1 019(5)	625(5)
H(22)	135(8)	1 129(5)	719(4)
H(23)	144(11)	1 091(7)	850(7)
H(24)	66(8)	951(5)	930(5)
H(25)	25(7)	857(4)	844(4)
H(26A)	164(6)	720(3)	738(3)
H(26B)	6(8)	725(5)	787(5)
H(27A)	120(7)	638(4)	633(4)
H(27B)	−48(6)	660(4)	656(3)
H(29)	334(6)	523(4)	689(4)
H(30)	569(6)	488(4)	748(4)
H(31)	571(5)	441(3)	889(3)
H(32)	366(6)	424(4)	972(4)
H(33)	115(6)	467(4)	935(4)
H(35)	−142(6)	387(4)	789(4)
H(36)	−171(7)	286(4)	714(4)
H(37)	−52(7)	270(4)	579(4)
H(38)	102(8)	380(4)	507(4)
H(39)	128(8)	482(5)	594(5)
H(40)	344(8)	635(5)	480(4)
H(42)	690(7)	479(4)	584(4)
H(43A)	614(11)	699(7)	524(6)
H(43B)	631(10)	641(6)	614(6)
H(43C)	484(12)	698(7)	600(7)

excess of 130 °C at low pressure for their release. In contrast, the benzene and *o*-xylene adducts, with lower host : guest ratios, undergo slow guest loss at ambient temperature. A critical dependence on prospective guest shape and size is suggested by the failure of ethylbenzene and *para*-diethylbenzene to form adducts. However, even with guests of favourable size and shape the formation of inclusion compounds occurs only when the onset of crystallisation is not above *ca.* 100 °C. Above this temperature, unsolvated crystals are produced which subsequently grow on cooling without incorporation of solvent.

Typical results of selective inclusion experiments are summarised in Table 2. In each case a very marked selectivity for the *para*-isomer is apparent. Interestingly, the high *para*-selectivity was retained in a sorption

TABLE 5

Bond lengths (Å) in the *p*-xylene adduct of (I), with e.s.d. in the least significant digits in parentheses

Se(1)–P(1)	2.094(2)	C(20)–C(21)	1.37(1)
Se(2)–P(2)	2.094(2)	C(20)–C(25)	1.35(1)
Se(3)–P(3)	2.099(2)	C(21)–C(22)	1.41(2)
P(1)–C(5)	1.807(9)	C(21)–H(21)	0.97(8)
P(1)–C(6)	1.807(8)	C(22)–C(23)	1.34(2)
P(1)–C(12)	1.809(8)	C(22)–H(22)	0.92(7)
P(2)–C(27)	1.807(9)	C(23)–C(24)	1.35(2)
P(2)–C(28)	1.797(7)	C(23)–H(23)	0.85(10)
P(2)–C(34)	1.814(7)	C(24)–C(25)	1.39(2)
P(3)–C(1)	1.809(8)	C(24)–H(24)	0.98(8)
P(3)–C(20)	1.821(8)	C(25)–H(25)	0.83(6)
P(3)–C(26)	1.801(8)	C(26)–C(27)	1.53(1)
C(1)–C(2)	1.38(2)	C(26)–H(26A)	0.92(5)
C(1)–C(19)	1.37(1)	C(26)–H(26B)	1.02(7)
C(2)–C(3)	1.39(2)	C(27)–H(27A)	0.98(6)
C(2)–H(2)	1.04(20)	C(27)–H(27B)	0.90(6)
C(3)–C(4)	1.38(2)	C(28)–C(29)	1.39(1)
C(3)–H(3)	0.93(14)	C(28)–C(33)	1.37(1)
C(4)–C(18)	1.35(2)	C(29)–C(30)	1.37(1)
C(4)–H(4)	1.01(10)	C(29)–H(29)	0.91(5)
C(5)–H(5A)	1.04(5)	C(30)–C(31)	1.37(1)
C(5)–H(5B)	0.93(7)	C(30)–H(30)	0.90(6)
C(5)–C(5′)	1.53(1)	C(31)–C(32)	1.35(1)
C(6)–C(7)	1.39(1)	C(31)–H(31)	0.85(5)
C(6)–C(11)	1.36(1)	C(32)–C(33)	1.38(1)
C(7)–C(8)	1.38(2)	C(32)–H(32)	0.82(6)
C(7)–H(7)	0.82(5)	C(33)–H(33)	1.09(6)
C(8)–C(9)	1.34(2)	C(34)–C(35)	1.37(1)
C(8)–H(8)	1.01(7)	C(34)–C(39)	1.38(1)
C(9)–C(10)	1.38(2)	C(35)–C(36)	1.37(1)
C(9)–H(9)	0.89(6)	C(35)–H(35)	0.90(6)
C(10)–C(11)	1.35(2)	C(36)–C(37)	1.36(2)
C(10)–H(10)	0.88(6)	C(36)–H(36)	0.83(6)
C(11)–H(11)	0.83(4)	C(37)–C(38)	1.33(2)
C(12)–C(13)	1.38(1)	C(37)–H(37)	0.87(6)
C(12)–C(17)	1.38(1)	C(38)–C(39)	1.39(1)
C(13)–C(14)	1.36(2)	C(38)–H(38)	1.05(7)
C(13)–H(13)	0.79(4)	C(39)–H(39)	0.83(7)
C(14)–C(15)	1.38(2)	C(40)–C(41)	1.34(1)
C(14)–H(14)	0.87(6)	C(40)–H(40)	0.87(7)
C(15)–C(16)	1.37(1)	C(40)–C(42′)	1.38(1)
C(15)–H(15)	1.02(7)	C(41)–C(42)	1.38(1)
C(16)–C(17)	1.36(1)	C(41)–C(43)	1.52(2)
C(16)–H(16)	0.98(6)	C(42)–H(42)	0.87(6)
C(17)–H(17)	0.79(5)	C(43)–H(43A)	1.10(10)
C(18)–C(19)	1.38(2)	C(43)–H(43B)	0.85(9)
C(18)–H(18)	0.92(8)	C(43)–H(43C)	0.94(10)
C(19)–H(19)	0.88(8)		

TABLE 6

Some bond angles (°) in the *p*-xylene adduct of (I)

C(5)–P(1)–Se(1)	111.8(3)
C(12)–P(1)–Se(1)	114.3(3)
C(28)–P(2)–Se(2)	113.3(3)
C(1)–P(3)–Se(3)	113.2(3)
C(26)–P(3)–Se(3)	113.9(3)
C(12)–P(1)–C(6)	102.9(4)
C(12)–P(1)–C(6)	105.4(4)
C(11)–C(6)–P(1)	120.7(7)
C(17)–C(12)–P(1)	121.6(7)
C(34)–P(2)–C(27)	106.7(4)
C(34)–P(2)–C(28)	105.4(3)
C(33)–C(28)–P(2)	120.8(6)
C(39)–C(34)–P(2)	121.7(6)
C(26)–P(3)–C(1)	104.7(4)
C(19)–C(1)–P(3)	120.6(7)
C(21)–C(20)–P(3)	118.5(7)
C(27)–C(26)–P(3)	114.4(6)
C(3)–C(2)–C(1)	119.0(13)
C(4)–C(3)–C(2)	121.2(15)
C(19)–C(18)–C(4)	122.0(13)
C(8)–C(7)–C(6)	121.8(10)
C(9)–C(8)–C(7)	119.2(11)
C(11)–C(10)–C(9)	119.1(11)
C(14)–C(13)–C(12)	122.5(10)
C(15)–C(14)–C(13)	119.3(10)
C(17)–C(16)–C(15)	120.8(10)
C(22)–C(21)–C(20)	120.1(10)
C(23)–C(22)–C(21)	120.7(11)
C(25)–C(24)–C(23)	119.9(11)
C(30)–C(29)–C(28)	122.1(8)
C(31)–C(30)–C(29)	119.0(9)
C(33)–C(32)–C(31)	121.5(9)
C(36)–C(35)–C(34)	120.2(10)
C(37)–C(36)–C(35)	120.4(11)
C(39)–C(38)–C(37)	120.4(10)
H(40)–C(40)–C(41)	125.0(45)
C(43)–C(41)–C(40)	121.6(10)
C(41)–C(42)–C(40′)	120.9(9)
C(43)–C(41)–C(42)	120.4(10)
H(43A)–C(43)–C(41)	105.4(51)
H(43C)–C(43)–C(41)	120.6(64)
H(43C)–C(43)–H(43A)	98.5(81)
C(6)–P(1)–Se(1)	113.4(3)
C(27)–P(2)–Se(2)	110.9(3)
C(34)–P(2)–Se(2)	113.4(2)
C(20)–P(3)–Se(3)	112.6(3)
C(6)–P(1)–C(5)	108.3(4)
C(5′)–C(5)–P(1)	113.1(7)
C(7)–C(6)–P(1)	123.2(7)
C(13)–C(12)–P(1)	121.6(7)
C(28)–P(2)–C(27)	106.7(4)
C(26)–C(27)–P(2)	111.7(6)
C(29)–C(28)–P(2)	121.2(6)
C(35)–C(34)–P(2)	119.9(6)
C(20)–P(3)–C(1)	106.3(3)
C(2)–C(1)–P(3)	120.0(7)
C(26)–P(3)–C(20)	105.4(4)
C(25)–C(20)–P(3)	123.7(6)
C(19)–C(1)–C(2)	119.4(8)
C(18)–C(19)–C(1)	120.1(10)
C(18)–C(4)–C(3)	118.2(12)
C(11)–C(6)–C(7)	116.1(9)
C(10)–C(11)–C(6)	123.1(10)
C(10)–C(9)–C(8)	120.7(11)
C(17)–C(12)–C(13)	116.8(8)
C(16)–C(17)–C(12)	121.4(9)
C(16)–C(15)–C(14)	119.2(11)
C(25)–C(20)–C(21)	117.8(8)
C(24)–C(25)–C(20)	121.9(9)
C(24)–C(23)–C(22)	119.4(11)
C(33)–C(28)–C(29)	117.9(7)
C(32)–C(33)–C(28)	119.8(8)
C(32)–C(31)–C(30)	119.6(9)
C(39)–C(34)–C(35)	118.4(8)
C(38)–C(39)–C(34)	120.1(9)
C(38)–C(37)–C(36)	120.5(11)
C(42′)–C(40)–C(41)	121.1(10)
C(42)–C(41)–C(40)	118.0(9)
H(40)–C(40)–C(42′)	113.9(45)
H(42)–C(42)–C(40′)	119.8(41)
H(42)–C(42)–C(41)	118.4(40)
H(43B)–C(43)–C(41)	117.7(64)
H(43B)–C(43)–H(43A)	102.8(79)
H(43C)–C(43)–H(43B)	108.3(90)

TABLE 7

Selected torsion angles (°) in the *p*-xylene adduct of (I)

P(1)–C(5)–C(5′)–P(1′)	180
P(2)–C(27)–C(26)–P(3)	−163(1)
Se(1)–P(1)–C(5)–C(5′)	54(1)
Se(2)–P(2)–C(27)–C(26)	58(1)
Se(3)–P(3)–C(26)–C(27)	−58(1)
H(43A)–C(43)–C(41)–C(42)	104(5)
H(43B)–C(43)–C(41)–C(42)	−10(7)
H(43C)–C(43)–C(41)–C(42)	−146(7)

experiment in which unsolvated (I), formed by removal of the guest component from the *p*-xylene adduct, was stirred for 20 h at ambient temperature (Table 2). A parallel experiment employing unsolvated material produced directly by recrystallisation led to no inclusion of solvent, consistent with the existence of two distinct unsolvated forms.

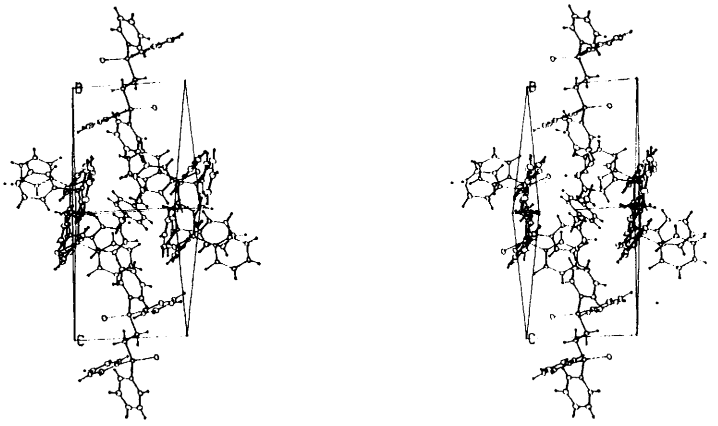

FIGURE 2 Molecular packing in the crystal

Inclusion Properties of Compounds (II)—(V) (*Table* 3).—Compounds (II) and (V), though closely related structurally to (I), were found to exhibit only limited inclusion behaviour (Table 3). On the other hand, compounds (III) and (IV), which have a three-atom chain linking the phosphorus atoms, form a number of adducts (Table 3) and (III) also shows some selective inclusion behaviour (Table 2). None of these hosts rivals the versatility and guest selectivity properties of the parent (I). A literature report [8] on PhBuAs(S)C_2H_4-As(S)PhBu indicates that it has a strong tendency to include organic molecules described as solvent of crystallisation. In particular a 3 : 1 adduct with cyclohexane remained unchanged after prolonged exposure to vacuum. It seems possible that other sulphur or selenium derivatives of ditertiary phosphines and arsines of these types might also show significant inclusion behaviour.

FIGURE 3 van der Waals surfaces of the guest and surrounding molecules, from the same viewpoint as in Figure 2

X-*Ray Crystal Structure of the* p-*Xylene Adduct of* (I).—Figure 1 shows the two crystallographically distinct host molecules and the single *p*-xylene guest molecule. One of the host molecules is centrosymmetric at $\frac{1}{2}$, 0, 0 while the other occupies a general position in the unit cell, the respective values of the torsion angles P(1)–C(5)–C(5′)–P(1′) and P(2)–C(27)–C(26)–P(3) being 180 and −163°. Significant differences for the backbone P–C(alkyl) bonds are observed (Table 7). Some of the ring bond lengths appear to be artificially shortened by thermal motion effects. The average P–C(aryl) bond length [1.810(4) Å)] may be compared with the corresponding value 1.81(1) Å in bis(diphenylphosphinoselenoyl)methane.[9] However, the average P–C(alkyl) bond length [1.805(6) Å] is possibly significantly shorter than 1.84(1) Å in that compound. The mean of the three independent P–Se bond lengths [2.096(1) Å] is close to 2.100(4) Å in the methane derivative.

Figure 2 shows a stereoview of the host–guest packing in the crystal, with the guest lying on a centre of symmetry at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$. The shortest contacts between host molecules are: Se ··· CH 3.63, CH ··· CH 3.54 Å; between host and guest molecules: C ··· CH 3.58, CH ··· CH 3.66, CH ··· CH_3 3.71 Å. There are some close intramolecular approaches involving phenyl and methylene groups, particularly C(25) ··· C(26) 3.16 Å. The nature of the void is best appreciated from Figure 3, which is a stereorepresentation of the free space available for guest accommodation, having allowed for the van der Waals volumes of the host atoms. The guest is accommodated in an effectively closed cage, all gaps in the cage wall being small compared with the dimensions of the guest, so the adduct is of the true clathrate type.

The accuracy of the fit is reflected in a highly ordered guest arrangement, which restricts motion of the guest. This enables the direct observation of *all* the hydrogen atoms, above the normal melting point of *p*-xylene. The carbon skeleton of the *p*-xylene is planar within 0.006(16) Å, and the geometrical parameters are included in Tables 5 and 6. In the present study, the direct observation of the methyl group conformation (Table 7) is noteworthy. A recent electron-diffraction study[10] determined accurate values of structural parameters for *p*-xylene in the vapour phase; for example C–C(Me) 1.512 Å, ring bond lengths 1.405 and 1.392 Å (all ±0.003 Å) ring angles 117.1 and 121.5° (±0.3°). In this work, unlike the present *X*-ray study, it was not possible to define the conformational situation for the methyl groups. Interestingly, the trend of bond angles in the guest *p*-xylene in the present study appears to parallel the very precise values obtained from the vapour-phase work.

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