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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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(*Received* 18 *May* 1992; *accepted* 22 *October* 1992)

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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0108-2701/93/040718-04$06.00

to 20; total data 8802; unique 6419 ($R_{\rm int} = 0.058$); unobserved data 5787; standards (114, $1\bar{5}7$, $3\bar{7}\bar{1}$) variation −2.2%; 2648 reflections with $I > 2.5\sigma(I)$ used in structure refinement. Data were corrected for Lorentz and polarization effects as well as for absorption (empirical); maximum and minimum transmission factors were 100.0 and 98.2%, respectively. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Blocked-matrix least squares (on F) with anisotropic thermal parameters for all non-H atoms gave $R = 0.037$ and $wR = 0.036$, $w = 1.0/[\sigma^2(F_o) + 4.8 \times 10^{-4}(F_o)^2]$; $S = 1.09$ (*SHELX*76; Sheldrick, 1976). H atoms were located by difference methods and their positional and isotropic thermal parameters refined. Maximum (Δ/σ) in the last cycle was 0.01 for all non-H atoms. Maximum and minimum difference peaks were 0.28 and -0.16 e Å^{-3}, respectively. Neutral-atom scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atom positional and thermal parameters are listed in Table 1*, while bond distances and angles are given in Table 2. The atom-numbering scheme is shown in Fig. 1.

Discussion. The crystallographic repeating unit in the structure of the title compound comprises two independent 1:1 adducts involving triphenylphosphine oxide (TPPO) (molecules *A* and *C*) and (3,4-dichlorophenoxy)acetic acid (3,4-D) (molecules *B* and *D*). Within each pair, the phosphoryl O atom is linked to the carboxylic acid proton by a single directed hydrogen bond (graph set *D*; Etter, 1990) (Fig. 2). The O···O distances and the hydrogen-bond angles are almost identical [2.60 (1) Å and 171 (1)° (*A* to *B*) and 2.61 (1) Å and 176 (1)° (*C* to *D*)]. These values compare with 2.58 (1), 2.61 (1) and 2.54 (1) Å for the TPPO adducts with 2,4-*D* (Lynch *et al.*, 1992*a*), 2,4,5-T (Lynch *et al.*, 1992*b*) and PCPA (Lynch *et al.*, 1993), respectively. The individual molecules in each independent pair are conformationally different and differ from their parent molecules. In both the parent 3,4-D (Smith *et al.*, 1981) and molecule *D*, the oxyacetic acid side chains are essentially planar, while in molecule *B* it is non-planar. Comparative torsion angles are C(2)—C(1)—O(7)—C(8) 178.2 (6) (3,4-D), −177.9 (5) (*D*), 175.3 (6)° (*B*); C(1)—O(7)—C(8)—C(9) 174.5 (6) (3,4-D), 176.9 (5) (*D*), 170.1 (5)° (*B*); O(7)—C(8)—C(9)—O(11) 178.6 (6) (3,4-D), 170.8 (5) (*D*), 159.4 (5)° (*B*). The dihedral angle between the planes of the benzene ring and the carboxylic acid group for 3,4-D is 7.0 (4)°, while for molecules *D* and *B* it is 8.89 (3) and 35.90 (3)°, respectively. Within the oxyacetic acid side chain, the O(7)(ether)···O(10)(carboxyl) distance remains relatively constant [2.698 (2) (*D*) and 2.664 (2) Å (*B*) compared with 2.671 (4) Å for the parent acid (Smith *et al.*, 1981)]. The important torsion angles in the

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
P(1*A*)	0.9442 (2)	1.1774 (1)	0.0680 (1)	0.0366 (6)
O(1*A*)	0.9098 (4)	1.2646 (2)	0.0885 (2)	0.045 (1)
C(11*A*)	1.1546 (6)	1.1852 (3)	0.0631 (3)	0.039 (2)
C(12*A*)	1.2533 (8)	1.2052 (4)	0.1270 (4)	0.050 (3)
C(13*A*)	1.4195 (9)	1.2213 (5)	0.1277 (5)	0.067 (3)
C(14*A*)	1.4864 (10)	1.2147 (5)	0.0656 (5)	0.069 (3)
C(15*A*)	1.3948 (9)	1.1940 (4)	0.0014 (4)	0.058 (3)
C(16*A*)	1.2276 (9)	1.1792 (4)	−0.0003 (4)	0.053 (3)
C(21*A*)	0.8395 (6)	1.1364 (4)	−0.0174 (3)	0.037 (2)
C(22*A*)	0.7255 (7)	1.0566 (4)	−0.0253 (3)	0.049 (3)
C(23*A*)	0.6414 (8)	1.0282 (5)	−0.0906 (3)	0.057 (3)
C(24*A*)	0.6707 (8)	1.0802 (5)	−0.1491 (4)	0.059 (3)
C(25*A*)	0.7775 (8)	1.1583 (5)	−0.1423 (3)	0.060 (3)
C(26*A*)	0.8620 (8)	1.1874 (4)	−0.0761 (3)	0.051 (3)
C(31*A*)	0.8794 (6)	1.0954 (4)	0.1322 (3)	0.033 (2)
C(32*A*)	0.9168 (8)	1.0133 (4)	0.1289 (3)	0.045 (3)
C(33*A*)	0.8556 (9)	0.9501 (5)	0.1751 (4)	0.052 (3)
C(34*A*)	0.7580 (9)	0.9686 (5)	0.2244 (4)	0.061 (3)
C(35*A*)	0.7217 (8)	1.0503 (6)	0.2296 (3)	0.058 (3)
C(36*A*)	0.7832 (7)	1.1140 (5)	0.1831 (3)	0.044 (3)
C(1*B*)	0.2149 (8)	0.4775 (4)	0.4220 (4)	0.060 (3)
C(2*B*)	0.1819 (9)	0.4530 (5)	0.4902 (4)	0.070 (3)
C(3*B*)	0.2597 (9)	0.5022 (5)	0.5486 (3)	0.073 (3)
Cl(3*B*)	0.2137 (3)	0.4695 (2)	0.6326 (1)	0.117 (1)
C(4*B*)	0.3743 (9)	0.5767 (5)	0.5398 (4)	0.070 (3)
Cl(4*B*)	0.4797 (3)	0.6414 (1)	0.6117 (1)	0.118 (1)
C(5*B*)	0.4086 (10)	0.5998 (5)	0.4712 (5)	0.074 (3)
C(6*B*)	0.3301 (9)	0.5518 (4)	0.4108 (4)	0.064 (3)
O(7*B*)	0.1311 (5)	0.4215 (3)	0.3678 (2)	0.074 (2)
C(8*B*)	0.1492 (11)	0.4457 (5)	0.2957 (3)	0.062 (3)
C(9*B*)	0.0703 (8)	0.3681 (5)	0.2471 (4)	0.065 (3)
O(10*B*)	0.0530 (7)	0.2924 (3)	0.2649 (2)	0.110 (2)
O(11*B*)	0.0354 (6)	0.3907 (3)	0.1823 (3)	0.071 (2)
P(1*C*)	0.2641 (2)	0.8475 (1)	0.3804 (1)	0.0379 (6)
O(1*C*)	0.1442 (4)	0.7875 (2)	0.3298 (2)	0.051 (2)
C(11*C*)	0.4568 (6)	0.8191 (3)	0.3861 (3)	0.036 (2)
C(12*C*)	0.4974 (9)	0.7757 (4)	0.3277 (3)	0.053 (3)
C(13*C*)	0.6457 (11)	0.7554 (5)	0.3282 (5)	0.071 (3)
C(14*C*)	0.7565 (10)	0.7792 (5)	0.3871 (6)	0.081 (4)
C(15*C*)	0.7200 (8)	0.8199 (4)	0.4458 (4)	0.066 (3)
C(16*C*)	0.5702 (8)	0.8415 (4)	0.4452 (3)	0.050 (3)
C(21*C*)	0.2927 (7)	0.9602 (3)	0.3548 (3)	0.033 (2)
C(22*C*)	0.1695 (8)	0.9848 (5)	0.3130 (3)	0.050 (3)
C(23*C*)	0.1801 (9)	1.0713 (5)	0.2956 (3)	0.060 (3)
C(24*C*)	0.3140 (9)	1.1336 (5)	0.3192 (3)	0.054 (3)
C(25*C*)	0.4376 (9)	1.1099 (5)	0.3591 (3)	0.054 (3)
C(26*C*)	0.4281 (8)	1.0241 (4)	0.3768 (3)	0.044 (3)
C(31*C*)	0.2026 (6)	0.8458 (4)	0.4692 (3)	0.034 (2)
C(32*C*)	0.1753 (7)	0.9188 (5)	0.5050 (3)	0.046 (3)
C(33*C*)	0.1198 (8)	0.9123 (5)	0.5717 (3)	0.059 (3)
C(34*C*)	0.0925 (8)	0.8324 (6)	0.6039 (4)	0.068 (3)
C(35*C*)	0.1174 (8)	0.7589 (5)	0.5695 (4)	0.061 (3)
C(36*C*)	0.1744 (7)	0.7658 (5)	0.5028 (3)	0.050 (3)
C(1*D*)	0.2361 (7)	0.4568 (4)	−0.0240 (3)	0.048 (3)
C(2*D*)	0.3203 (7)	0.4306 (4)	0.0360 (3)	0.050 (3)
C(3*D*)	0.3742 (7)	0.4893 (5)	0.0923 (3)	0.053 (3)
Cl(3*D*)	0.4759 (2)	0.4543 (1)	0.1672 (1)	0.079 (1)
C(4*D*)	0.3483 (8)	0.5729 (4)	0.0903 (3)	0.056 (3)
Cl(4*D*)	0.4184 (3)	0.6475 (1)	0.1613 (1)	0.114 (1)
C(5*D*)	0.2675 (8)	0.5969 (5)	0.0308 (4)	0.063 (3)
C(6*D*)	0.2117 (8)	0.5402 (4)	−0.0266 (3)	0.052 (3)
O(7*D*)	0.1879 (5)	0.3933 (2)	−0.0781 (2)	0.067 (2)
C(8*D*)	0.1068 (10)	0.4165 (4)	−0.1413 (3)	0.056 (3)
C(9*D*)	0.0737 (8)	0.3400 (4)	−0.1940 (3)	0.051 (3)
O(10*D*)	0.1250 (5)	0.2743 (3)	−0.1863 (2)	0.061 (2)
O(11*D*)	−0.0221 (6)	0.3534 (3)	−0.2498 (2)	0.068 (2)

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* Lists of observed and calculated structure factors, H-atom coordinates, torsion angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55735 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1016]

TPPO molecules are O(1)—P(1)—C(11)—C(12) 65.5 (4) (*A*), 26.5 (4)° (*C*); O(1)—P(1)—C(21)—C(22), −119.2 (4) (*A*), 24.2 (4)° (*C*); O(1)—P(1)—C(31)—C(32) −171.9 (3) (*A*), −118.8 (4)° (*C*).

Table 2. *Bond distances* (Å) *and angles* (°)

O(1*A*)—P(1*A*)	1.499 (4)	C(11*A*)—P(1*A*)	1.786 (6)
C(21*A*)—P(1*A*)	1.799 (5)	C(31*A*)—P(1*A*)	1.805 (5)
C(12*A*)—C(11*A*)	1.392 (8)	C(16*A*)—C(11*A*)	1.403 (9)
C(13*A*)—C(12*A*)	1.39 (1)	C(14*A*)—C(13*A*)	1.36 (1)
C(15*A*)—C(14*A*)	1.37 (1)	C(16*A*)—C(15*A*)	1.39 (1)
C(22*A*)—C(21*A*)	1.403 (8)	C(26*A*)—C(21*A*)	1.372 (8)
C(23*A*)—C(22*A*)	1.378 (9)	C(24*A*)—C(23*A*)	1.39 (1)
C(25*A*)—C(24*A*)	1.353 (9)	C(26*A*)—C(25*A*)	1.395 (8)
C(32*A*)—C(31*A*)	1.382 (9)	C(36*A*)—C(31*A*)	1.381 (9)
C(33*A*)—C(32*A*)	1.37 (1)	C(34*A*)—C(33*A*)	1.37 (1)
C(35*A*)—C(34*A*)	1.38 (1)	C(36*A*)—C(35*A*)	1.38 (1)
C(2*B*)—C(1*B*)	1.38 (1)	C(6*B*)—C(1*B*)	1.383 (9)
O(7*B*)—C(1*B*)	1.371 (7)	C(3*B*)—C(2*B*)	1.360 (9)
Cl(3*B*)—C(3*B*)	1.719 (7)	C(4*B*)—C(3*B*)	1.37 (1)
Cl(4*B*)—C(4*B*)	1.730 (7)	C(5*B*)—C(4*B*)	1.38 (1)
C(6*B*)—C(5*B*)	1.38 (1)	C(8*B*)—O(7*B*)	1.423 (8)
C(9*B*)—C(8*B*)	1.50 (1)	O(10*B*)—C(9*B*)	1.213 (9)
O(11*B*)—C(9*B*)	1.298 (9)	O(1*C*)—P(1*C*)	1.486 (3)
C(11*C*)—P(1*C*)	1.787 (6)	C(21*C*)—P(1*C*)	1.799 (5)
C(31*C*)—P(1*C*)	1.791 (5)	C(12*C*)—C(11*C*)	1.386 (9)
C(16*C*)—C(11*C*)	1.391 (8)	C(13*C*)—C(12*C*)	1.37 (1)
C(14*C*)—C(13*C*)	1.38 (1)	C(15*C*)—C(14*C*)	1.36 (1)
C(16*C*)—C(15*C*)	1.39 (1)	C(22*C*)—C(21*C*)	1.378 (9)
C(26*C*)—C(21*C*)	1.381 (7)	C(23*C*)—C(22*C*)	1.38 (1)
C(24*C*)—C(23*C*)	1.367 (9)	C(25*C*)—C(24*C*)	1.36 (1)
C(26*C*)—C(25*C*)	1.37 (1)	C(32*C*)—C(31*C*)	1.384 (9)
C(36*C*)—C(31*C*)	1.390 (9)	C(33*C*)—C(32*C*)	1.376 (9)
C(34*C*)—C(33*C*)	1.38 (1)	C(35*C*)—C(34*C*)	1.37 (1)
C(36*C*)—C(35*C*)	1.38 (1)	C(2*D*)—C(1*D*)	1.395 (9)
C(6*D*)—C(1*D*)	1.359 (9)	O(7*D*)—C(1*D*)	1.375 (7)
C(3*D*)—C(2*D*)	1.365 (8)	Cl(3*D*)—C(3*D*)	1.740 (6)
C(4*D*)—C(3*D*)	1.37 (1)	Cl(4*D*)—C(4*D*)	1.730 (6)
C(5*D*)—C(4*D*)	1.357 (9)	C(6*D*)—C(5*D*)	1.364 (9)
C(8*D*)—O(7*D*)	1.411 (8)	C(9*D*)—C(8*D*)	1.496 (9)
O(10*D*)—C(9*D*)	1.202 (9)	O(11*D*)—C(9*D*)	1.317 (8)
C(11*A*)—P(1*A*)—O(1*A*)	111.3 (2)	C(21*A*)—P(1*A*)—O(1*A*)	111.1 (2)
C(21*A*)—P(1*A*)—C(11*A*)	108.3 (3)	C(31*A*)—P(1*A*)—O(1*A*)	111.6 (2)
C(31*A*)—P(1*A*)—C(11*A*)	107.5 (3)	C(31*A*)—P(1*A*)—C(21*A*)	106.9 (2)
C(12*A*)—C(11*A*)—P(1*A*)	116.5 (5)	C(16*A*)—C(11*A*)—P(1*A*)	125.1 (4)
C(16*A*)—C(11*A*)—C(12*A*)	118.2 (6)	C(13*A*)—C(12*A*)—C(11*A*)	120.9 (7)
C(14*A*)—C(13*A*)—C(12*A*)	119.4 (7)	C(15*A*)—C(14*A*)—C(13*A*)	122.0 (8)
C(16*A*)—C(15*A*)—C(14*A*)	119.1 (8)	C(15*A*)—C(16*A*)—C(11*A*)	120.3 (6)
C(22*A*)—C(21*A*)—P(1*A*)	122.1 (4)	C(26*A*)—C(21*A*)—P(1*A*)	119.4 (4)
C(26*A*)—C(21*A*)—C(22*A*)	118.3 (5)	C(23*A*)—C(22*A*)—C(21*A*)	121.3 (6)
C(24*A*)—C(23*A*)—C(22*A*)	118.8 (6)	C(25*A*)—C(24*A*)—C(23*A*)	120.8 (6)
C(26*A*)—C(25*A*)—C(24*A*)	120.4 (6)	C(25*A*)—C(26*A*)—C(21*A*)	120.4 (5)
C(32*A*)—C(31*A*)—P(1*A*)	121.4 (5)	C(36*A*)—C(31*A*)—P(1*A*)	118.8 (5)
C(36*A*)—C(31*A*)—C(32*A*)	119.7 (6)	C(33*A*)—C(32*A*)—C(31*A*)	120.0 (7)
C(34*A*)—C(33*A*)—C(32*A*)	119.8 (7)	C(35*A*)—C(34*A*)—C(33*A*)	121.1 (7)
C(36*A*)—C(35*A*)—C(34*A*)	119.0 (7)	C(35*A*)—C(36*A*)—C(31*A*)	120.3 (7)
C(6*B*)—C(1*B*)—C(2*B*)	121.1 (6)	O(7*B*)—C(1*B*)—C(2*B*)	115.3 (5)
O(7*B*)—C(1*B*)—C(6*B*)	123.6 (6)	C(3*B*)—C(2*B*)—C(1*B*)	120.9 (6)
Cl(3*B*)—C(3*B*)—C(2*B*)	119.3 (5)	C(4*B*)—C(3*B*)—C(2*B*)	119.8 (7)
C(4*B*)—C(3*B*)—Cl(3*B*)	120.9 (5)	Cl(4*B*)—C(4*B*)—C(3*B*)	122.1 (6)
C(5*B*)—C(4*B*)—C(3*B*)	118.8 (7)	C(5*B*)—C(4*B*)—Cl(4*B*)	119.0 (5)
C(6*B*)—C(5*B*)—C(4*B*)	122.7 (7)	C(5*B*)—C(6*B*)—C(1*B*)	116.6 (7)
C(8*B*)—O(7*B*)—C(1*B*)	118.6 (5)	C(9*B*)—C(8*B*)—O(7*B*)	108.5 (6)
O(10*B*)—C(9*B*)—C(8*B*)	123.7 (6)	O(11*B*)—C(9*B*)—C(8*B*)	112.3 (6)
O(11*B*)—C(9*B*)—O(10*B*)	123.7 (6)	C(11*C*)—P(1*C*)—O(1*C*)	112.0 (2)
C(21*C*)—P(1*C*)—O(1*C*)	112.1 (2)	C(21*C*)—P(1*C*)—C(11*C*)	107.2 (2)
C(31*C*)—P(1*C*)—O(1*C*)	111.9 (2)	C(31*C*)—P(1*C*)—C(11*C*)	107.2 (2)
C(31*C*)—P(1*C*)—C(21*C*)	106.1 (3)	C(12*C*)—C(11*C*)—P(1*C*)	118.3 (4)
C(16*C*)—C(11*C*)—P(1*C*)	123.1 (5)	C(16*C*)—C(11*C*)—C(12*C*)	118.5 (6)
C(13*C*)—C(12*C*)—C(11*C*)	120.7 (6)	C(14*C*)—C(13*C*)—C(12*C*)	119.7 (8)
C(15*C*)—C(14*C*)—C(13*C*)	121.3 (8)	C(16*C*)—C(15*C*)—C(14*C*)	119.1 (7)
C(15*C*)—C(16*C*)—C(11*C*)	120.6 (6)	C(22*C*)—C(21*C*)—P(1*C*)	117.9 (4)
C(26*C*)—C(21*C*)—P(1*C*)	123.9 (4)	C(26*C*)—C(21*C*)—C(22*C*)	118.2 (5)
C(23*C*)—C(22*C*)—C(21*C*)	120.5 (6)	C(24*C*)—C(23*C*)—C(22*C*)	120.2 (7)
C(25*C*)—C(24*C*)—C(23*C*)	119.9 (7)	C(26*C*)—C(25*C*)—C(24*C*)	120.4 (6)
C(25*C*)—C(26*C*)—C(21*C*)	120.8 (6)	C(32*C*)—C(31*C*)—P(1*C*)	123.6 (4)
C(36*C*)—C(31*C*)—P(1*C*)	118.2 (5)	C(36*C*)—C(31*C*)—C(32*C*)	118.2 (5)
C(33*C*)—C(32*C*)—C(31*C*)	120.9 (6)	C(34*C*)—C(33*C*)—C(32*C*)	119.9 (7)
C(35*C*)—C(34*C*)—C(33*C*)	120.5 (7)	C(36*C*)—C(35*C*)—C(34*C*)	119.5 (7)
C(35*C*)—C(36*C*)—C(31*C*)	121.0 (7)	C(6*D*)—C(1*D*)—C(2*D*)	120.1 (5)
O(7*D*)—C(1*D*)—C(2*D*)	114.6 (5)	O(7*D*)—C(1*D*)—C(6*D*)	125.2 (5)
C(3*D*)—C(2*D*)—C(1*D*)	118.9 (6)	Cl(3*D*)—C(3*D*)—C(2*D*)	118.0 (5)
C(4*D*)—C(3*D*)—C(2*D*)	121.1 (6)	C(4*D*)—C(3*D*)—Cl(3*D*)	120.9 (4)
Cl(4*D*)—C(4*D*)—C(3*D*)	121.0 (5)	C(5*D*)—C(4*D*)—C(3*D*)	118.7 (6)
C(5*D*)—C(4*D*)—Cl(4*D*)	120.4 (6)	C(6*D*)—C(5*D*)—C(4*D*)	122.1 (7)
C(5*D*)—C(6*D*)—C(1*D*)	119.1 (6)	C(8*D*)—O(7*D*)—C(1*D*)	117.5 (5)
C(9*D*)—C(8*D*)—O(7*D*)	108.6 (6)	O(10*D*)—C(9*D*)—C(8*D*)	124.9 (6)
O(11*D*)—C(9*D*)—C(8*D*)	111.0 (6)	O(11*D*)—C(9*D*)—O(10*D*)	124.1 (6)

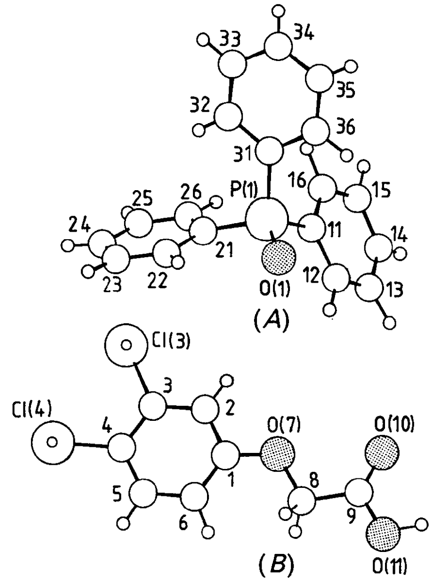

Fig. 1. Molecular conformation and atom-labelling scheme for the individual molecule pairs in the adduct. Only one pair [molecule *A* (TPPO) and molecule *B* (3,4-D)] is shown. Unless otherwise indicated, atoms are C.

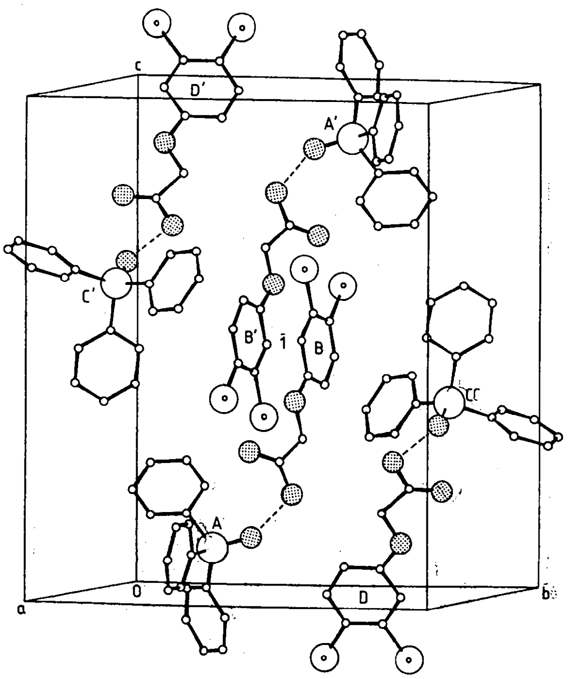

Fig. 2. Perspective view of the packing in the unit cell.

The authors thank the Australian Research Council, The University of Queensland and the Queensland University of Technology for financial support.

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Polymorphism in Dethoxyprone, a Steroidal Anaesthetic. I. Structure of 11α-Dimethylamino-2β-ethoxy-3α-hydroxy-5α-pregnan-20-one (Dethoxyprone Form I)

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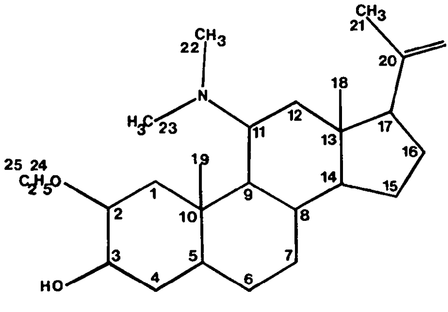
(*Received* 5 *May* 1992; *accepted* 21 *August* 1992)

Abstract. $C_{25}H_{43}NO_3$, $M_r = 405$, monoclinic, $P2_1$, $a = 8.654\,(2)$, $b = 6.428\,(1)$, $c = 21.032\,(3)$ Å, $\beta = 95.7\,(2)°$, $V = 1164\,(2)$ Å^3, $Z = 2$, $D_x = 1.16$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 5.05$ cm^{-1}, $F(000) = 448$, room temperature, $R = 0.042$ for 2185 observed reflections. All rings of the steroid skeleton are *trans* connected. Rings *A*, *B* and *C* are all in the chair conformation. Ring *D* is in a half-chair conformation. The molecules are hydrogen bonded in a head-to-head fashion through H(O3) and O(2) in a staggered arrangement linking molecules stacked along **b**.

Introduction. The anaesthetic properties of certain hormonal steroids have been known for over fifty years. The synthesis of Dethoxyprone [(2β,3α,5α,11α)-11-dimethylamino-2-ethoxy-3-hydroxy-5-pregnan-20-one] was a direct response to the need for a soluble steroid with potent anaesthetic properties. Initial animal studies (Davies, 1978) have demonstrated that it produces rapid onset of and recovery from anaesthesia and is non-irritant on intravenous administration. Early clinical trials (Aveling, 1979; Dundee, 1979; Dunn, 1980) have shown equal promise. At present two polymorphic forms of dethoxyprone are known to exist: Form I (monoclinic, $P2_1$) and Form II (orthorhombic, $P2_12_12_1$). We report here the crystal and molecular structure of Form I as part of an investigation into the polymorphism of this compound.



Experimental. Sample provided by Glaxo Research Laboratories, UK. Colourless prisms by slow

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0108-2701/93/040721-03$06.00