Investigation of Phosphorus–Carbon Bond Lengths in Aromatic Phosphines. Part I. Crystal and Molecular Structures of Tri-*o*-tolylphosphine, -phosphine Oxide, -phosphine Sulphide, and -phosphine Selenide

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The crystal and molecular structure of the four title compounds from four circle have been determined. Tri-*o*-tolylphosphine (I), triclinic, $a = 12.081(5)$, $b = 10.915(5)$, $c = 14.348(7)$ Å; $\alpha = 91.95(5)°$, $\beta = 110.58(4)°$, $\gamma = 98.22(5)°$, space group $P\bar{1}$, $Z = 4$; R 0.045, 4 698 independent reflections. Tri-*o*-tolylphosphine oxide (II), monoclinic, $a = 9.039(5)$, $b = 17.282(6)$, $c = 35.192(12)$ Å, $\beta = 95.12(1)°$ space group $P2_1/c$, $Z = 12$; R 0.075, 5 428 independent reflections. Tri-*o*-tolylphosphine sulphide (III), triclinic, $a = 15.377(4)$, $b = 15.346(4)$, $c = 7.979(4)$ Å; $\alpha = 103.1(1)°$, $\beta = 86.6(1)°$, $\gamma = 96.5(1)°$, space group $P\bar{1}$, $Z = 4$; R 0.094, 2 890 independent reflections. Tri-*o*-tolylphosphine selenide (IV), monoclinic, $a = 33.497(10)$, $b = 8.004(2)$, $c = 14.701(10)$ Å, $\beta = 110.67(4)°$, space group $C2/c$, $Z = 8$; R 0.067, 2 343 independent reflections.

The differences in P–C bond lengths appear to be determined by charge density on the aromatic group and the phosphorus atom, and by steric hindrance and crystal packing forces, and not by any extension of the π system of the aromatic groups to the phosphorus atom.

In molecules with aryl phosphine groups where the phosphorus atom is present either as trivalent P^{III} or pentavalent P^{V}, a wide variation in phosphorus–carbon bond lengths has been observed.[1] These variations occur both between the P–C bond lengths in one molecule, and between the mean bond lengths of different molecules. In an attempt to identify the factors responsible for these variations the structures of tri-*o*-, tri-*m*-, and tri-*p*-tolyl-phosphine-, -phosphine oxide, -phosphine sulphide, and -phosphine selenide have been determined.[2,3] We report here the structures of the tri-*o*-compounds, (I)—(IV).

TABLE 1

Bond angles (deg.) and their estimated standard deviations for non-hydrogen atoms in (I)

C(1)–P(1)–C(11)	101.9(1)	C(31)–P(2)–C(41)	101.6(1)
C(1)–P(1)–C(21)	103.1(1)	C(31)–P(2)–C(51)	102.7(1)
C(11)–P(1)–C(21)	103.4(1)	C(41)–P(2)–C(51)	102.9(1)
P(1)–C(1)–C(2)	118.9(2)	P(2)–C(31)–C(32)	118.7(2)
P(1)–C(1)–C(6)	121.1(2)	P(2)–C(31)–C(36)	122.4(2)
C(2)–C(1)–C(6)	118.9(2)	C(32)–C(31)–C(36)	118.8(2)
C(1)–C(2)–C(3)	118.3(3)	C(31)–C(32)–C(33)	118.2(3)
C(1)–C(2)–C(7)	122.1(2)	C(31)–C(32)–C(37)	121.7(2)
C(3)–C(2)–C(7)	119.6(2)	C(33)–C(32)–C(37)	120.1(2)
C(2)–C(3)–C(4)	122.1(2)	C(32)–C(33)–C(34)	121.8(3)
C(3)–C(4)–C(5)	120.4(3)	C(33)–C(34)–C(35)	120.2(3)
C(4)–C(5)–C(6)	119.3(3)	C(34)–C(35)–C(36)	119.3(3)
C(1)–C(6)–C(5)	121.2(2)	C(31)–C(36)–C(35)	121.7(2)
P(1)–C(11)–C(12)	118.5(2)	P(2)–C(41)–C(42)	117.7(2)
P(1)–C(11)–C(16)	122.5(2)	P(2)–C(41)–C(46)	122.8(2)
C(12)–C(11)–C(16)	119.0(2)	C(42)–C(41)–C(46)	119.5(2)
C(11)–C(12)–C(13)	118.8(3)	C(41)–C(42)–C(43)	119.1(3)
C(11)–C(12)–C(17)	121.8(2)	C(41)–C(42)–C(47)	121.9(2)
C(13)–C(12)–C(17)	119.4(3)	C(43)–C(42)–C(47)	118.9(3)
C(12)–C(13)–C(14)	120.8(3)	C(42)–C(43)–C(44)	120.5(3)
C(13)–C(14)–C(15)	121.0(3)	C(43)–C(44)–C(45)	120.4(3)
C(14)–C(15)–C(16)	119.4(3)	C(44)–C(45)–C(46)	120.8(3)
C(11)–C(16)–C(15)	121.1(3)	C(41)–C(46)–C(45)	119.7(2)
P(1)–C(21)–C(22)	119.1(2)	P(2)–C(51)–C(52)	118.7(2)
P(1)–C(21)–C(26)	122.3(2)	P(2)–C(51)–C(56)	122.6(2)
C(22)–C(21)–C(26)	118.4(2)	C(52)–C(51)–C(56)	118.7(2)
C(21)–C(22)–C(23)	118.8(3)	C(51)–C(52)–C(53)	118.6(2)
C(21)–C(22)–C(27)	121.1(2)	C(51)–C(52)–C(57)	121.2(2)
C(23)–C(22)–C(27)	120.1(2)	C(53)–C(52)–C(57)	120.2(2)
C(22)–C(23)–C(24)	121.8(3)	C(52)–C(53)–C(54)	121.9(2)
C(23)–C(24)–C(25)	119.9(3)	C(53)–C(54)–C(55)	119.7(3)
C(24)–C(25)–C(26)	119.7(3)	C(54)–C(55)–C(56)	119.8(3)
C(21)–C(26)–C(25)	121.4(2)	C(51)–C(56)–C(55)	121.4(2)

TABLE 2

Bond angles (deg.) and their estimated standard deviations for non-hydrogen atoms in (II)

O(1)–P(1)–C(1)	112.2(3)	C(81)–C(86)–C(85)	120.9(5)
O(1)–P(1)–C(11)	113.5(2)	C(11)–C(16)–C(15)	122.3(5)
O(1)–P(1)–C(21)	112.9(2)	P(1)–C(21)–C(22)	120.8(5)
C(1)–P(1)–C(11)	106.0(2)	P(1)–C(21)–C(26)	119.8(4)
C(1)–P(1)–C(21)	106.3(2)	C(22)–C(21)–C(26)	119.4(5)
C(11)–P(1)–C(21)	105.2(3)	C(21)–C(22)–C(23)	116.5(6)
P(1)–C(1)–C(2)	120.6(4)	C(21)–C(22)–C(27)	124.4(6)
P(1)–C(1)–C(6)	119.7(4)	C(23)–C(22)–C(27)	119.1(6)
C(2)–C(1)–C(6)	119.5(5)	C(22)–C(23)–C(24)	125.1(7)
C(1)–C(2)–C(3)	118.3(5)	C(23)–C(24)–C(25)	118.2(6)
C(1)–C(2)–C(7)	122.7(5)	C(24)–C(25)–C(26)	118.6(7)
C(3)–C(2)–C(7)	119.0(6)	C(21)–C(26)–C(25)	122.1(6)
C(2)–C(3)–C(4)	120.9(6)	O(2)–P(2)–C(31)	113.3(2)
C(3)–C(4)–C(5)	120.4(7)	O(2)–P(2)–C(41)	112.5(2)
C(4)–C(5)–C(6)	120.5(7)	O(2)–P(2)–C(51)	112.7(2)
C(1)–C(5)–C(5)	120.3(6)	C(31)–P(2)–C(41)	106.8(2)
P(1)–C(11)–C(12)	120.0(4)	C(31)–P(2)–C(51)	105.5(2)
P(1)–C(11)–C(16)	119.6(4)	C(41)–P(2)–C(51)	105.4(2)
C(12)–C(11)–C(16)	120.4(5)	P(2)–C(31)–C(32)	121.0(4)
C(11)–C(12)–C(13)	115.5(6)	P(2)–C(31)–C(36)	118.6(4)
C(11)–C(12)–C(17)	124.6(5)	C(32)–C(31)–C(36)	120.4(5)
C(13)–C(12)–C(17)	119.9(6)	C(31)–C(32)–C(33)	118.2(6)
C(12)–C(13)–C(14)	121.6(6)	C(31)–C(32)–C(37)	123.2(6)
C(13)–C(14)–C(15)	123.1(7)	C(33)–C(32)–C(37)	118.6(7)
C(14)–C(15)–C(16)	117.1(6)	C(32)–C(33)–C(34)	119.8(7)
C(34)–C(35)–C(36)	118.5(6)	C(33)–C(34)–C(35)	123.3(7)
C(31)–C(36)–C(35)	119.8(6)	C(71)–P(3)–C(81)	103·3(2)
P(2)–C(41)–C(42)	121.3(4)	P(3)–C(61)–C(62)	121.0(4)
P(2)–C(41)–C(46)	120.3(4)	P(3)–C(6)–C(66)	120.6(4)
C(42)–C(41)–C(46)	118.4(5)	C(62)–C(61)–C(66)	118.3(5)
C(41)–C(42)–C(43)	118.0(5)	C(61)–C(62)–C(63)	118.3(5)
C(41)–C(42)–C(47)	122.1(6)	C(61)–C(62)–C(67)	122.8(5)
C(43)–C(42)–C(47)	119.9(6)	C(63)–C(62)–C(67)	118.9(5)
C(42)–C(43)–C(44)	122.4(6)	C(62)–C(63)–C(64)	122.1(6)
C(43)–C(44)–C(45)	120.3(6)	C(63)–C(64)–C(65)	119.3(6)
C(44)–C(45)–C(46)	118.8(6)	C(64)–C(65)–C(66)	120.4(6)
C(41)–C(46)–C(45)	122.0(5)	C(61)–C(66)–C(65)	121.6(5)
P(2)–C(51)–C(52)	121.3(4)	P(3)–C(71)–C(72)	119.8(4)

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[1] D. E. C. Corbridge, 'The Structural Chemistry of Phosphorus,' Elsevier, Amsterdam, 1974, pp. 330, 395.

[2] (*a*) R. A. Shaw, M. Woods, T. S. Cameron, and B. Dahlèn, *Chem. and Ind.*, 1971, 151; (*b*) T. S. Cameron, K. D. Howlett, R. A. Shaw, and M. Woods, *Phosphorus*, 1973, **3**, 71.

[3] T. S. Cameron and K. Millar, *Cryst. Struct. Comm.*, 1974, **3**, 489.

TABLE 2 (*Continued*)

P(2)–C(51)–C(56)	120.1(4)	P(3)–C(71)–C(76)	119.8(4)
C(52)–C(51)–C(56)	118.6(5)	C(72)–C(71)–C(76)	120.3(5)
C(51)–C(52)–C(53)	118.7(5)	C(71)–C(72)–C(73)	117.2(6)
C(51)–C(52)–C(57)	121.4(5)	C(71)–C(72)–C(77)	123.9(6)
C(53)–C(52)–C(57)	119.9(5)	C(73)–C(72)–C(77)	118.9(6)
C(52)–C(53)–C(54)	122.8(6)	C(72)–C(73)–C(74)	121.8(7)
C(53)–C(54)–C(55)	118.7(6)	C(73)–C(74)–C(75)	120.9(6)
C(54)–C(55)–C(56)	119.8(6)	C(74)–C(75)–C(76)	119.2(6)
C(51)–C(56)–C(55)	121.4(5)	C(71)–C(76)–C(75)	120.6(6)
O(3)–P(3)–C(61)	112.1(2)	P(3)–C(81)–C(82)	122.8(4)
O(3)–P(3)–C(71)	113.7(2)	C(81)–C(82)–C(83)	118.2(5)
O(3)–P(3)–C(81)	113.7(2)	C(81)–C(82)–C(87)	123.5(5)
C(61)–P(3)–C(71)	106.9(2)	C(81)–C(82)–C(83)	118.2(5)
C(61)–P(3)–C(81)	106.2(2)	C(81)–C(82)–C(87)	123.5(5)
C(71)–P(3)–C(81)	103.3(2)	C(83)–C(82)–C(87)	118.3(5)
C(82)–C(83)–C(84)	122.6(6)	P(3) –C(81)–C(86)	118.6(4)
C(83)–C(84)–C(85)	119.8(5)	C(82)–C(81)–C(86)	118.5(5)
C(84)–C(85)–C(86)	119.9(6)	C(83)–C(82)–C(87)	118.3(5)

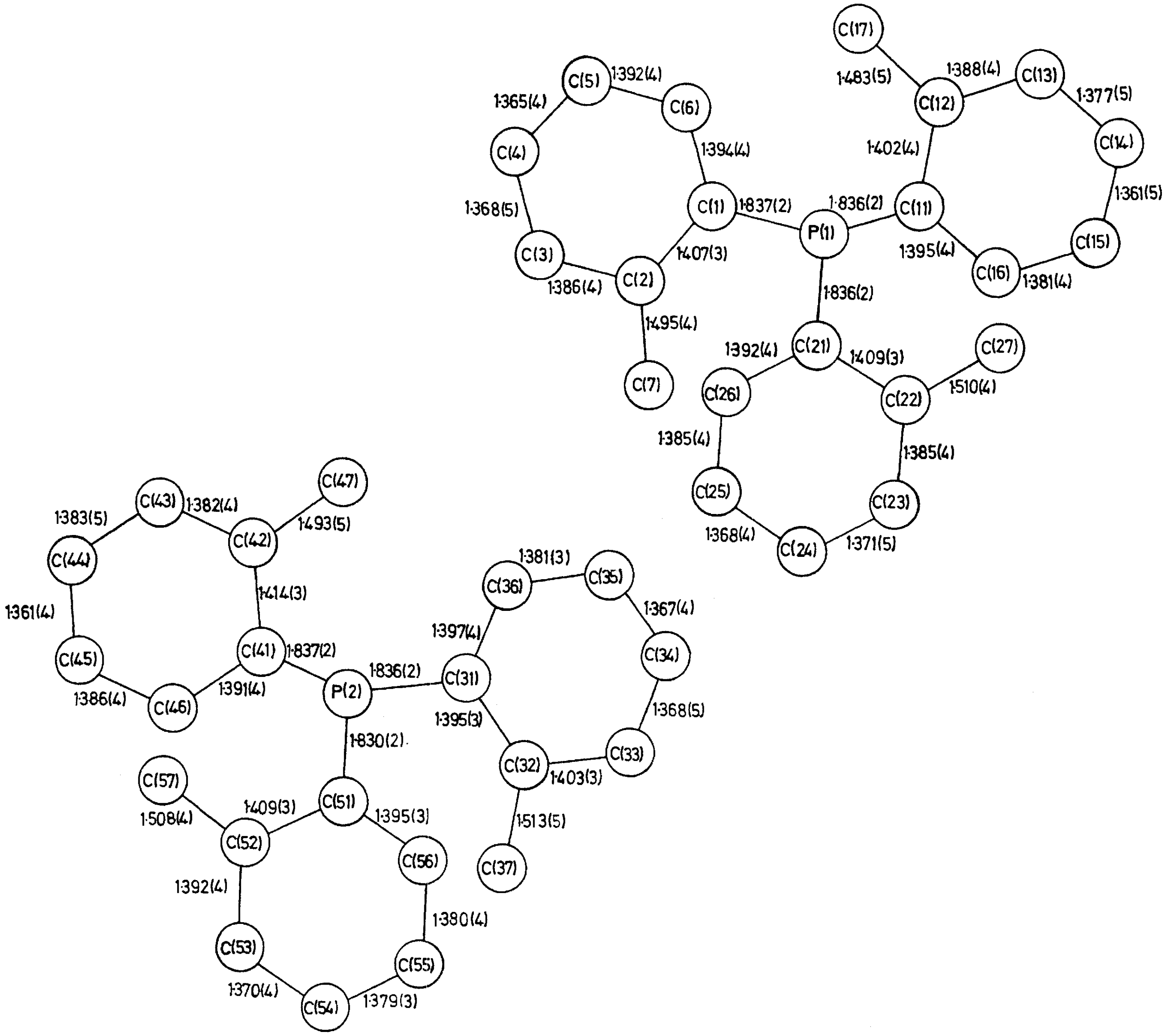

FIGURE 1 Interatomic distances in (I)

RESULTS AND DISCUSSION

Interatomic distances for the four compounds are given in Figures 1—4, and interbond angles in Tables 1—4. Torsion angles about the P–C bonds between the plane of the tolyl groups and the P⋯X axis are given in Table 5. Stereoscopic projections of the four structures are given in Figures 5—8 and certain enlarged details of the structures in Figures 9—11.

*Tri-*o*-tolylphosphine,* (I).—The crystal contains two independent phosphine molecules, with similar conformations, and which pack in layers almost parallel to the (101) plane. The orientations of adjacent non-equivalent molecules are approximately related by a reflection through a mirror in this plane. In each molecule, the co-ordination sphere about the phosphorus atom is a regular trigonal pyramid with the phosphorus at the apex. The *o*-methyl groups are on the same 'side' of the molecule as the phosphorus lone-pair electrons. The torsion angles about the P–C bonds between the plane of a phenyl group and the axis of the trigonal pyramid

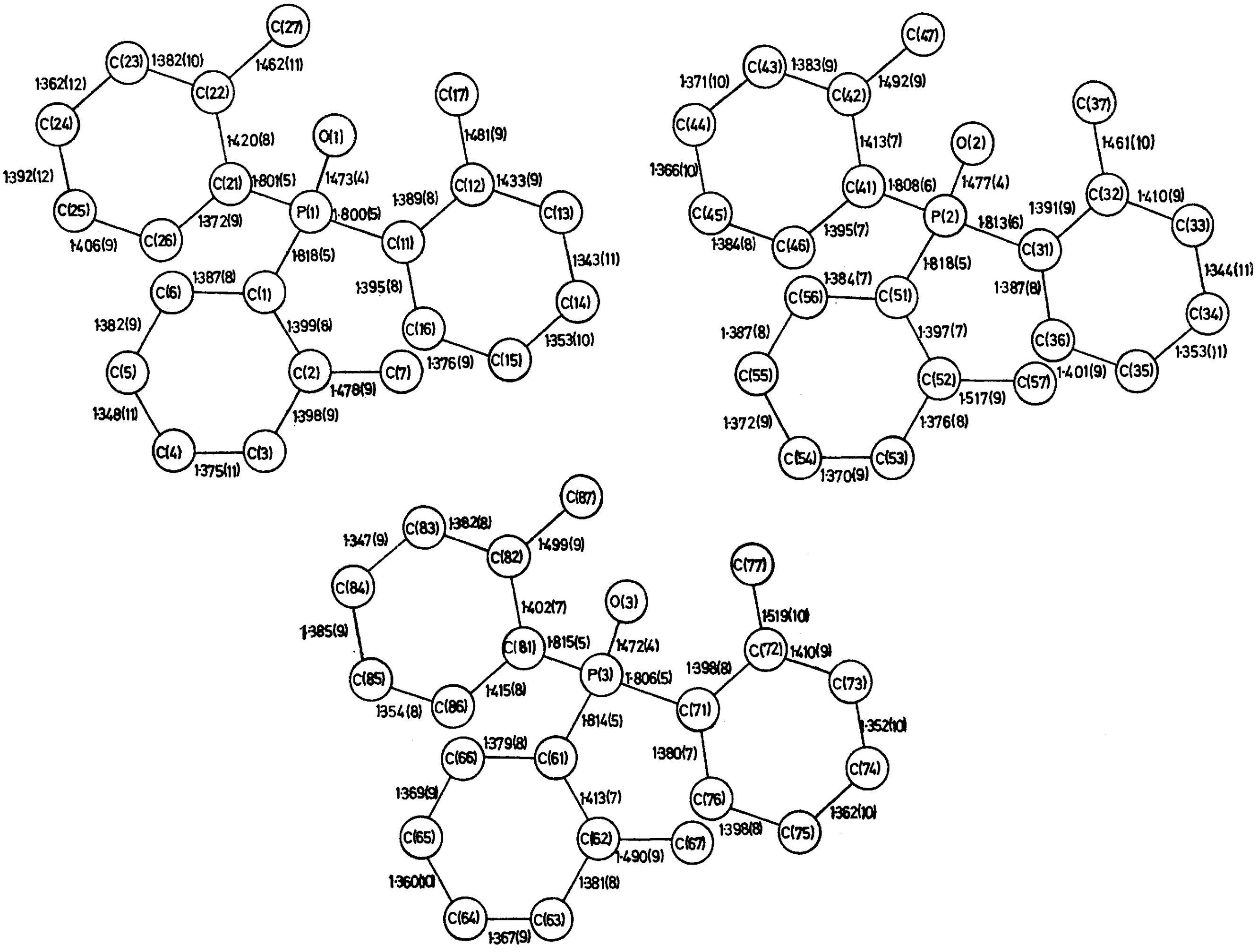

FIGURE 2 Interatomic distances in (II)

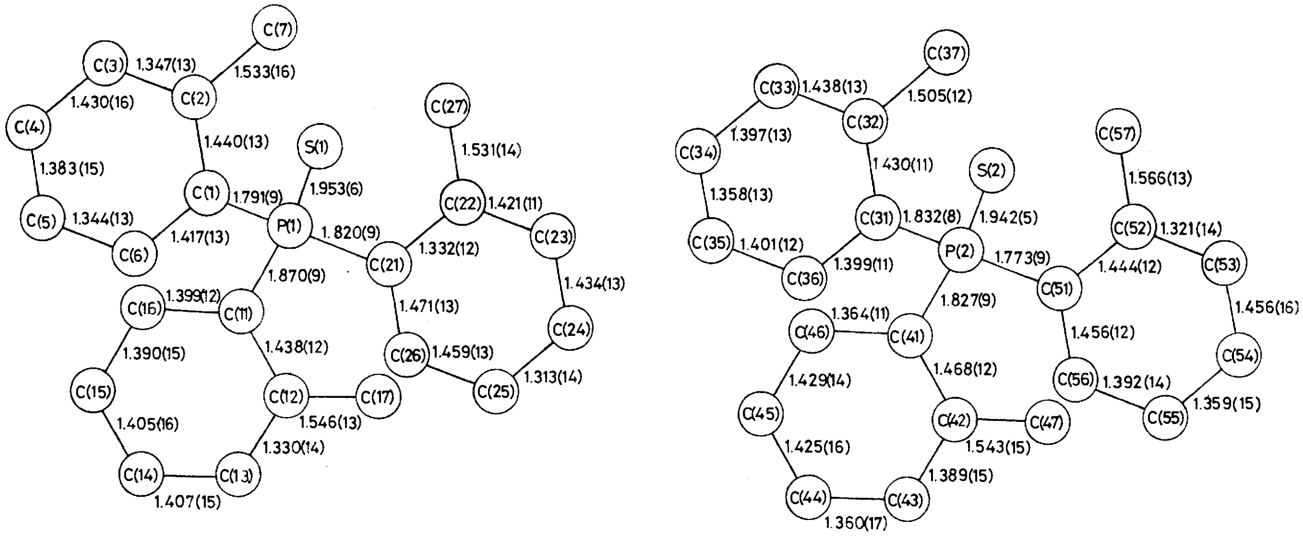

FIGURE 3 Interatomic distances in (III)

are in the range 36.7—49.0°, with the rotation always in the same direction. The molecule therefore has almost C_3 symmetry.

TABLE 3

Interbond angles (deg.) in (III)

S(1)–P(1)–C(1)	110.7(3)	S(2)–P(2)–C(31)	112.4(2)
S(1)–P(1)–C(11)	112.5(2)	S(2)–O(2)–C(41)	111.6(2)
S(1)–P(1)–C(21)	114.2(3)	S(2)–P(2)–C(51)	114.3(2)
C(1)–P(1)–C(11)	106.9(3)	C(31)–P(2)–C(41)	104.9(3)
C(1)–P(1)–C(21)	110.6(4)	C(31)–P(2)–C(51)	105.1(3)
C(11)–P(1)–C(21)	101.4(3)	C(41)–P(2)–C(51)	107.9(3)
P(1)–C(1)–C(2)	122.9(6)	P(2)–C(31)–C(32)	123.9(5)
P(1)–C(1)–C(6)	120.6(6)	P(2)–C(31)–C(36)	116.3(5)
C(2)–C(1)–C(6)	116.1(7)	C(32)–C(31)–C(36)	119.6(7)
C(1)–C(2)–C(3)	119.8(8)	C(31)–C(32)–C(33)	116.9(7)
C(1)–C(2)–C(7)	122.7(8)	C(31)–C(32)–C(37)	124.8(7)
C(3)–C(2)–C(7)	117.4(8)	C(33)–C(32)–C(37)	118.1(7)
C(2)–C(3)–C(4)	123.2(9)	C(32)–C(33)–C(34)	119.7(8)
C(3)–C(4)–C(5)	115.9(9)	C(33)–C(34)–C(35)	123.7(8)
C(4)–C(5)–C(6)	122.6(9)	C(34)–C(35)–C(36)	116.9(8)
C(1)–C(6)–C(5)	122.3(8)	C(31)–C(36)–C(35)	122.8(7)
P(1)–C(11)–C(12)	125.3(6)	P(2)–C(41)–C(42)	121.9(6)
P(1)–C(11)–C(16)	114.6(6)	P(2)–C(41)–C(46)	118.4(6)
C(12)–C(11)–C(16)	119.9(7)	C(42)–C(41)–C(46)	119.4(7)
C(11)–C(12)–C(13)	117.0(8)	C(41)–C(42)–C(43)	115.2(8)
C(11)–C(12)–C(17)	121.6(7)	C(41)–C(42)–C(47)	121.3(8)
C(13)–C(12)–C(17)	121.4(8)	C(43)–C(42)–C(47)	123.5(8)
C(12)–C(13)–C(14)	124.8(9)	C(42)–C(43)–C(44)	125.8(10)
C(13)–C(14)–C(15)	118.3(9)	C(43)–C(44)–C(45)	119.6(10)
C(14)–C(15)–C(16)	118.8(9)	C(44)–C(45)–C(46)	116.2(9)
C(11)–C(16)–C(15)	121.2(8)	C(41)–C(46)–C(45)	123.8(8)
P(1)–C(21)–C(22)	123.4(6)	P(2)–C(51)–C(52)	123.4(6)
P(1)–C(21)–C(26)	115.3(6)	P(2)–C(51)–C(56)	119.8(6)
C(22)–C(21)–C(26)	121.1(8)	C(52)–C(51)–C(56)	116.8(7)
C(21)–C(22)–C(23)	122.1(8)	C(51)–C(52)–C(53)	121.4(8)
C(21)–C(22)–C(27)	124.7(8)	C(51)–C(52)–C(57)	119.6(7)
C(23)–C(22)–C(27)	113.5(7)	C(53)–C(52)–C(57)	118.9(8)
C(22)–C(23)–C(24)	117.4(7)	C(52)–C(53)–C(54)	121.7(9)
C(23)–C(24)–C(25)	121.5(8)	C(53)–C(54)–C(55)	118.0(9)
C(24)–C(25)–C(26)	122.6(8)	C(54)–C(55)–C(56)	122.6(9)
C(21)–C(26)–C(25)	114.8(8)	C(51)–C(56)–C(55)	119.3(8)

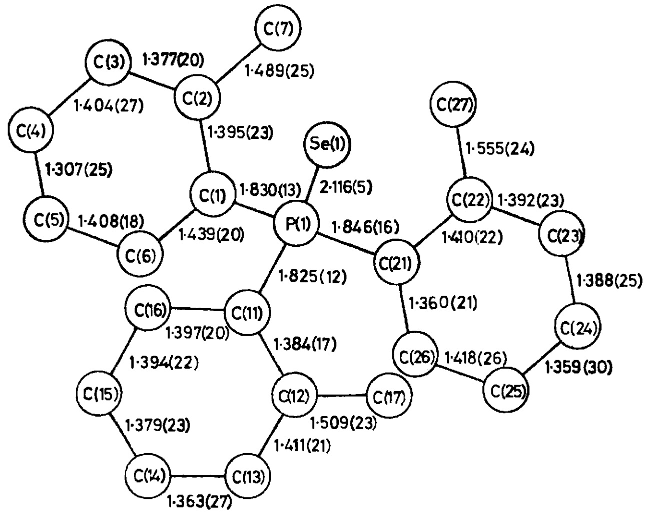

FIGURE 4 Interatomic distances in (IV)

The dimensions of the molecules are very close to those reported[4] for triphenylphosphine where the P–C bond lengths are 1.822(5), 1.831(5), and 1.836(7) Å, and the C–P–C interbond angles are 102.1(2), 103.3(2), and 103.5(2)°. In the *o*-tolylphosphine molecules the six P–C bond lengths [mean 1.835(1) Å] do not vary significantly, and the C–P–C interbond angles [mean

TABLE 4

Bond angles, with standard deviations in parentheses, for (IV)

Se(1)–P(1)–C(1)	111.1(0.4)	C(12)–C(11)–C(16)	119.3(1.2)
Se(1)–P(1)–C(11)	114.0(0.4)	C(11)–C(12)–C(13)	119.1(1.4)
Se(1)–P(1)–C(21)	112.1(0.4)	C(11)–C(12)–C(17)	123.6(1.2)
C(1)–P(1)–C(11)	107.2(0.6)	C(13)–C(12)–C(17)	117.3(1.3)
C(1)–P(1)–C(21)	106.7(0.6)	C(12)–C(13)–C(14)	121.1(1.4)
C(11)–P(1)–C(21)	105.4(0.7)	C(13)–C(14)–C(15)	120.3(1.6)
P(1)–C(1)–C(2)	122.8(1.1)	C(14)–C(15)–C(16)	119.5(1.5)
P(1)–C(1)–C(6)	116.3(1.1)	C(11)–C(16)–C(15)	120.7(1.3)
C(2)–C(1)–C(6)	120.7(1.2)	P(1)–C(21)–C(22)	123.7(1.1)
C(1)–C(2)–C(3)	117.3(1.5)	P(1)–C(21)–C(26)	115.8(1.3)
C(1)–C(2)–C(7)	124.9(1.3)	C(22)–C(21)–C(26)	120.5(1.5)
C(3)–C(2)–C(7)	117.8(1.6)	C(21)–C(22)–C(23)	117.4(1.4)
C(2)–C(3)–C(4)	121.7(1.7)	C(21)–C(22)–C(27)	125.7(1.4)
C(3)–C(4)–C(5)	121.5(1.4)	C(23)–C(22)–C(27)	116.9(1.5)
C(4)–C(5)–C(6)	120.7(1.5)	C(22)–C(23)–C(24)	121.4(1.7)
C(1)–C(6)–C(5)	118.0(1.4)	C(23)–C(24)–C(25)	121.3(1.8)
P(1)–C(11)–C(12)	122.9(1.0)	C(24)–C(25)–C(26)	117.7(1.6)
P(1)–C(11)–C(16)	117.8(0.9)	C(21)–C(26)–C(25)	121.7(1.7)

TABLE 5

Torsion angles (deg.) about the P–C bond between the P–X axis and the planes of the phenyl rings, shortest intermolecular contacts at carbon atom *para* to the P–C bond, and corresponding P–C bond length (Å)

P–C	Torsional angle		Contact
Tri-*o*-tolylphosphine, (I)			
1.837(2)	46.8	C(4) · · · C(3$^{\mathrm{I}}$)	3.86
1.836(2)	40.7	C(14) · · · C(44$^{\mathrm{II}}$)	3.84
1.836(2)	45.6	C(24) · · · C(34$^{\mathrm{III}}$)	3.90
1.837(2)	36.7	C(34) · · · C(23$^{\mathrm{III}}$)	3.72
1.837(2)	49.0	C(44) · · · C(14$^{\mathrm{IV}}$)	3.84
1.830(2)	43.1	C(54) · · · C(7$^{\mathrm{V}}$)	3.88
Tri-*o*-tolylphosphine, (II)			
1.818(5)	52.4	C(4) · · · C(15$^{\mathrm{IV}}$)	3.72
1.800(5)	44.5	C(14) · · · C(3$^{\mathrm{II}}$)	3.76
1.801(5)	43.2	C(24)	>4.0
1.813(6)	44.6	C(34) · · · C(43$^{\mathrm{IV}}$)	3.74
1.808(6)	51.7	C(44) · · · C(35$^{\mathrm{II}}$)	3.81
1.818(5)	44.3	C(54) · · · C(39$^{\mathrm{III}}$)	3.95
1.814(5)	51.1	C(64) · · · C(75$^{\mathrm{II}}$)	3.81
1.806(5)	47.6	C(74) · · · C(84$^{\mathrm{VI}}$)	3.70
1.815(5)	33.8	C(84) · · · C(73$^{\mathrm{VII}}$)	3.63
Tri-*o*-tolylphosphine sulphide, (III)			
1.791(6)	66.9	C(4) · · · C(57)	3.60
1.870(6)	3.4	C(14) · · · C(36)	3.78
1.820(7)	52.6	C(24) · · · S(2$^{\mathrm{V}}$)	3.72
		C(34) · · · C(34$^{\mathrm{I}}$)	3.49 *
1.831(6)	17.0	C(34) · · · C(57$^{\mathrm{VIII}}$)	3.77
1.826(7)	56.6	C(44) · · · C(27)	3.96
1.773(8)	56.5	C(54) · · · C(37$^{\mathrm{IX}}$)	3.64
Tri-*o*-tolylphosphine selenide, (IV)			
1.830(12)	56.3	C(4) · · · C(6$^{\mathrm{I}}$)	3.44 *
1.825(12)	58.9	C(14) · · · C(23$^{\mathrm{X}}$)	3.67
1.846(16)	13.0	C(24) · · · C(13$^{\mathrm{XI}}$)	3.88

* Plane-to-plane contact. Roman numerals denote the following equivalent positions relative to the reference molecule at x, y, z:

I $-x, -y, -z$
II $1 + x, y, z$
III $1 - x, 1 - y, 1 - z$
IV $x - 1, y, z$
V $-x, 1 - y, -z$
VI $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
VII $x, \frac{1}{2} + y, \frac{1}{2} - z$
VIII $x, \frac{1}{2} - y, \frac{1}{2} + y$
IX $x, 1 + y, z$
X $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
XI $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

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[4] J. J. Daly, *J. Chem. Soc.*, 1964, 3799.

TABLE 6

Fractional atomic co-ordinates ($\times 10^4$; $\times 10^3$ for the H atoms) in (I), with thermal parameters *

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
P(1)	4 156(1)	0 292(1)	1 063(0)	479(3)	506(3)	524(3)	87(3)	204(3)	62(2)
C(1)	2 640(2)	−0 508(2)	0 880(2)	508(12)	437(11)	561(12)	69(9)	149(10)	57(9)
C(2)	1 757(2)	−0 652(2)	−0 085(2)	625(15)	553(13)	617(14)	44(11)	118(12)	95(11)
C(3)	0 644(2)	−1 341(3)	−0 228(2)	589(16)	714(17)	808(18)	37(14)	2(14)	25(13)
C(4)	0 384(2)	−1 868(3)	0 537(3)	531(15)	765(18)	1 054(23)	185(16)	115(15)	−62(13)
C(5)	1 225(2)	−1 724(3)	1 481(2)	623(16)	793(18)	964(20)	323(16)	244(15)	−18(14)
C(6)	2 355(2)	−1 041(2)	1 653(2)	545(14)	666(15)	673(15)	178(12)	140(12)	−7(11)
C(7)	1 976(3)	−0 063(3)	−0 944(2)	846(20)	1 084(24)	551(15)	99(15)	114(14)	175(17)
C(11)	4 995(2)	0 025(2)	2 361(2)	428(12)	567(13)	651(14)	153(11)	167(10)	36(10)
C(12)	5 483(2)	−1 073(2)	2 542(2)	431(12)	582(14)	933(18)	222(13)	187(12)	40(10)
C(13)	6 137(2)	−1 269(3)	3 519(2)	566(15)	785(18)	1 049(22)	409(16)	166(15)	110(13)
C(14)	6 305(3)	−0 405(3)	4 299(2)	767(19)	1 132(25)	842(20)	491(19)	94(16)	107(17)
C(15)	5 832(3)	0 662(3)	4 133(2)	939(21)	983(22)	607(16)	199(15)	138(15)	100(17)
C(16)	5 178(2)	0 880(2)	3 167(2)	685(16)	718(16)	577(14)	164(12)	175(12)	120(13)
C(17)	5 300(3)	−2 033(3)	1 722(3)	826(20)	665(18)	1 288(27)	42(17)	253(19)	229(15)
C(21)	4 017(2)	1 942(2)	1 149(2)	518(12)	528(12)	416(11)	106(9)	140(9)	23(9)
C(22)	4 967(2)	2 847(2)	1 136(2)	571(14)	664(14)	493(12)	118(11)	138(11)	−73(11)
C(23)	4 810(3)	4 079(2)	1 099(2)	808(18)	624(15)	603(15)	133(12)	143(13)	−138(13)
C(24)	3 768(3)	4 412(2)	1 093(2)	986(20)	506(14)	614(15)	88(11)	90(14)	53(13)
C(25)	2 848(2)	3 575(2)	1 124(2)	764(17)	610(15)	642(15)	71(12)	189(13)	183(13)
C(26)	2 968(2)	2 332(2)	1 145(2)	594(14)	540(13)	582(13)	77(10)	200(11)	63(11)
C(27)	6 141(3)	2 492(3)	1 165(3)	607(16)	969(23)	1 042(22)	142(18)	305(16)	−91(15)
P(2)	1 168(1)	4 445(1)	3 080(0)	451(3)	484(3)	437(3)	106(2)	140(2)	54(2)
C(31)	2 342(2)	4 988(2)	4 300(2)	475(12)	492(12)	542(12)	109(10)	139(10)	76(9)
C(32)	3 350(2)	5 817(2)	4 333(2)	552(14)	565(13)	683(15)	95(11)	155(12)	36(11)
C(33)	4 279(2)	6 159(3)	5 261(2)	571(15)	748(18)	850(19)	16(14)	79(14)	−47(13)
C(34)	4 211(3)	5 711(3)	6 122(2)	776(19)	735(17)	700(18)	−17(14)	−65(14)	92(14)
C(35)	3 212(3)	4 923(3)	6 097(2)	933(20)	703(17)	518(14)	77(12)	94(13)	92(14)
C(36)	2 292(2)	4 553(2)	5 191(2)	689(15)	643(15)	534(13)	102(11)	155(12)	0(12)
C(37)	3 459(3)	6 338(3)	3 399(3)	917(21)	844(20)	1 033(23)	177(17)	436(18)	−166(16)
C(41)	0 344(2)	3 062(2)	3 381(2)	528(12)	508(12)	424(11)	76(9)	91(9)	10(10)
C(42)	0 839(2)	1 955(2)	3 459(2)	716(15)	514(13)	463(12)	72(10)	108(11)	70(11)
C(43)	0 229(3)	0 892(2)	3 666(2)	947(20)	536(14)	649(16)	101(12)	170(14)	11(13)
C(44)	−0 855(3)	0 908(2)	3 789(2)	945(21)	607(15)	687(17)	153(13)	123(15)	−164(14)
C(45)	−1 341(2)	1 968(3)	3 695(2)	585(15)	916(20)	691(16)	147(14)	146(13)	−129(14)
C(46)	−0 753(2)	3 055(2)	3 496(2)	549(14)	650(15)	598(14)	122(11)	179(11)	−9(11)
C(47)	2 008(3)	1 903(3)	3 336(2)	903(20)	705(17)	918(21)	239(15)	374(17)	327(15)
C(51)	0 148(2)	5 574(2)	2 927(2)	496(12)	497(12)	495(12)	148(9)	184(10)	38(9)
C(52)	−0 765(2)	5 574(2)	1 989(2)	518(13)	582(13)	553(13)	170(10)	166(10)	43(10)
C(53)	−1 516(2)	6 459(2)	1 865(2)	557(14)	723(16)	694(16)	279(13)	173(12)	144(12)
C(54)	−1 383(2)	7 330(2)	2 623(2)	689(16)	678(16)	858(18)	282(14)	353(14)	242(13)
C(55)	−0 490(3)	7 335(2)	3 543(2)	834(18)	564(14)	721(16)	131(12)	341(14)	180(13)
C(56)	0 268(2)	6 468(2)	3 690(2)	653(14)	559(13)	554(13)	138(11)	200(11)	113(11)
C(57)	−0 931(2)	4 642(3)	1 130(2)	721(17)	869(19)	529(14)	79(13)	78(12)	109(14)

Hydrogen atom parameters

	x	y	z	B/Å^2		x	y	z	B/Å^2
H(3)	−004	−141	−091	5.8	H(33)	500	675	526	5.9
H(4)	−046	−235	044	5.9	H(34)	486	590	675	6.2
H(5)	109	−209	211	5.9	H(35)	310	456	676	5.8
H(6)	296	−092	234	5.0	H(36)	164	399	519	4.9
H(71)	278	003	912	6.5	H(371)	350	567	305	6.5
H(72)	447	−045	−155	6.5	H(372)	278	682	325	6.5
H(73)	175	075	−100	6.5	H(373)	415	595	348	6.5
H(13)	654	−204	362	6.0	H(43)	057	002	375	5.7
H(14)	674	−066	499	7.1	H(44)	−124	017	397	5.8
H(15)	597	127	471	6.8	H(45)	−203	208	377	5.6
H(16)	478	166	305	5.3	H(46)	−112	383	344	4.8
H(171)	450	−234	138	7.0	H(471)	271	234	390	6.2
H(172)	580	−276	185	7.0	H(472)	216	111	328	6.2
H(173)	544	−162	120	7.0	H(473)	219	247	286	6.2
H(23)	549	471	109	5.4	H(53)	−217	648	123	5.1
H(24)	369	534	106	5.7	H(54)	−188	801	249	5.4
H(25)	212	382	119	5.2	H(55)	−042	793	407	5.3
H(26)	229	168	116	4.4	H(56)	088	645	435	4.6
H(271)	660	321	110	6.5	H(571)	−151	481	052	5.9
H(272)	610	175	070	6.5	H(572)	000	487	100	5.9
H(273)	646	230	177	6.5	H(573)	−100	382	134	5.9

* Anisotropic thermal parameters in the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2lha^*c^*U_{31} + 2hka^*b^*U_{12})]$.

102.4(1)°] are evenly spread over the range 101.6—103.4°.

There are no unusually short intermolecular contacts between the molecules and it would appear that the P–C bond length is unaffected by the 12° variation in torsion angle. The mean torsional angle (43.7) compares with a predicted [5] value of 36.5°.

*Tri-*o-*tolylphosphine Oxide,* (II).—The crystal is con-

TABLE 7

Fractional atomic co-ordinates (× 10⁴; × 10³ for H) in (II) (the anisotropic temperature factor is defined in Table 6)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
P(1)	9 150(2)	4 537(1)	0 886(0)	554(8)	510(7)	613(8)	87(6)	47(6)	−135(6)
O(1)	8 659(4)	4 320(2)	1 261(1)	767(27)	798(27)	800(26)	178(21)	191(21)	−120(21)
C(1)	8 117(5)	5 356(3)	0 671(2)	514(30)	585(31)	803(35)	130(27)	51(25)	−116(25)
C(2)	7 961(6)	6 035(3)	0 882(2)	595(35)	682(35)	864(39)	22(29)	147(29)	−174(28)
C(3)	7 049(8)	6 621(4)	0 714(2)	828(46)	579(36)	522(65)	96(39)	223(44)	−32(33)
C(4)	6 319(8)	6 533(4)	0 352(3)	857(50)	700(42)	1 684(75)	337(45)	−17(48)	−46(36)
C(5)	6 498(8)	5 884(4)	0 148(2)	923(51)	881(47)	1 194(56)	324(42)	−270(42)	−72(39)
C(6)	7 382(7)	5 287(3)	0 304(2)	760(41)	693(37)	932(41)	191(32)	−87(33)	−125(31)
C(7)	8 725(8)	6 155(4)	1 271(2)	1 038(54)	804(44)	1 082(51)	−136(38)	311(42)	−65(39)
C(11)	11 082(6)	4 805(3)	0 912(1)	575(31)	549(29)	625(30)	−44(24)	37(24)	−181(24)
C(12)	12 141(7)	4 370(3)	1 133(2)	697(37)	763(38)	728(35)	−75(29)	−19(29)	−67(31)
C(13)	13 633(8)	4 657(5)	1 156(2)	791(46)	1 199(58)	949(47)	−34(42)	−144(37)	58(42)
C(14)	13 972(8)	5 298(5)	0 960(2)	860(50)	1 037(54)	1 347(63)	−26(47)	108(44)	−363(42)
C(15)	12 950(8)	5 712(4)	0 736(2)	860(46)	740(40)	1 112(50)	1(36)	167(38)	−191(35)
C(16)	11 500(6)	5 461(3)	0 716(2)	507(32)	714(35)	1 861(38)	−56(30)	96(27)	−146(28)
C(17)	11 827(8)	3 638(4)	1 330(2)	937(50)	981(49)	923(46)	201(39)	−104(38)	106(40)
C(21)	8 937(6)	3 765(3)	0 538(2)	722(36)	509(29)	713(53)	103(25)	−183(28)	−125(26)
C(22)	7 619(7)	3 314(3)	0 495(2)	895(46)	518(32)	1 140(44)	219(33)	−384(38)	−194(31)
C(23)	7 576(9)	2 722(4)	0 228(2)	1 392(67)	576(37)	1 440(64)	132(40)	−772(54)	−253(40)
C(24)	8 682(10)	2 551(4)	0 004(2)	1 753(78)	484(34)	1 183(56)	−76(35)	−647(54)	−124(41)
C(25)	9 967(10)	3 000(4)	0 045(2)	1 441(65)	710(40)	826(43)	−136(34)	−194(41)	139(41)
C(26)	10 073(8)	3 597(4)	0 319(2)	1 078(51)	699(37)	654(35)	22(29)	7(33)	−100(35)
C(27)	6 322(8)	3 449(4)	0 705(3)	851(51)	817(47)	1 739(77)	285(49)	−98(50)	−104(40)
P(2)	6 627(2)	4 197(1)	4 134(4)	633(9)	481(7)	540(7)	56(6)	−37(6)	74(6)
O(2)	7 397(5)	3 773(2)	4 462(1)	938(30)	708(25)	726(24)	217(20)	−178(22)	115(22)
C(31)	4 670(6)	3 958(3)	4 045(2)	648(35)	456(27)	736(33)	44(24)	9(27)	−31(24)
C(32)	3 777(7)	3 908(3)	4 347(2)	855(43)	577(32)	856(39)	37(29)	248(33)	13(30)
C(33)	2 265(8)	3 718(4)	4 259(2)	839(46)	732(40)	1 198(53)	137(38)	394(40)	135(35)
C(34)	1 721(8)	3 604(4)	3 891(3)	752(46)	832(46)	1 533(67)	93(45)	201(44)	80(37)
C(35)	2 563(8)	3 646(4)	3 592(2)	773(44)	787(42)	1 108(51)	−4(37)	−147(37)	51(34)
C(36)	4 072(6)	3 830(3)	3 669(2)	624(36)	743(37)	839(39)	87(31)	−82(30)	61(30)
C(37)	4 328(11)	4 050(6)	4 748(2)	1 527(79)	1 571(80)	813(48)	−129(51)	310(49)	−144(64)
C(41)	0.7441(6)	0.4019(3)	0.3689(1)	578(32)	515(28)	657(30)	−66(24)	−85(24)	70(24)
C(42)	0.7679(6)	0.3259(3)	0.3560(2)	674(36)	558(32)	894(40)	−182(29)	−126(30)	3(28)
C(43)	0.8356(7)	0.3169(4)	0.3224(2)	741(42)	464(47)	994(46)	−537(38)	−99(34)	157(36)
C(44)	0.8796(8)	0.3787(4)	0.3017(2)	858(47)	1 162(55)	767(40)	−277(38)	53(34)	−34(41)
C(45)	0.8567(7)	0.4526(4)	0.3137(2)	809(43)	935(45)	708(36)	−149(33)	106(31)	−40(36)
C(46)	0.7869(6)	0.4637(3)	0.3468(1)	656(34)	587(31)	619(30)	−43(25)	−24(25)	87(26)
C(47)	0.7245(9)	0.2564(4)	0.3776(2)	1 356(65)	532(35)	1 179(55)	−122(35)	−38(47)	71(38)
C(51)	0.6693(6)	0.5240(3)	0.4200(1)	605(32)	533(27)	484(26)	−12(21)	27(23)	−8(24)
C(52)	0.7996(6)	0.5612(3)	0.4350(1)	639(33)	682(33)	529(28)	−64(24)	105(24)	12(27)
C(53)	0.7984(7)	0.6405(3)	0.4389(2)	821(42)	729(37)	795(38)	−218(30)	221(32)	−202(32)
C(54)	0.6755(8)	0.6846(3)	0.4281(2)	1 024(50)	612(35)	1 014(46)	−191(33)	261(38)	−88(34)
C(55)	0.5472(8)	0.6484(3)	0.4134(2)	1 012(50)	556(33)	983(45)	33(31)	241(37)	290(33)
C(56)	0.5448(6)	0.5686(3)	0.4093(2)	670(37)	622(33)	786(36)	−2(28)	−70(29)	137(28)
C(57)	0.9412(8)	0.5163(4)	0.4465(2)	795(45)	1 096(53)	888(44)	−15(39)	−82(35)	−150(40)
P(3)	0.6620(2)	0.1247(1)	0.2383(0)	533(8)	487(7)	536(7)	−31(6)	−15(6)	−71(6)
O(3)	0.7437(5)	0.1679(2)	0.2700(1)	871(29)	731(25)	672(23)	−184(20)	−105(21)	−190(22)
C(61)	0.7366(5)	0.1420(3)	0.1926(1)	467(29)	544(28)	647(30)	−22(23)	−12(23)	−41(23)
C(62)	0.7616(6)	0.2181(3)	0.1800(2)	529(32)	579(30)	789(35)	37(26)	−42(26)	−74(25)
C(63)	0.8297(6)	0.2275(4)	0.1466(2)	604(36)	812(39)	842(39)	230(32)	53(29)	−104(31)
C(64)	0.8704(7)	0.1659(4)	0.1254(2)	668(39)	1 100(50)	742(39)	244(36)	198(31)	8(36)
C(65)	0.8434(8)	0.0929(4)	0.1374(2)	879(46)	957(46)	787(39)	−6(35)	244(34)	232(37)
C(66)	0.7779(6)	0.0811(3)	0.1706(2)	676(37)	637(33)	729(34)	28(28)	42(28)	41(28)
C(67)	0.7200(9)	0.2882(3)	0.2013(2)	1 267(61)	507(33)	1 216(54)	−115(35)	388(46)	−131(36)
C(71)	0.4660(6)	0.1470(3)	0.2315(1)	546(31)	547(29)	636(30)	−36(23)	73(24)	−59(24)
C(72)	0.3821(7)	0.1465(4)	0.2630(2)	628(37)	807(40)	965(44)	−46(33)	163(32)	−13(31)
C(73)	0.2283(7)	0.1607(4)	0.2557(2)	726(42)	921(47)	1 172(53)	−4(40)	252(38)	−151(36)
C(74)	0.1635(6)	0.1741(4)	0.2197(2)	420(32)	814(41)	1 442(68)	−7(40)	77(34)	−75(30)
C(75)	0.2454(7)	0.1744(3)	0.1840(2)	734(41)	648(36)	1 120(50)	200(34)	−191(36)	8(31)
C(76)	0.3983(6)	0.1606(3)	0.1950(2)	582(33)	548(30)	828(37)	80(27)	21(28)	−20(25)
C(77)	0.4469(10)	0.1312(6)	0.3042(2)	1 149(65)	1 949(97)	845(49)	49(56)	140(45)	−42(65)
C(81)	0.6651(6)	0.0206(3)	0.2453(1)	688(35)	616(30)	481(27)	72(23)	−46(24)	−78(27)
C(82)	0.7106(6)	−0.0191(3)	0.2618(2)	653(36)	734(35)	604(31)	99(27)	−32(26)	−44(28)
C(83)	0.7817(7)	−0.0986(4)	0.2653(2)	832(44)	718(37)	821(39)	191(31)	58(32)	43(32)
C(84)	0.6585(8)	−0.1389(3)	0.2531(2)	1 055(52)	488(32)	1 112(49)	223(32)	152(40)	24(33)
C(85)	0.5336(8)	−0.1003(4)	0.2367(2)	873(47)	696(38)	981(45)	78(33)	16(36)	−132(33)
C(86)	0.5369(7)	−0.0226(3)	0.2322(2)	771(39)	509(29)	737(34)	110(26)	−105(29)	−105(27)
C(87)	0.9342(7)	0.0199(4)	0.2756(2)	767(44)	1 103(53)	891(44)	16(39)	−135(35)	−141(39)

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[5] E. J. Halpern and K. Mislow, *J. Amer. Chem. Soc.*, 1967, **89**, 5224.

Table 7 (*Continued*)

Hydrogen atom parameters

	x	y	z	$B/Å^2$
H(3)	688	707	092	7.1
H(4)	586	700	028	7.9
H(5)	619	585	−010	7.8
H(6)	753	481	015	6.2
H(71)	872	656	134	7.6
H(72)	943	595	133	7.6
H(73)	841	575	147	7.6
H(13)	1 393	445	137	7.6
H(14)	1 471	549	095	8.4
H(15)	1 327	627	057	7.0
H(16))	1 073	580	054	5.4
H(171	1 288	341	149	7.5
H(172)	1 110	364	152	7.5
H(173)	1 132	329	118	7.5
H(23)	680	240	017	8.3
H(24)	862	207	−019	7.9
H(25)	1 062	293	−007	7.5
H(26)	1 059	372	024	6.2
H(271)	611	374	078	8.4
H(272)	599	285	086	8.4
H(273)	659	299	051	8.4
H(33)	180	372	453	7.1
H(34)	068	346	378	7.8
H(35)	216	357	331	6.9
H(36)	476	390	344	5.8
H(371)	416	440	489	9.9
H(372)	423	381	493	9.9
H(373)	507	439	480	9.9
H(43)	850	276	312	7.0
H(44)	927	366	279	7.2
H(95)	896	506	297	6.4
H(46)	775	517	359	4.9
H(471)	739	211	366	7.5
H(472)	786	254	403	7.5
H(473)	663	255	397	7.5
H(53)	883	670	451	6.2
H(54)	681	744	436	6.8
H(55)	462	678	404	6.5
H(56)	453	546	397	5.4
H(571)	005	547	454	7.3
H(572)	983	486	417	7.3
H(573)	927	482	464	7.3
H(63)	839	281	139	5.9
H(64)	919	173	101	6.6
H(65)	874	051	127	6.9
H(66)	765	035	179	5.4
H(671)	767	342	195	7.3
H(672)	585	320	182	7.3
H(673)	688	291	219	7.3
H(73)	177	161	277	7.3
H(74)	1 063	178	220	6.2
H(75)	203	188	163	6.4
H(76)	454	162	172	5.1
H(771)	562	118	309	9.8
H(772)	459	064	306	9.8
H(773)	479	161	316	9.8
H(83)	865	−127	280	6.2
H(84)	644	−194	254	6.6
H(85)	460	−126	225	6.6
H(86)	457	005	215	5.2
H(871)	986	044	253	7.2
H(872)	1 029	−031	288	7.2
H(873)	923	064	291	7.2

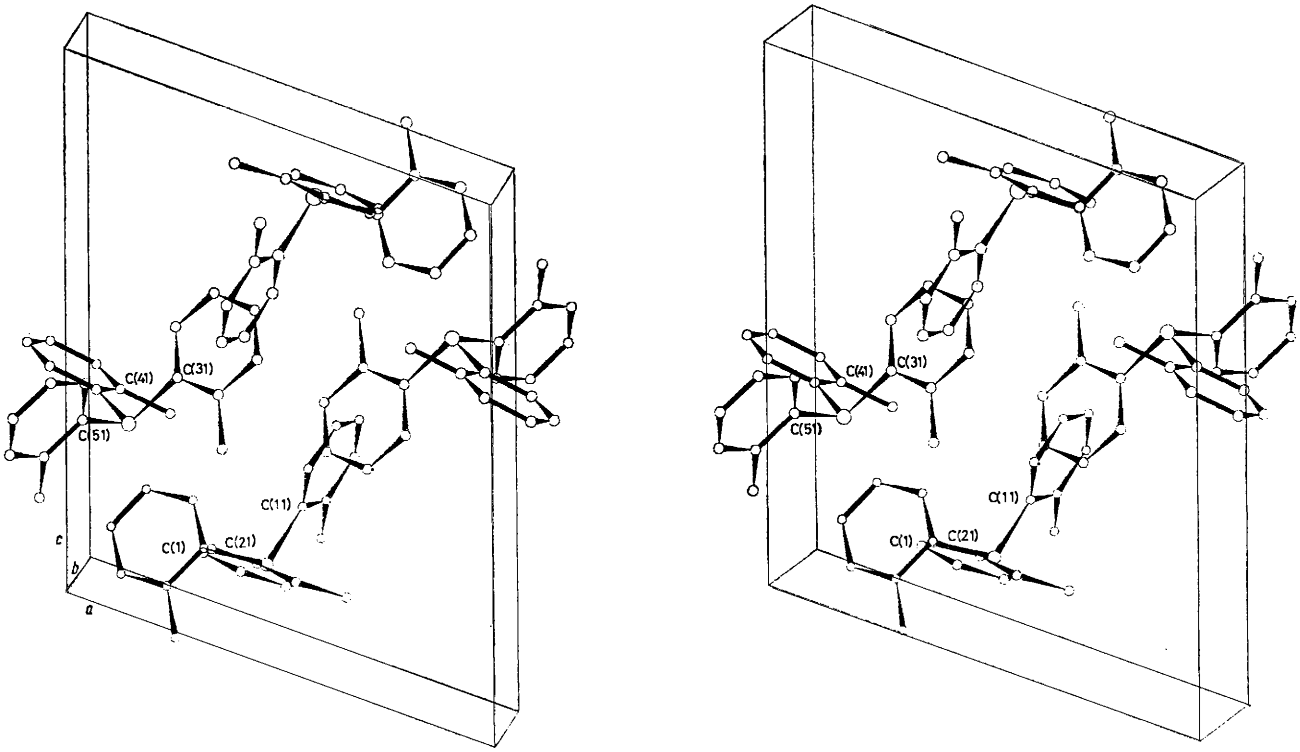

Figure 5 Stereoscopic projection of the structure of (I). Axis b is at 4° to the normal to the page

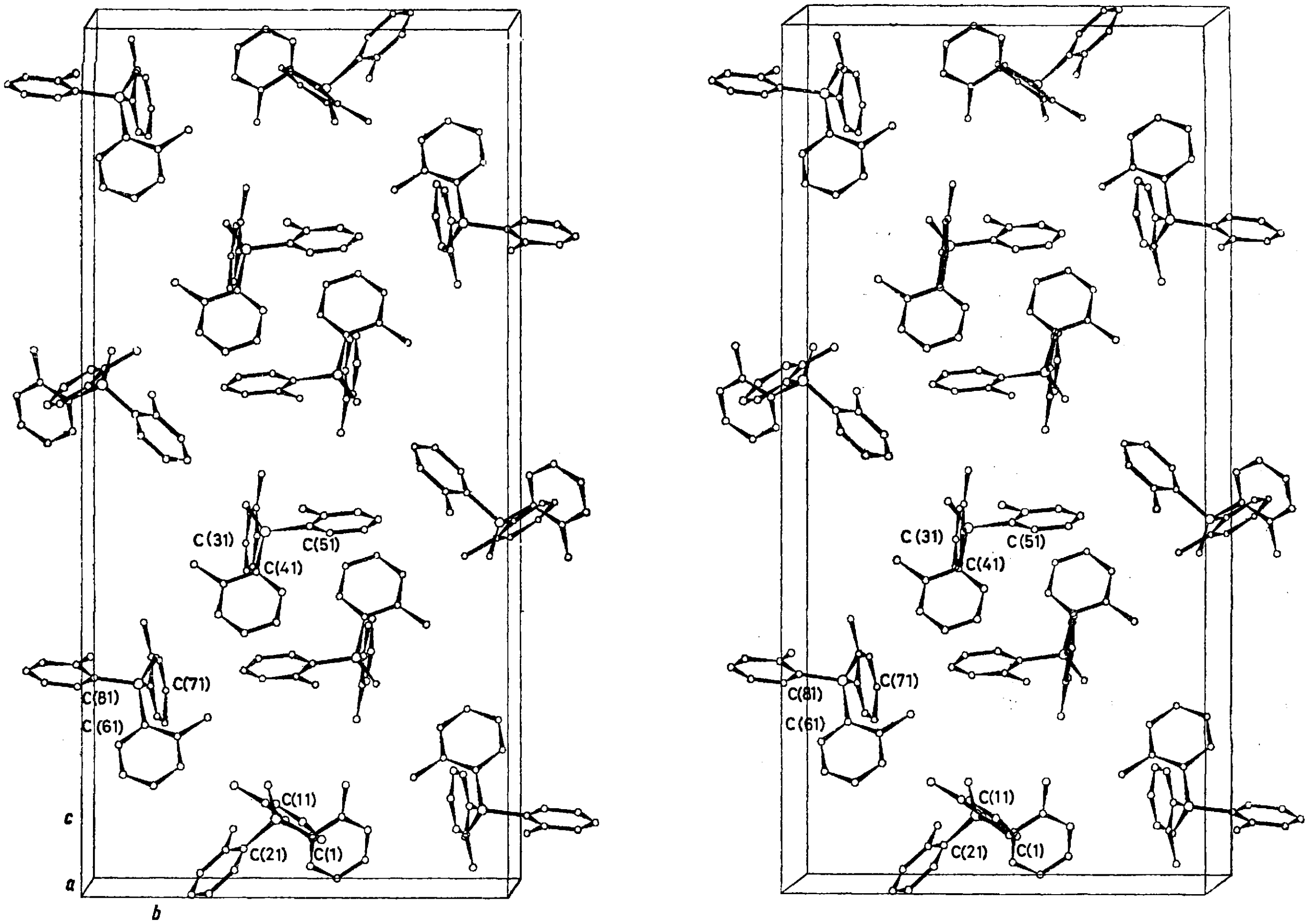

FIGURE 6 Stereoscopic projection of the structure of (II). Axis *a* is at 4° to the normal to the page

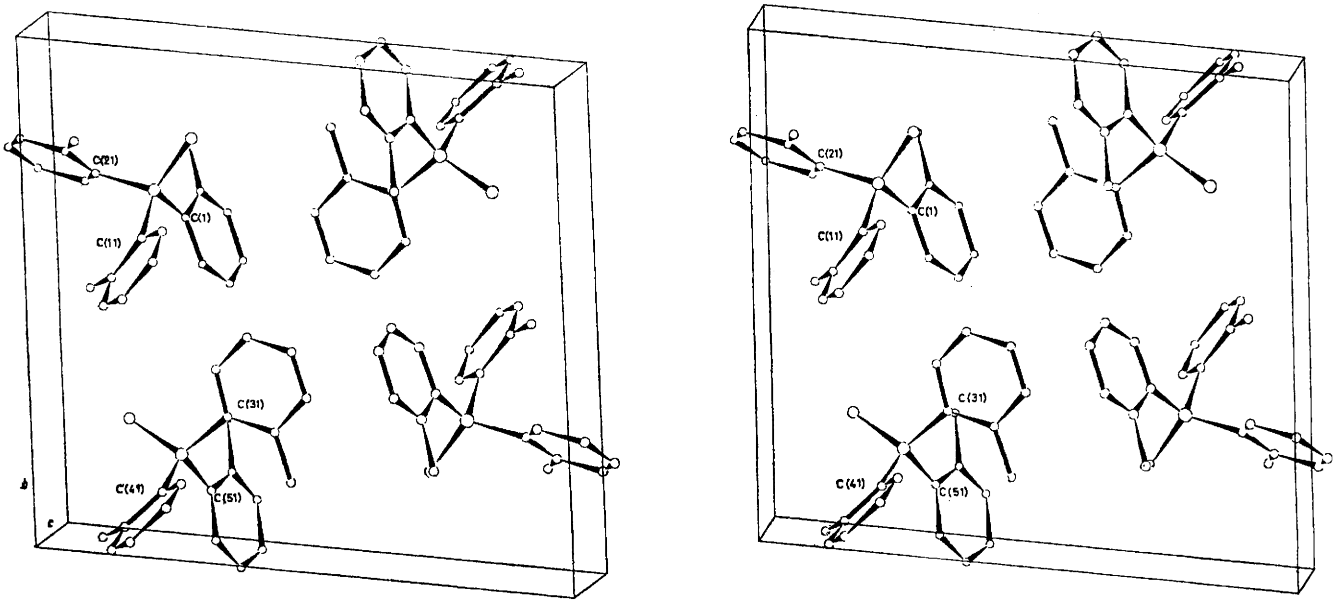

FIGURE 7 Stereoscopic projection of the structure of (III). Axis *c* is at 4° to the normal to the page

structed from three independent molecules with similar conformations. In the structure two of these molecules pack ' back-to-back ' with the conformation of the tolyl groups so arranged that the plane of each tolyl group of one molecule is perpendicular to that of the closest tolyl group of the second molecule. The third independent molecule packs similarly with a centrosymmetrically related molecule. These two pairs of molecules form a layer along the (013) plane.

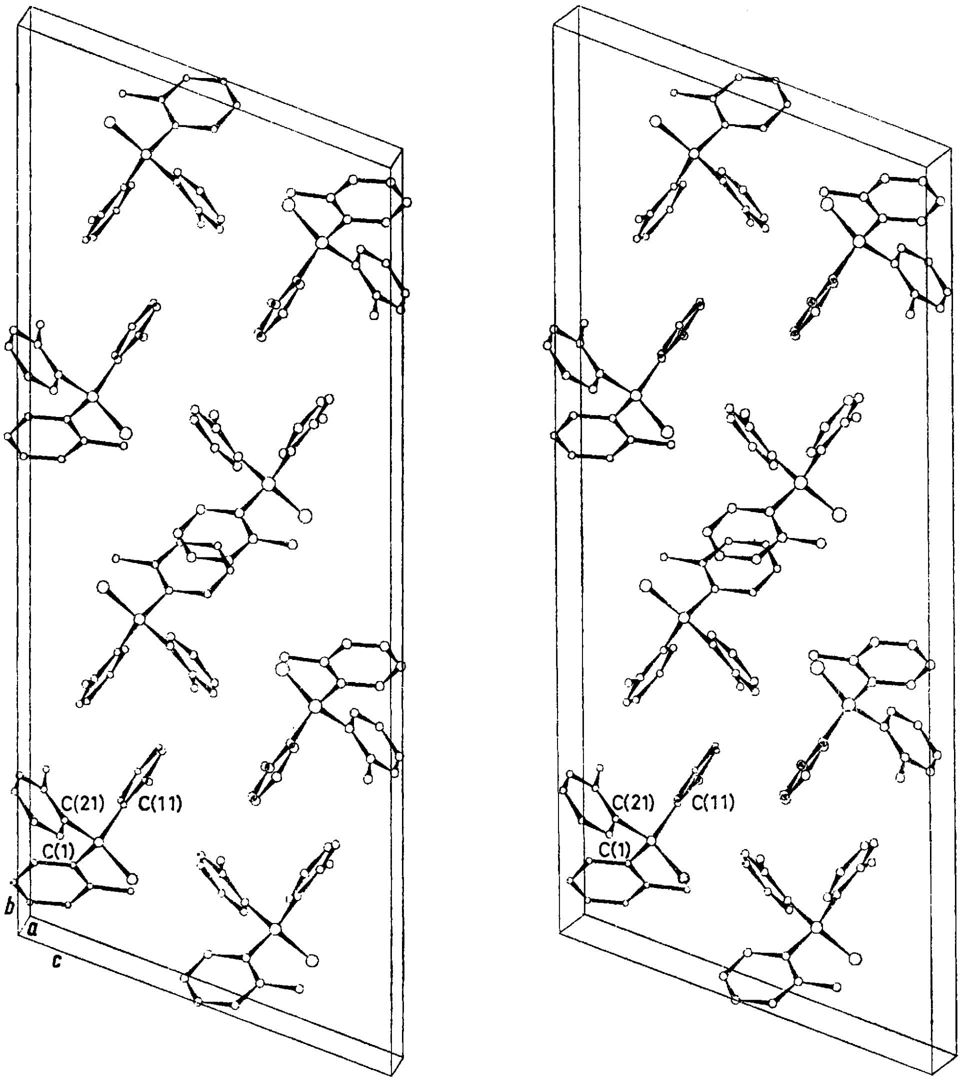

FIGURE 8 Stereoscopic projection of the structure of (IV). Axis *b* is at 4° to the normal to the page

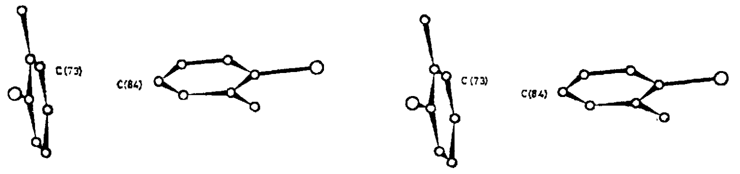

FIGURE 9 Detail of the steric interaction between tolyl groups C(71)—(77) and C(81)—(87) in (II)

The co-ordination sphere about each phosphorus atom is a distorted tetrahedron. The O–P–C interbond angles are evenly distributed over the range 112.1—113.7°, mean 112.9(1)°, while the C–P–C interbond angles are equivalent, with the exception of C(71)–P(3)–C(81), mean 106.0(1)° *vs.* 102.3° in (I). Atoms C(73) and C(84) have the closest intermolecular contact 3.63 Å (Figure 5) and the closing of the C(71)–P(3)–C(81) interbond angle to 103.3(2)° would relieve this steric interaction. The increase in C–P–C interbond angle in (II) compared to (I) probably reflects[6] a greater repulsion between the phosphorus lone-pair electrons and σ bond

[6] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **11**, 339.

electrons of the P–C bond than between the electrons of the P=O and P–C bonds.

The tolyl groups in each molecule assume the ' paddle ' conformation frequently observed in molecules containing the PPh_3 group and have the three *o*-methyl groups close to the phosphoryl oxygen atom. The torsion angles about the P–C bonds are in the range 36.7—53.3° so there is an approximate three-fold axis in the molecule which passes along the phosphoryl P=O bond.

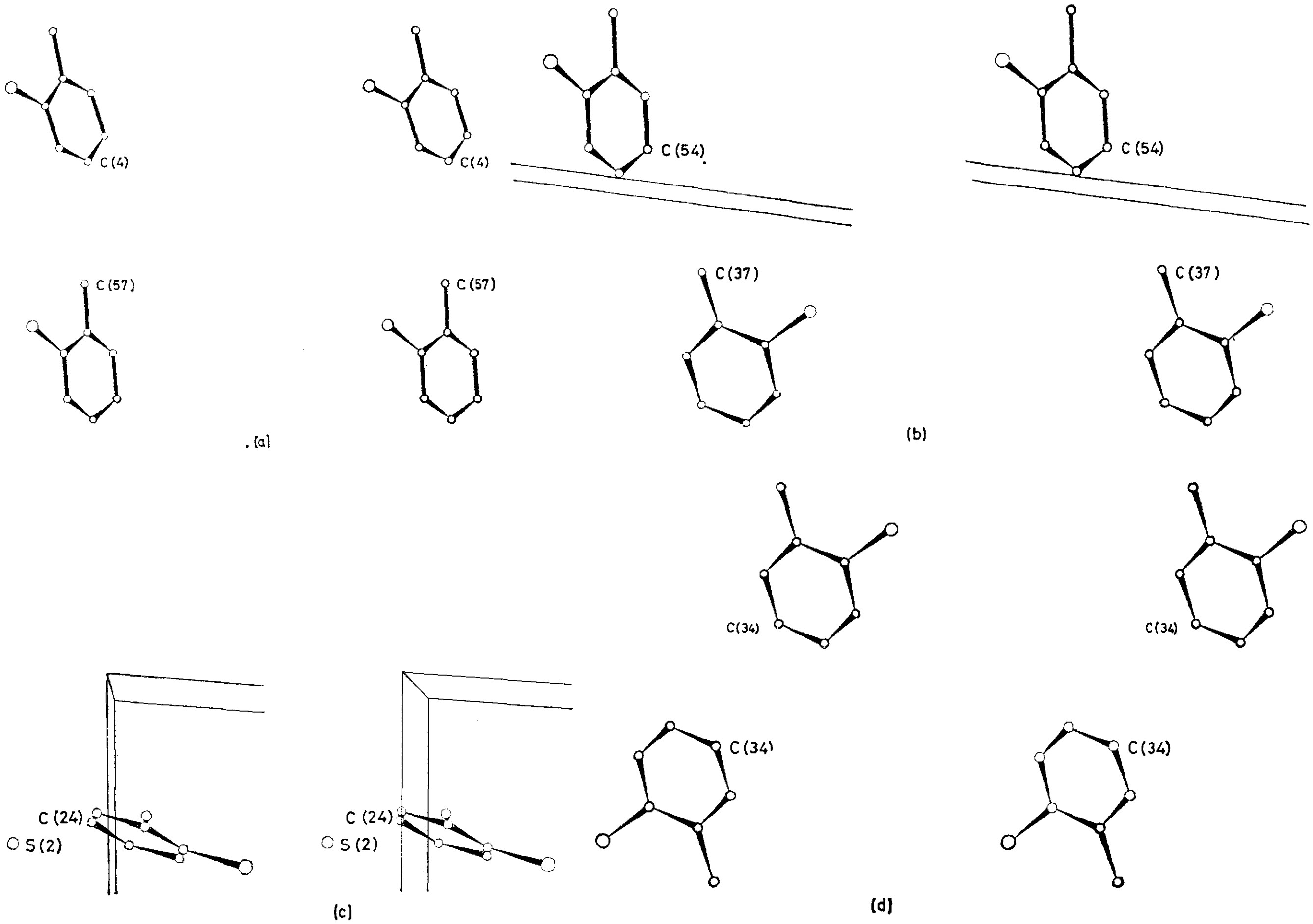

FIGURE 10 Detail of the steric interaction in (III) between tolyl groups (a) C(1)—(7) and C(51)—(57), (b) C(51)—(57) and C(31)—(37), (c) C(21)—(27) and S(2), and (d) C(31)—(37) and C(31)—(37) in the centrosymmetrically related molecule

The P–C bond lengths are all equivalent, mean 1.810(2) Å; this compares [7,8] with means of 1.76(1) Å in triphenylphosphine oxide and 1.785(4) Å in the hydroxytriphenylphosphonium ion, $[Ph_3POH]^+$. All the P–C bond lengths are shorter than those in triphenylphosphine, and this could be the result of the electron-withdrawing properties of the phosphoryl oxygen atom, which produces a reduced electron density at the phosphorus atom, a small charge separation along the P–C bond and a consequent shortening of its length. The P–C bond lengths in (II) however are significantly longer than those of triphenylphosphine oxide, reflecting, perhaps, the steric strain within the molecules. The intramolecular *o*-methyl carbon–phosphoryl oxygen atom contact distances are in the range 3.01—3.19 Å, and the plane through the three methyl carbon atoms of each molecule cuts across the corresponding phosphoryl P=O bond. These contact distances are short and the steric strain that this represents can most easily be relieved by an increase in P–C bond length.

Tri-o-*tolylphosphine Sulphide*, (III).—The structure contains two independent molecules with similar conformations. The crystal is best described as being constructed from groups of four molecules (the two independent molecules and the pair related to them by the centre of symmetry in the centre of the unit cell) arranged with the phosphorus atoms approximately on the corners of a square; four tolyl groups come within this square, with the planes of adjacent groups approximately perpendicular. The four sulphur atoms are outside the square with a projection of the P=S bond on the plane of the square parallel to its diagonals.

In molecules of (III), unlike (I) and (II), the three

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[7] G. Bandoli, G. Bartolozzo, D. A. Clemente, U. Croatto, and C. Panattoni, *J. Chem. Soc.* (*A*), 1970, 2778.

[8] T. S. Cameron and C. K. Prout, *J. Chem. Soc.* (*C*), 1969, 2289.

o-methyl groups do not occupy similar positions. Two are on the same side of the molecule as the sulphur atom, the *exo*-groups,[5] but the third is on the opposite side, the *endo*-group, and is close to the continuation of the line passing from the sulphur to the phosphorus atom. The change in conformation for this compound is probably the result of the increased space occupied by the sulphur atom compared with that occupied by the oxygen atom or lone-pair electrons, and an examination of a ' space filling ' model suggests that it is not possible to place all three methyl groups close to the sulphur atom without serious steric strain.

TABLE 8

Fractional atomic co-ordinates (× 10^4; × 10^3 for H atoms) in (III) (the anisotropic temperature factor is defined in Table 6)

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	2 232(1)	7 024(1)	4 150(3)	407	563	646	−67	−389	260
S(1)	7 147(1)	1 992(1)	4 219(3)	619	671	998	−231	−779	195
C(1)	2 912(5)	6 662(6)	2 275(12)	493	844	696	−79	−581	445
C(2)	3 270(5)	7 253(6)	1 181(12)	431	779	830	105	−103	304
C(3)	6 159(5)	3 038(7)	115(14)	499	958	1 015	−76	−390	165
C(4)	4 114(6)	6 075(7)	−493(14)	556	994	913	−234	−454	315
C(5)	3 789(6)	5 533(6)	618(13)	542	703	811	75	−285	261
C(6)	3 210(4)	5 796(5)	1 912(11)	413	685	836	−340	−351	411
C(7)	3 061(6)	8 231(7)	1 471(15)	690	623	1 024	412	−110	410
C(11)	1 899(5)	6 017(5)	5 080(10)	533	564	558	89	−320	267
C(12)	1 354(5)	5 228(6)	4 264(11)	458	868	639	107	−68	461
C(13)	8 874(6)	5 393(6)	4 823(12)	631	865	747	547	148	391
C(14)	8 628(7)	5 327(7)	3 125(15)	882	1 083	1 040	360	−170	953
C(15)	8 081(7)	4 566(7)	2 337(13)	713	1 016	758	431	−350	636
C(16)	7 819(6)	3 906(7)	3 254(11)	600	931	631	364	−143	693
C(17)	1 073(5)	5 091(6)	2 387(12)	732	824	646	−357	−654	214
C(21)	1 181(5)	7 275(5)	3 545(12)	343	500	921	−33	−413	406
C(22)	556(5)	7 580(6)	4 684(11)	408	538	794	31	−54	249
C(23)	−259(4)	7 768(5)	4 173(11)	399	618	911	295	−212	222
C(24)	−367(5)	7 684(6)	2 368(12)	443	786	801	238	−401	493
C(25)	242(6)	7 393(6)	1 219(13)	619	696	991	133	−571	180
C(26)	1 091(5)	7 203(6)	1 692(11)	617	691	656	−45	−427	297
C(27)	−605(6)	2 318(7)	3 370(13)	741	985	723	−74	−309	731
P(2)	2 663(1)	1 984(1)	2 052(3)	364	523	674	−54	−435	273
S(2)	1 758(1)	2 626(1)	1 426(3)	487	753	978	80	−606	492
C(31)	3 456(4)	2 728(5)	3 483(10)	477	508	609	−236	−254	323
C(32)	4 299(5)	2 494(5)	3 780(11)	270	617	681	45	−453	263
C(33)	4 853(6)	3 166(6)	4 905(11)	514	617	752	24	−313	48
C(34)	5 432(6)	5 990(6)	4 400(13)	458	602	890	31	−476	−65
C(35)	6 235(5)	5 766(5)	4 660(12)	691	478	785	−111	−503	18
C(36)	3 234(5)	3 599(5)	4 189(11)	572	469	744	−33	−59	216
C(37)	4 609(4)	1 377(5)	3 133(11)	518	698	797	−37	−333	616
C(41)	2 204(5)	1 147(5)	3 253(10)	415	777	561	68	−294	461
C(42)	1 519(5)	432(6)	2 557(12)	576	773	763	−92	−457	383
C(43)	1 187(7)	−109(7)	3 675(15)	777	913	826	199	−10	476
C(44)	1 425(7)	−12(7)	5 326(16)	866	935	1 086	5	−375	327
C(45)	2 082(7)	686(7)	6 028(14)	786	845	811	512	−370	257
C(46)	2 449(5)	1 248(6)	4 907(10)	534	970	570	94	−113	693
C(47)	1 221(6)	289(7)	693(15)	670	1 055	972	−304	−847	−329
C(51)	3 298(5)	1 434(5)	283(11)	497	648	701	89	−655	245
C(52)	6 225(5)	8 108(6)	934(11)	647	658	587	199	−287	584
C(53)	5 708(6)	8 530(7)	2 160(14)	794	865	743	153	−355	249
C(54)	5 634(7)	9 489(7)	2 414(13)	950	868	633	−65	−102	834
C(55)	6 110(7)	54(6)	1 339(13)	675	686	733	−146	−270	410
C(56)	3 360(5)	472(5)	11(22)	517	523	963	−203	−497	284
C(57)	3 716(6)	2 922(6)	−755(13)	831	558	725	−261	−418	188

Hydrogen atom parameters

	x	*y*	*z*	*B*/Å^2		*x*	*y*	*z*	*B*/Å^2
H(3)	299	534	260	6.0	H(33)	544	304	520	5.6
H(4)	398	491	47	6.1	H(34)	496	448	633	5.8
H(5)	451	584	−148	6.1	H(35)	357	482	596	5.3
H(6)	406	741	−80	5.3	H(36)	267	377	385	4.9
H(13)	257	663	729	7.1	H(43)	73	−61	324	8.9
H(14)	211	550	836	9.4	H(44)	112	−44	600	8.4
H(15)	116	419	750	8.4	H(45)	227	77	72	8.1
H(16)	75	406	455	7.2	H(46)	291	175	531	7.8
H(23)	−73	795	504	5.7	H(53)	462	186	−287	8.3
H(24)	−89	783	187	6.3	H(54)	474	16	−333	9.4
H(25)	5	731		6.8	H(55)	393	−60	−154	6.0
H(26)	157	703	81	6.7	H(56)	303	9	76	5.1

The co-ordination spheres around the phosphorus atoms are distorted tetrahedra but the change in conformation of the molecules of (III) produces a more irregular sphere than was observed for (II). The

TABLE 9

Fractional atomic co-ordinates ($\times 10^4$; $\times 10^3$ for H) in (IV) (the anisotropic temperature factor is defined in Table 6)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se(1)	0 889(1)	2 146(2)	2 805(1)	573	645	513	−119	259	70
P(1)	1 123(1)	0 771(4)	1 870(3)	314	288	280	−19	117	19
C(1)	0 723(4)	—0 718(17)	1 138(10)	343	305	354	−69	102	−15
C(2)	0 527(5)	—1 889(19)	1 545(11)	416	394	490	−57	174	−87
C(3)	0 208(5)	−2 851(21)	0 915(13)	437	395	715	−2	143	−184
C(4)	0 084(5)	−2 674(20)	−0 097(4)	311	431	774	−211	102	−39
C(5)	0 263(4)	−1 572(19)	−0 487(11)	286	491	464	−58	42	34
C(6)	0 595(4)	−0 545(17)	0 100(10)	375	357	378	−72	94	−63
C(7)	0 634(6)	−2 158(26)	2 607(13)	513	787	490	77	320	−15
C(11)	1 608(4)	−0 411(16)	2 501(9)	301	414	276	26	173	27
C(12)	1 983(4)	0 334(18)	3 091(11)	439	435	363	−42	196	−2
C(13)	2 346(5)	−0 671(25)	3 528(13)	366	765	597	51	0	−31
C(14)	2 332(6)	−2 356(23)	3 385(15)	482	684	765	−2	71	108
C(15)	1 961(6)	−3 107(20)	2 790(13)	575	457	564	3	223	173
C(16)	1 597(5)	−2 139(20)	2 363(11)	490	363	419	38	104	−93
C(17)	2 032(6)	2 192(22)	3 272(13)	516	586	554	−72	228	−184
C(21)	1 258(4)	2 133(18)	1 007(9)	299	309	317	22	56	−100
C(22)	1 492(4)	1 593(18)	0 431(9)	437	424	231	−49	54	−49
C(23)	1 577(5)	2 767(22)	−0 175(11)	556	557	376	−90	157	−110
C(24)	1 419(6)	4 384(22)	−0 249(13)	494	744	510	169	−33	−202
C(25)	1 185(6)	4 897(22)	0 289(12)	730	271	502	−48	36	−121
C(26)	1 109(5)	3 727(19)	0 934(12)	404	362	477	−86	119	18
C(27)	1 676(5)	−0 192(24)	0 435(12)	442	747	457	−140	11	−93

Hydrogen atom parameters

	x	y	z	B/Å^2		x	y	z	B/Å^2
H(3)	003	−375	120	4.3	H(171)	197	234	373	4.6
H(4)	014	−348	−065	4.1	H(172)	198	271	286	4.6
H(5)	023	−127	−134	3.5	H(173)	235	275	365	4.6
H(6)	068	035	021	2.9	H(23)	174	206	−052	4.0
H(71)	045	−298	258	4.7	H(24)	137	507	−085	4.7
H(72)	087	−255	282	4.7	H(25)	105	616	020	3.7
H(73)	053	−162	296	4.7	H(26)	093	419	107	3.2
H(13)	266	−017	399	4.8	H(271)	150	−023	116	4.3
H(14)	257	−336	403	5.6	H(272)	188	006	086	4.3
H(15)	190	−420	263	4.6	H(273)	152	−046	017	4.3
H(16)	134	−265	188	4.0					

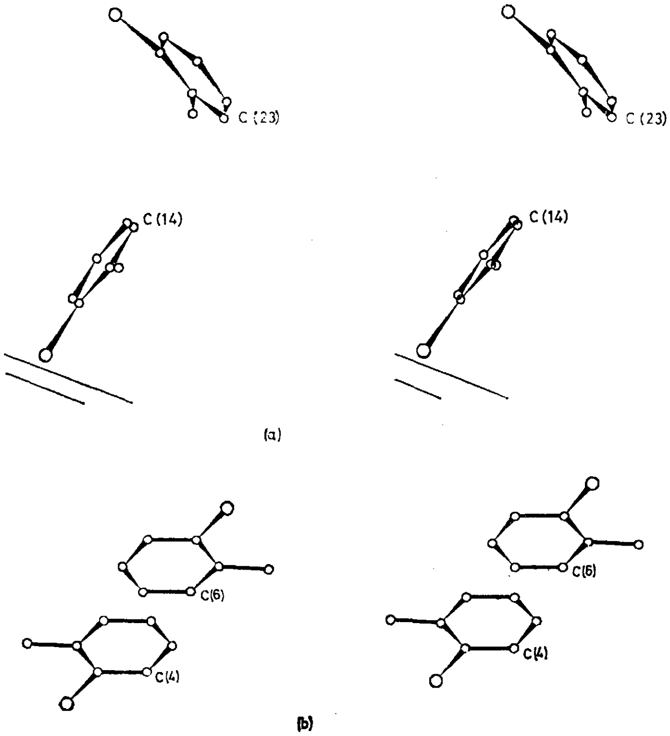

FIGURE 11 Detail of the steric interaction in (IV) between tolyl groups (a) C(11)—(17) and C(21)—(27) and (b) C(1)—(7) and C(1′)—(7′) in the centrosymmetrically related molecule

S–P–C interbond angles are in the range 110.7—114.3°, mean value of 112.6(2)°, and the C–P–C angles have values between 101.5 and 110.6°. The torsion angles come in two groups: these for the tolyl groups with *exo*-methyl substituents are in the range of 52.6—66.9°, and those with the *endo*-methyl groups are 3.4 [C(11)—C(17)], and 17.0° [C(31)—C(37)]. The rotation is in the same direction when each phenyl group is viewed from a similar perspective. Because of the small torsion angle of the *endo*-tolyl groups, the *o*-carbon atom, without the methyl group, comes close to the sulphur atom [S(1) · · · C(16) 3.24, S(1) · · · C(36) 3.25 Å]. This distance is less than the sum of the van der Waals radii and probably produces considerable steric strain, which could be relieved by lengthening the P–C bond.

In group C(11)—C(17), with the P–C torsion angle near zero and the S(1) · · · C(16) interaction close to its maximum, this lengthening is dramatic; P(1)–C(11) (1.870 Å) is one of the longer reported[1] P–C bonds lengths. In the group C(31)—C(37) the increase in P–C torsion angles relieves most of the steric hindrance between C(36) and S(2), and the P(2)–C(31) bond length is only slightly longer than the other P–C bond lengths in the molecule.

In the ' paddle ' conformation present in (II) the balance between the intramolecular nonbonded interactions produced a regular structure; the small torsional angle of one tolyl group and the non-equivalent conformation in (III) disturbs the balance. The general increase in P–C torsion angles in the *exo*-tolyl groups of one molecule brings carbon C(26) close to the tolyl group C(1)—C(7), while the small torsion angle at the *endo*-group results in a wide separation between groups C(11)—C(17) and C(21)—C(27). Consequently tolyl group C(21)—C(27) moves away from group C(1)—C(7) and towards group C(11)—C(17), and this is reflected in the interbond angles C(1)–P(1)–C(21) and C(11)–P(1)–C(21) (110.7 and 101.6°). The increase from 3.4 to 17.0° in the P–C torsion angle of the *endo*-tolyl group in the second molecule reduces the disparity between these intramolecular interactions. The close contact between the *exo*-tolyl groups remains, but the distances between these and the *endo*-group C(31)—C(37) are shortened. A large deformation from the regular structure is therefore energetically less profitable, as can be seen from the C–P–C bond angles: C(31)–P(2)–C(41) 104.9(4), C(31)–P(1)–C(51) 105.1(4)°, and angles between the *exo*-tolyl groups C(41)–P(1)–C(51) 107.9(4)°.

There is a close plane-to-plane contact [C(34) · · · C(34′), 3.49 Å] between the *endo*-tolyl group of this second molecule and the group centrosymmetrically related to it, the steric requirement of which is thought to be responsible for the difference in conformation between the two independent molecules.

The mean P=S bond length [1.948(2) Å] compares [2] with those [1.939(4) and 1.923(5) Å] in tri-*m*- and tri-*p*-tolylphosphine sulphide. In the *para*-compound there is also a marked decrease [2a] in the mean P–C bond lengths and the shortening of both the P–C and P=S bond lengths may be a consequence of the increased electron density at the P–C bond from the electron-donating *para*-substituent. A similar decrease in bond lengths would be expected for (III) with the *ortho*-substituents and the lengths observed are perhaps a compromise between steric crowding tending to lengthen, and electron donation from the substituent tending to shorten them.

The P–C bond lengths are in the range 1.773—1.870(9) Å, mean 1.819 Å. The three shortest contacts between the carbon of the phenyl rings *para* to phosphorus are: C(41) · · · C(57) 3.60, C(54) · · · C(37) 3.64, and C(24) · · · S(2) 3.72 Å. Corresponding P–C bond lengths are 1.791(9), 1.773(9), and 1.820(9) Å, and are the three shortest P–C bond lengths in the molecule. Details of these contacts are shown in Figure 10, where it can be seen that a large proportion of the interaction will be a compression force resolved along the axis of the P–C bond, and this could be responsible for their shortened lengths.

On the other hand there appears to be no obvious correlation in (III) between the torsion angle about the P–C bond and its length, *e.g.* in the four *exo*-groups the torsion angles vary by only 14° while the P–C bond lengths are in the range 1.733(9)—1.827(9) Å.

*Tri-*o*-tolylphosphine Selenide,* (IV).—The structure contains one independent molecule and the crystal is constructed from layers of molecules approximately parallel to the (101) plane. The molecule itself has a similar conformation to that of (III), with two *exo*- and one *endo*-tolyl groups; the co-ordination sphere about the phosphorus atom is also a similar distorted tetrahedron with mean Se–P–C and C–P–C angles of 112.7 and 106.4. The torsion angles about the P–C bonds are 13° for the *endo*-tolyl group C(21)—C(27), and 56.3 and 58.9° for the two *exo* groups C(1)—C(7) and C(11)—C(17). The dimensions in (IV) are less accurate than those in (I)—(III), so that the C–P–C interbond angles and the P–C bond lengths are not strictly significantly different. They do display, however, the same trends as in (III); the close intramolecular contact is between the two *exo*-tolyl groups and the C–P–C interbond angles are C(1)–P(1)–C(21) 106.7 and C(11)–P(1)–C(21) 105.4°, with C(1)–P(1)–C(11) 107.2°. Similarly the longest P–C bond length is in the *endo*-tolyl group and the shortest length [P(1)–C(11)] occurs in the tolyl group where there is the shortest intermolecular contact with the carbon atom *para* to phosphorus [C(14) · · · C(23) 3.67 Å, Figure 7].

The mean P–C bond length (1.834 Å) is longer than any observed in (II) or (III) and is similar to 1.835 in (I). This probably reflects the very weak polarising power of selenium compared to phosphorus (electronegativities: P 2.1 and Se 2.4 on the Pauling scale).

Conclusions.—The mean P–C bond lengths in these aryl phosphines appear to be influenced by two factors: the variation in σ electron density along the P–C bond, and intramolecular steric hindrance.

The P–C bond length will be shortened either by an electron-withdrawing atom bonded to phosphorus, *e.g.* phosphoryl oxygen, attracting the electrons of the aromatic system towards the phosphorus atom or an electron-donating substituent in the *ortho*- or *para*-positions in the phenyl ring, donating electrons to the carbon bonded to phosphorus.

In (II), the *ortho*-substituent is sterically hindered within the molecule and this is relieved by an increase in the P–C bond length. A similar conformation in the sulphide and selenide would be so severely hindered that the molecule adopts an alternative arrangement of atoms.

The individual P–C bond lengths appear to be affected by inter- and intra-molecular steric factors but not apparently to any great extent by an interaction between the phenyl π electrons and the phosphorus *d* orbitals. An alteration in the P–C bond length to relieve a close nonbonded atom contact seems to occur only when a large proportion of the resulting force can be resolved along the axis of the P–C bond; close contacts which produce forces that cannot be so resolved tend to distort the co-ordination sphere around the phosphorus atom. Consequently, most intramolecular steric interactions alter the molecular configuration, while crystal packing forces alter the P–C bond lengths. An exception to this occurs in the (II) where with the molecule already highly hindered, a decrease in P–C bond length to relieve a close intermolecular contact is unfavourable and instead the co-ordination sphere is distorted. It might be possible, if a sufficient crystal packing force is applied at the *p*-carbon of the phenyl ring, to form a similar conformation in (II) to that observed in (III) or (IV) and in this context it would be interesting to observe the structure of tris-(2,4-dimethylphenyl)phosphine oxide where the *p*-methyl groups which extend beyond the main body of the molecule could be particularly prone [9] to unusually short intermolecular contacts. The torsion angles about the P–C bonds present no coherent picture. In (III) two tolyl groups with torsion angles 56.6 and 56.5° have differences in P–C bond-length six times greater than the σ values of their lengths, while in the (II) and (IV) torsion angles distributed over the range 13—59° have corresponding P–C bond lengths which are not significantly different. Any extension of the aromatic π system to the phosphorus atom should be dependent on the torsion angle about the P–C bond and be reflected in its length.

EXPERIMENTAL

The structures were determined by the heavy-atom method. The positions of the phosphorus atom(s) were found from unsharpened three-dimensional Patterson functions and the positions of the remaining non-hydrogen atoms were determined from successive Fourier and difference-Fourier syntheses. Preliminary atomic parameters were refined by full-matrix least-squares; initially to convergence with isotropic temperature factors and unit weights, subsequently with anisotropic temperature factors and individual weights (w) for each reflection where $w = \{1 + [(|F_o(\text{abs})| - a_1)/a_2]^2\}^{-1}$. The positions of the hydrogen atoms were determined from difference syntheses calculated when refinement was almost complete. Hydrogen atoms were assigned the isotropic temperature factor of the atom bonded to them and their parameters were included in, but not altered by, the final cycles of refinement.

Crystal Data.—(*a*) *Tri*-o-*tolylphosphine*, (I). $2(C_{21}H_{21}P)$, $M = 608.7$. Triclinic, $a = 12.081(5)$, $b = 10.915(5)$, $c = 14.348(7)$ Å, $\alpha = 91.95(5)°$, $\beta = 110.58(4)°$, $\gamma = 98.22(5)°$, $U = 1\,745.8$ Å^3, $D_m = 1.157$ g cm^{-3}, $Z = 4$, $D_c = 1.158$ g cm^{-3}, $F(000) = 324$. Space group $P\bar{1}$ (C_i^1, No. 2). Cu-K_α radiation, $\lambda = 1.54051$ Å, $\mu(\text{Cu-}K_\alpha) = 13.18$ cm^{-1}.

The space group was assumed to be $P\bar{1}$ and this was not contradicted in the structure refinement.

A single crystal was mounted along the *a* axis and intensity data were measured on a Picker FACS 1 automatic four-circle diffractometer. Graphite monochromated Cu-K_α radiation was used to measure the reflections by use of the θ—2θ scanning mode, with a 2° scan across each peak at a scanning rate of 1° min^{-1}, with a 10 s background count at each end of the scan. With $2\theta_{\text{max.}}$ 124°, 5 526 independent reflections were measured of which 828 having $I < 4\sigma(I)$ were considered unobserved and excluded from the calculations. Intensity data were corrected for Lorentz and polarisation factors but not for absorption or extinction.

Refinement with isotropic temperature factors converged with *R* 0.12, and that with anisotropic temperature factors at *R* 0.045. The parameters of the weighting function were $a_1 = 300$ and $a_2 = 250$.

(*b*) *Tri*-o-*tolylphosphine oxide*, (II). $3(C_{21}H_{21}OP)$, $M = 961.1$. Monoclinic, $a = 9.039(5)$, $b = 17.282(6)$, $c = 35.192(12)$ Å, $\beta = 95.12(1)°$, $U = 5\,427.6$ Å^3, $D_m = 1.178$ g cm^{-3}, $Z = 12$, $D_c = 1.176$ g cm^{-3}, $F(000) = 510$. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences: $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$. Cu-K_α radiation, $\mu(\text{Cu-}K_\alpha) = 13.39$ cm^{-1}.

A single crystal was mounted along the *a* axis and intensity data were measured as before. With $2\theta_{\text{max.}}$ 124°, 5 428 reflections had $I > 4\sigma(I)$. Data were corrected for Lorentz and polarisation factors but not for absorption or extinction.

Refinement with isotropic temperature factors converged with *R* 0.137, and that with anisotropic temperature factors at *R* 0.075. The parameters of the weighting function were $a_1 = 600$ and $a_2 = 600$.

(*c*) *Tri*-o-*tolylphosphine sulphide*, (III). $2(C_{21}H_{21}PS)$, $M = 672.9$. Triclinic, $a = 15.377(4)$, $b = 15.346(4)$, $c = 7.979(4)$ Å, $\alpha = 103.1(1)°$, $\beta = 86.6(1)°$, $\gamma = 96.5(1)°$, $U = 1\,820.7$ Å^3, $D_m = 1.221$ g cm^{-3}, $Z = 4$, $D_c = 1.227$ g cm^{-3}, $F(000) = 356$. Space group $P\bar{1}$ (C_i^1, No. 2). Cu-K_α radiation, $\mu(\text{Cu-}K_\alpha) = 22.90$ cm^{-1}.

A single crystal was mounted about the needle axis, (*c*), in a thin-walled glass capillary. The compound is somewhat volatile (with an unpleasant and pervasive odour even from a single crystal) and under the action of *X*-rays cracks develop in the crystal along the axis of the needle, which cause individual reflections first to broaden and then divide into multiplets. With three separate crystals, 2 890 independent reflections with $I > 4\sigma(I)$ were measured with a Hilger and Watts four-circle diffractometer. Balanced filters were used up to a Bragg angle of 30° and data were collected by the ordinate analysis technique.[10] Data were corrected for Lorentz and polarisation factors but not for absorption or extinction.

The cell dimensions were determined during the calculation of the orientation matrix necessary for data collection, and two axes (*a* and *b*) were found to have very nearly equal lengths. The estimated standard deviations of these lengths indicate that they should be significantly different, however the unit-cell face defined by axes *a* and *b* will have diagonals which intersect at or near 90° and these could be axes of a monoclinic (or even higher symmetry) unit call. A crystal was mounted and photographed about one of these diagonals but no reflection symmetry was observed.

The structure determination confirmed the space group as $P\bar{1}$; refinement with isotropic temperature factors converged with *R* 0.15 and with anisotropic temperature factors at *R* 0.09. The parameters of the weighting function were $a_1 = 400$ and $a_2 = 350$.

(*d*) *Tri*-o-*tolylphosphine selenide*, (IV). $C_{21}H_{21}PSe$, $M = 383.33$. Monoclinic, $a = 33.497(10)$, $b = 8.004(2)$, $c = 14.701(10)$ Å, $\beta = 110.67(4)°$, $U = 3\,687.7$ Å^3, $D_m = 1.375$ g cm^{-3}, $Z = 8$, $D_c = 1.381$ g cm^{-3}, $F(000) = 196$. Space group $C2/c$ (C_{2h}^6, No. 15) from systematic absences: hkl, $h + k = 2n + 1$, $h0l$, $l = 2n + 1$. Cu-K_α radiation, $\mu(\text{Cu-}K_\alpha) = 38.48$ cm^{-1}.

The crystal was mounted about the needle axis (*c*), and data were measured as in (*a*) and (*b*). 2 343 Independent reflections having $I > 4\sigma(I)$ were used in the subsequent calculations. Data were corrected for polarisation and Lorentz factors but not for extinction or absorption.

Refinement with isotropic temperature factors converged at *R* 0.113 and with anisotropic temperature factors at

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R 0.067. The parameters of the weighting function were $a_1 = 400$ and $a_2 = 400$.

The structure factors for the four compounds calculated from the atomic parameters in Tables 6—9 are deposited at the University of Ulster Library,* Serial No. QD 921, C33 and in Supplementary Publication No. SUP 21436 (47 pp., 1 microfiche).† Scattering factors were taken from ref. 11 and were corrected for the real part of the anomalous dispersion.

The structures of (I), (II), and (IV) were computed with the system of Abrahamsson [12] and of (III) with the N.U.U crystal system.[13] Diagrams were drawn by use of. STRPL.[13]

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* Copies may be obtained on application to the Librarian for Science, University of Ulster.

† See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

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