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Structure of 7,8-Ph_2-10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9$ Methylene Chloride Solvate

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Abstract. 7,8-Diphenyl-10-*endo*-(triphenylphosphinomercury)-7,8-dicarba-*nido*-undecaborane(9) methylene chloride solvate, $C_{32}H_{34}B_9HgP.CH_2Cl_2$, M_r = 832.41, monoclinic, $P2_1$, a = 10.9534 (15), b = 13.274 (3), c = 11.5283 (17) Å, β = 90.074 (12)°, V = 1676.1 Å^3, Z = 2, D_x = 1.649 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 4.82 mm^{-1}, F(000) = 816, T = 185 (1) K, R = 0.0214 for 2656 independent observed reflections. The Hg atom is slipped by 1.1 Å away from the C(cage) atoms and the cage-bound phenyl groups are cooperatively twisted about their C(cage)—C(aryl) bonds by an average of 29.1° as the result of $Ph_3P\cdots Ph$ intramolecular crowding. The C(7)—C(8) connectivity, 1.589 (9) Å, the shortest C(cage)—C(cage) distance yet recorded in a diarylcarbaborane, is a direct consequence of the twisting of the phenyl groups.

Introduction. In the two preceding papers (Lewis & Welch, 1993; Cowie, Donohoe, Douek & Welch, 1993), we describe the molecular structures of 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ and [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}]^-$. These studies were stimulated by our previous observation (Lewis & Welch, 1992) of an unusual polyhedral deformation in 1,2-Ph_2-3-(η-C_5Me_5)-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ (to our knowledge the only reported transition-metal derivative of diphenylcarbaborane) resulting from mutual repulsion between the cage-bound phenyl groups, forced to adopt near-90° θ values [θ is the average difference between 90° and the moduli of the C(cage)—C(cage)—C—C torsion angles] by the sterically demanding η-C_5Me_5 ligand bound to Rh(3). In 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$ and [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}]^-$, θ values are much more modest, 20° at most, and consequently the overall molecular structures are essentially as expected.

It was clearly of importance, therefore, to synthesize and characterize structurally a wide range of transition-metal derivatives of diphenylcarbaborane, paying particular regard to intramolecular steric factors. In [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}]^-$, a (zero-electron one-orbital) proton is bound to a [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9]^{2-}$ ion in an *endo* position at B(10). Since the $\{R_3PHg\}^{2+}$ fragment is isolobal (Hoffmann, 1982) with H^+, but obviously has a much greater steric demand, one of our initial targets was the title compound, 7,8-Ph_2-10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9$, and accordingly the studies described herein were undertaken.

Experimental. Degassed CH_2Cl_2 (15 cm^3) was added to a solid mixture of Tl_2[7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$] (0.349 g, 0.504 mmol) (Lewis & Welch, 1992) and $[PPh_3HgCl_2]_2$ (0.269 g, 0.252 mmol) (Evans, Mann, Peiser & Purdie, 1940) in a foil-covered vessel at 77 K. The mixture was warmed to room temperature with stirring, and then filtered to afford a pale yellow solution. The solution was concentrated and excess hexane added, yielding a white flocculate and a green oil. The former was isolated by filtration. Crystals of the title compound were grown by the slow evaporation of a CH_2Cl_2 solution. Crystal, 0.2 × 0.15 × 0.15 mm, mounted on a glass fibre and set on an Enraf–Nonius CAD-4 diffractometer (graphite monochromator); cell parameters and orientation matrix from least-squares refinement of the setting angles ($12 < \theta < 13°$) of 25 centred reflections; data collection by ω–2θ scans in 96 steps with ω-scan width (0.8 + 0.34tanθ)°; one quadrant of data (h 0 to 13, k 0 to 15, l −13 to 13) measured for $1 \le \theta \le 25°$ over 67 X-ray hours with no appreciable decay or movement; corrections for Lorentz and polarization effects applied (Gould & Smith, 1986); of 2677 data measured, 2656 [$F \ge 2.0\sigma(F)$] used to solve [Patterson synthesis for Hg atom, difference Fourier syntheses for P, C, B, Cl and cage H atoms (Sheldrick, 1976)] and refine (least squares on F) the structure to isotropic convergence; cage H atoms allowed positional refinement subject to a common B—H distance of 1.06 (1) Å; phenyl H atoms set in idealized positions (C—H 1.08 Å); absolute configuration established by parallel refinements of models with y coordinates inverted; empirical absorption correction (Walker & Stuart, 1983) applied (correction factors 0.87–1.15); all non-H atoms refined with anisotropic thermal parameters; cage and phenyl H atoms refined with single group thermal parameter, 0.038 (5) Å^2 at convergence; weights assigned according to $w^{-1} = [\sigma^2(F) + 0.000200F^2]$; model refined in

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two blocks (182 and 264 variable parameters); $R = 0.0214$, $wR = 0.0241$, $S = 1.078$; max. shift/e.s.d. in final cycle < 0.10 on positional parameters and < 0.62 on thermal parameters (U_H); max. and min. residues in final ΔF synthesis 0.20 and -0.18 e Å^{-3}, respectively; scattering factors for P, Cl, C, H and B inlaid in *SHELX*76; those for Hg from *International Tables for X-ray Crystallography* (1974, Vol. IV); Fig. 1 drawn using *EASYORTEP* (Mallinson & Muir, 1985); molecular geometry calculations *via CALC* (Gould & Taylor, 1986).

Discussion. In Table 1[*] are listed coordinates of refined non-H atoms and equivalent isotropic thermal parameters, while Table 2 details selected internuclear distances and interbond angles. A perspective view of a single molecule and the atomic numbering scheme adopted is shown in Fig. 1. The title compound crystallizes as a CH_2Cl_2 solvate and there are no contacts of significance between molecules in the crystal. Although the precision of the final model is not particularly high (a number of factors, *e.g.* poor crystal quality, imperfect absorption correction, could be responsible for this), the atomic connectivities and overall molecular stereochemistry are established beyond doubt.

The basic architecture of the $\{PHgC_2B_9\}$ fragment of the molecule is the same as that previously observed in 10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_{11}$ (Colquhoun, Greenhough & Wallbridge, 1979) and [10-*endo*-PPh_3Au-7,8-*nido*-$C_2B_9H_{11}$]$^-$ (Hamilton & Welch, 1990), with the d^{10} metal atom *endo* σ-bonded to B(10) [2.178 (8) Å in the present study] although also involved in weaker bonding to B(9) and B(11) (2.53–2.62 Å). Thus, 7,8-Ph_2-10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9$ is structurally a direct analogue of [7,8-Ph_2-7,8-*nido*-$C_2B_9H_{10}$]$^-$ through the isolobal relationship between H and $\{Ph_3PHg\}^+$. Molecular-orbital calculations on the parent species [7,8-*nido*-$C_2B_9H_{11}$]$^{2-}$ (Buchanan, Hamilton, Reed & Welch, 1990) suggest that the *endo* atom to B(9)/B(11) interaction is real.

In 7,8-Ph_2-10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9$, the Hg···C(7)/C(8) distances are >3 Å, and the slip parameter Δ (Mingos, Forsyth & Welch, 1978) is 1.10 Å, nearly 0.2 Å more than in 10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9$, thus suggesting some degree of steric congestion between the Ph_3P ligand and the cage-bound Ph groups (see below). Note that the greatest slip distortion yet recorded across the C_2B_3 face of a *nido* icosahedral C_2B_9 carbaborane is 1.26 Å in 10-*endo*-$SnPh_3$-7,8-*nido*-$C_2B_9H_{11}$ (Kim, Kim & Do, 1992).

Table 1. *Coordinates of non-*H *atoms and equivalent isotropic thermal parameters* (Å^2) *for* 7,8-Ph_2-10-*endo*-PPh_3Hg-7,8-*nido*-$C_2B_9H_9.CH_2Cl_2$

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

	x	y	z	U_{eq}
Hg	0.23330 (2)	0.50000	0.33860 (2)	0.0188 (1)
P	0.36870 (15)	0.57300 (13)	0.19669 (15)	0.0189 (8)
C(11)	0.5157 (5)	0.5124 (10)	0.1941 (5)	0.024 (4)
C(12)	0.6000 (6)	0.5311 (6)	0.2838 (6)	0.035 (5)
C(13)	0.7136 (7)	0.4857 (11)	0.2795 (7)	0.049 (6)
C(14)	0.7401 (7)	0.4153 (7)	0.1908 (7)	0.041 (5)
C(15)	0.6571 (7)	0.3965 (6)	0.1064 (7)	0.035 (4)
C(16)	0.5453 (6)	0.4449 (5)	0.1053 (6)	0.026 (4)
C(21)	0.3896 (6)	0.7059 (5)	0.2221 (5)	0.018 (3)
C(22)	0.5009 (7)	0.7548 (6)	0.2033 (6)	0.029 (4)
C(23)	0.5077 (7)	0.8597 (6)	0.2119 (7)	0.034 (4)
C(24)	0.4031 (8)	0.9127 (6)	0.2372 (7)	0.039 (5)
C(25)	0.2932 (7)	0.8668 (6)	0.2575 (7)	0.037 (5)
C(26)	0.2863 (6)	0.7612 (6)	0.2503 (6)	0.031 (4)
C(31)	0.3073 (5)	0.5621 (5)	0.0514 (5)	0.018 (3)
C(32)	0.3568 (6)	0.6247 (6)	−0.0342 (6)	0.030 (4)
C(33)	0.3132 (7)	0.6205 (6)	−0.1459 (6)	0.037 (5)
C(34)	0.2182 (7)	0.5568 (6)	−0.1730 (6)	0.033 (4)
C(35)	0.1697 (7)	0.4955 (11)	−0.0890 (6)	0.036 (4)
C(36)	0.2122 (6)	0.4980 (10)	0.0258 (6)	0.029 (3)
B(10)	0.0920 (7)	0.4604 (6)	0.4633 (8)	0.019 (4)
B(6)	0.0771 (7)	0.3888 (6)	0.5922 (7)	0.019 (4)
B(2)	0.1719 (7)	0.2826 (6)	0.5940 (7)	0.019 (4)
B(3)	0.1320 (7)	0.2041 (6)	0.4795 (7)	0.019 (4)
B(4)	0.0064 (10)	0.2584 (7)	0.4047 (7)	0.019 (5)
B(5)	−0.0290 (7)	0.3729 (6)	0.4700 (8)	0.022 (4)
B(11)	0.2251 (7)	0.3983 (5)	0.5329 (7)	0.017 (4)
B(9)	0.0614 (7)	0.3721 (6)	0.3435 (7)	0.021 (4)
B(1)	0.0143 (9)	0.2680 (7)	0.5569 (9)	0.019 (5)
C(7)	0.2474 (5)	0.2927 (5)	0.4649 (6)	0.016 (3)
C(8)	0.1554 (5)	0.2784 (5)	0.3596 (5)	0.016 (3)
C(71)	0.3757 (6)	0.2512 (5)	0.4547 (6)	0.018 (4)
C(72)	0.4014 (7)	0.1504 (6)	0.4353 (6)	0.028 (4)
C(73)	0.5211 (6)	0.1159 (6)	0.4291 (6)	0.030 (4)
C(74)	0.6185 (6)	0.1826 (6)	0.4434 (6)	0.027 (4)
C(75)	0.5939 (6)	0.2830 (6)	0.4589 (7)	0.031 (4)
C(76)	0.4740 (6)	0.3182 (6)	0.4645 (6)	0.027 (4)
C(81)	0.2008 (6)	0.2245 (5)	0.2523 (5)	0.019 (3)
C(82)	0.1483 (6)	0.1353 (5)	0.2125 (6)	0.026 (4)
C(83)	0.1874 (7)	0.0929 (6)	0.1088 (6)	0.031 (4)
C(84)	0.2780 (7)	0.1375 (6)	0.0428 (6)	0.035 (4)
C(85)	0.3314 (7)	0.2259 (6)	0.0847 (6)	0.030 (4)
C(86)	0.2940 (6)	0.2682 (5)	0.1872 (6)	0.027 (4)
Cl(1)	0.01917 (20)	0.11089 (16)	−0.16521 (19)	0.0429 (12)
Cl(2)	−0.05671 (24)	0.27340 (21)	−0.01263 (22)	0.0610 (15)
C	0.0430 (8)	0.2378 (6)	−0.1248 (7)	0.039 (5)

In the title compound, the B(2)–B(6) ring is, as expected, essentially planar $\{\sigma = 0.020$ Å $[\sigma = (\sum z_i^2)^{1/2}$, where z_i is the displacement of the ith atom from the least-squares plane]$\}$ but the upper C_2B_3 face is not ($\sigma = 0.054$ Å), adopting a 4.4° concave envelope fold across B(9)···B(11). As Fig. 1 clearly shows, the cage-bound phenyl groups are significantly conrotated about their C(cage)—C(aryl) bonds, θ values being 31.0 [ring C(71)–C(76)] and 27.7° [ring C(81)–C(86)]. The likely origin of these twists is crowding between Ph and Ph_3P groups (as previously noted), C(75)···C(13) being 3.639 (13) Å and H(85)···H(16) being 2.40 Å in the structure adopted. Clearly, both phenyl rings must twist in the same sense, and by approximately equal amounts, otherwise unfavourable cage phenyl–cage phenyl contacts would be set up, and it generally appears

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete geometry and have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55797 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1028]

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *for* 7,8-$\mathrm{Ph_2}$-10-*endo*-$\mathrm{PPh_3PHg}$-7,8-*nido*-$\mathrm{C_2B_9H_9.CH_2Cl_2}$

Hg—P	2.4127 (17)	B(2)—C(7)	1.709 (10)
Hg—B(10)	2.178 (8)	B(3)—B(4)	1.775 (12)
Hg—B(11)	2.616 (7)	B(3)—B(1)	1.783 (13)
Hg—B(9)	2.536 (8)	B(3)—C(7)	1.735 (10)
P—C(11)	1.800 (9)	B(3)—C(8)	1.718 (10)
P—C(21)	1.802 (7)	B(4)—B(5)	1.740 (13)
P—C(31)	1.809 (6)	B(4)—B(9)	1.773 (13)
B(10)—B(6)	1.772 (11)	B(4)—B(1)	1.761 (14)
B(10)—B(5)	1.765 (12)	B(4)—C(8)	1.734 (12)
B(10)—B(11)	1.855 (11)	B(5)—B(9)	1.764 (11)
B(10)—B(9)	1.842 (12)	B(5)—B(1)	1.779 (13)
B(6)—B(2)	1.751 (11)	B(11)—C(7)	1.625 (10)
B(6)—B(5)	1.837 (11)	B(9)—C(8)	1.625 (10)
B(6)—B(11)	1.765 (11)	C(7)—C(8)	1.589 (9)
B(6)—B(1)	1.792 (13)	C(7)—C(71)	1.514 (9)
B(2)—B(3)	1.737 (11)	C(8)—C(81)	1.513 (9)
B(2)—B(11)	1.788 (11)	Cl(1)—C	1.767 (9)
B(2)—B(1)	1.789 (13)	Cl(2)—C	1.758 (9)

P—Hg—B(10)	169.23 (22)	B(10)—B(5)—B(6)	58.9 (4)
P—Hg—B(11)	144.04 (17)	B(10)—B(5)—B(9)	62.9 (5)
P—Hg—B(9)	137.83 (19)	B(6)—B(5)—B(1)	59.4 (5)
Hg—P—C(11)	112.5 (3)	B(4)—B(5)—B(9)	60.8 (5)
Hg—P—C(21)	111.15 (22)	B(4)—B(5)—B(1)	60.0 (5)
Hg—P—C(31)	111.55 (21)	Hg—B(11)—B(10)	55.2 (3)
C(11)—P—C(21)	109.0 (4)	B(10)—B(11)—B(6)	58.5 (4)
C(11)—P—C(31)	106.2 (4)	B(6)—B(11)—B(2)	59.1 (4)
C(21)—P—C(31)	106.0 (3)	B(2)—B(11)—C(7)	59.9 (4)
P—C(11)—C(12)	119.7 (6)	Hg—B(9)—B(10)	57.1 (3)
P—C(11)—C(16)	120.4 (6)	Hg—B(9)—C(8)	92.6 (4)
P—C(21)—C(22)	122.7 (5)	B(10)—B(9)—B(5)	58.6 (4)
P—C(21)—C(26)	116.9 (5)	B(4)—B(9)—B(5)	59.0 (5)
P—C(31)—C(32)	117.4 (5)	B(4)—B(9)—C(8)	61.2 (5)
P—C(31)—C(36)	121.9 (6)	B(6)—B(1)—B(2)	58.6 (5)
Hg—B(10)—B(11)	80.4 (4)	B(6)—B(1)—B(5)	61.9 (5)
Hg—B(10)—B(9)	77.7 (4)	B(2)—B(1)—B(3)	58.2 (5)
B(6)—B(10)—B(5)	62.6 (5)	B(3)—B(1)—B(4)	60.1 (5)
B(6)—B(10)—B(11)	58.2 (4)	B(4)—B(1)—B(5)	58.9 (5)
B(5)—B(10)—B(9)	58.5 (4)	B(2)—C(7)—B(3)	60.6 (4)
B(10)—B(6)—B(5)	58.5 (4)	B(2)—C(7)—B(11)	64.8 (4)
B(10)—B(6)—B(11)	63.3 (4)	B(2)—C(7)—C(71)	119.3 (5)
B(2)—B(6)—B(11)	61.1 (4)	B(3)—C(7)—C(8)	62.1 (4)
B(2)—B(6)—B(1)	60.7 (5)	B(3)—C(7)—C(71)	115.9 (5)
B(5)—B(6)—B(1)	58.7 (5)	B(11)—C(7)—C(71)	119.5 (5)
B(6)—B(2)—B(11)	59.8 (4)	C(8)—C(7)—C(71)	119.0 (5)
B(6)—B(2)—B(1)	60.8 (5)	B(3)—C(8)—B(4)	61.9 (5)
B(3)—B(2)—B(1)	60.7 (5)	B(3)—C(8)—C(7)	63.1 (4)
B(3)—B(2)—C(7)	60.4 (4)	B(3)—C(8)—C(81)	115.8 (5)
B(2)—B(3)—B(1)	61.1 (5)	B(4)—C(8)—B(9)	63.6 (5)
B(2)—B(3)—C(7)	59.0 (4)	B(4)—C(8)—C(81)	118.9 (6)
B(4)—B(3)—B(1)	59.3 (5)	B(9)—C(8)—C(81)	118.6 (5)
B(4)—B(3)—C(8)	59.5 (4)	C(7)—C(8)—C(81)	118.2 (5)
C(7)—B(3)—C(8)	54.8 (4)	C(7)—C(71)—C(72)	123.6 (6)
B(3)—B(4)—B(1)	60.6 (5)	C(7)—C(71)—C(76)	118.4 (6)
B(3)—B(4)—C(8)	58.6 (4)	C(8)—C(81)—C(82)	122.3 (6)
B(5)—B(4)—B(9)	60.3 (5)	C(8)—C(81)—C(86)	119.0 (6)
B(5)—B(4)—B(1)	61.1 (5)	Cl(1)—C—Cl(2)	111.0 (5)
B(9)—B(4)—C(8)	55.2 (4)		

that structural cooperation of this sort is, and will be, a recurrent feature of the structural chemistry of diarylcarbaboranes and their derivatives, so long as massive structural deformation, *e.g.* as in 1,2-$\mathrm{Ph_2}$-3-(η-$\mathrm{C_5Me_5}$)-3,1,2-*pseudocloso*-$\mathrm{RhC_2B_9H_9}$ (Lewis & Welch, 1992), does not occur. The twists in 7,8-$\mathrm{Ph_2}$-10-*endo*-$\mathrm{PPh_3Hg}$-7,8-*nido*-$\mathrm{C_2B_9H_9}$ are substantially greater than those in 1,2-$\mathrm{Ph_2}$-1,2-*closo*-$\mathrm{C_2B_{10}H_{10}}$ and $[\mathrm{7,8\text{-}Ph_2\text{-}7,8\text{-}\mathit{nido}\text{-}C_2B_9H_{10}}]^-$. Furthermore, they approach the limiting values of θ calculated for 1,2-$\mathrm{Ph_2}$-1,2-*closo*-$\mathrm{C_2B_{10}H_{10}}$ (Fig. 4 of Lewis & Welch, 1993) before *ortho–ortho* contacts cause massive molecular destabilization [$\theta \simeq 90°$ in 1,2-$\mathrm{Ph_2}$-3-(η-$\mathrm{C_5Me_5}$)-3,1,2-*pseudocloso*-$\mathrm{RhC_2B_9H_9}$ (Lewis & Welch, 1992) but destabilization is obviated by deformation to the *pseudocloso* structure observed]. The synchronous rotation of the Ph rings in 1,2-$\mathrm{Ph_2}$-1,2-*closo*-$\mathrm{C_2B_{10}H_{10}}$ away from $\theta = 0°$ was predicted to result in strengthening of the C(cage)—C(cage) connectivity, and it is encouraging to note that in 7,8-$\mathrm{Ph_2}$-10-*endo*-$\mathrm{PPh_3Hg}$-7,8-*nido*-$\mathrm{C_2B_9H_9}$ the C(7)—C(8) distance, 1.589 (9) Å, is the shortest C(cage)—C(cage) bond yet recorded in a diarylcarbaborane derivative.

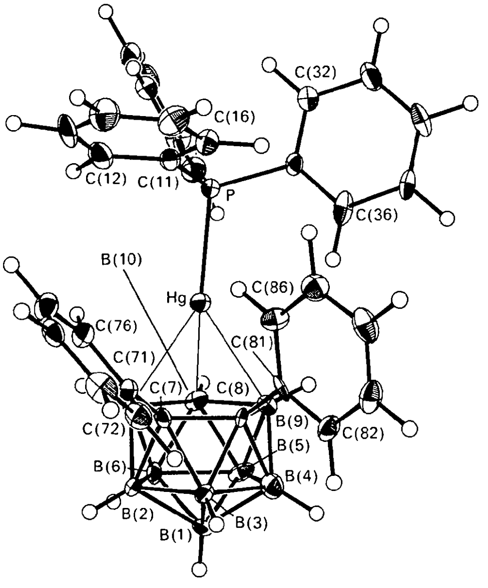

Fig. 1. Perspective view of 7,8-$\mathrm{Ph_2}$-10-*endo*-$\mathrm{PPh_3Hg}$-7,8-*nido*-$\mathrm{C_2B_9H_9}$ (50% thermal ellipsoids, except for H atoms which have artificial radii of 0.1 Å for clarity).

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Molecular Co-Crystals of Carboxylic Acids. 11.* Structure of the 1:1 Adduct of Triphenylphosphine Oxide with (3,4-Dichlorophenoxy)acetic Acid

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Abstract. $C_{18}H_{15}OP.C_8H_6Cl_2O_3$, $M_r = 499.3$, triclinic, $P\bar{1}$, $a = 8.539\,(4)$, $b = 15.564\,(7)$, $c = 18.768\,(10)$ Å, $\alpha = 90.97\,(3)$, $\beta = 95.25\,(3)$, $\gamma = 102.24\,(3)°$, $V = 2426\,(2)$ Å^3, $Z = 4$, $D_x = 1.367$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.36$ mm^{-1}, $F(000) = 1032$, $T = 295$ K, $R = 0.037$ for 2648 observed reflections. The compound was prepared by interacting 1:1 molar ratios of triphenylphosphine oxide and (3,4-dichlorophenoxy)acetic acid in toluene/ethanol and allowing the mixture to crystallize from the oil which resulted from evaporation of the solvent. The crystallographic repeating unit consists of two independent 1:1 molecular pairs. The two molecules of triphenylphosphine oxide and (3,4-dichlorophenoxy)acetic acid in each pair associate through single directed hydrogen bonds between the carboxylic acid group and the phosphoryl O atom [OH···O 2.60 (1), 2.61 (1) Å]. The independent molecules of triphenylphosphine oxide and (3,4-dichlorophenoxy)acetic acid are conformationally dissimilar.

Introduction. Structural studies in this laboratory of the molecular adducts formed with commercially important herbicides have shown a number of combinations. 1:1 adducts are readily formed between phenoxyalkanoic acids and triphenylphosphine oxide (TPPO), the adducts already characterized being TPPO with (2,4-dichlorophenoxy)acetic acid (2,4-D) (Lynch, Smith, Byriel & Kennard, 1992*a*), (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) (Lynch, Smith, Byriel & Kennard, 1992*b*) and (2,3,4,5,6-pentachlorophenoxy)acetic acid (PCPA) (Lynch, Smith, Byriel & Kennard, 1993). Invariably, the interaction between the phosphoryl O atom of triphenylphosphine oxide and the carboxylic acid donor proton is *via* a single directed hydrogen bond which makes TPPO a useful crystallizing acid (Etter & Baures, 1988). Another member of the phenoxyalkanoic acid series is (3,4-dichlorophenoxy)acetic acid which also has useful herbicidal properties. Although not as commercially important as 2,4-D or 2,4,5-T, 3,4-D has particular value as a wettable powder or paste of low water solubility for direct application to soils as a pre-emergence herbicide in regions of high rainfall (Crafts, 1957). In this latest study, the 1:1 adduct of 3,4-D with TPPO has been structurally characterized. Conformational comparisons with both parent molecules can also be made since their structures are known [3,4-D: Smith Kennard & White (1981); TPPO: Spek (1987); Ruban & Zabel (1976); Bandoli, Bortolozzo, Clemente, Croatto & Panattoni (1970)].

Experimental. The title compound was prepared by refluxing equimolar amounts of triphenylphosphine oxide (TPPO) and (3,4-dichlorophenoxy)acetic acid (3,4-D) in 50% ethanol/toluene for 20 min at 423 K. Colourless plates (m.p. 341–343 K) were obtained after crystallization of the resultant oil at room temperature. A crystal with dimensions 0.36 × 0.12 × 0.12 mm was used to collect data at 295 K on an Enraf–Nonius CAD-4 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters were obtained using data from 25 reflections with $2\theta < 25°$. Data collection details: $2\theta/\omega$ collection mode, variable scanning rate; $2\theta_{max} = 50°$; collection range h −10 to 10, k −18 to 18, l 0

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* Part 10: Lynch, Smith, Byriel & Kennard (1993).

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