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α,α-Bis(*p*-chlorophenyl)-3-pyridinemethanol (Parinol)

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Abstract. $C_{18}H_{13}Cl_2NO$, $M_r = 330$, orthorhombic, $Pna2_1$, $a = 11{\cdot}557$ (1), $b = 13{\cdot}958$ (2), $c = 9{\cdot}652$ (1) Å, $Z = 4$, $D_x = 1{\cdot}41$ Mg m^{-3}, $F(000) = 680$, μ(Cu $K\alpha$) = 3·72 mm^{-1}; $R = 0{\cdot}053$ for 1305 observed reflections. The molecules are linked by a single intermolecular hydrogen bond (N···O, 2·746 Å) between the pyridine N and the hydroxyl O. The pyridine ring is approximately perpendicular to the plane of C–C–O. The dihedral angle between the planes of the benzene ring is 80·7°, giving torsion angles [C(8–7–13–14)] and [C(2–1–13–14)] down the ring-C to α-C vectors of −87·0 (3) and +38·7 (3)° respectively.

Introduction. Parinol is the common name for α,α-bis(*p*-chlorophenyl)-3-pyridinemethanol which was introduced under the trade name Parnon as a commercial fungicide (EL-241) by Eli Lilly & Co. (Thayer, Ford & Hall, 1967). The structure–fungicidal-activity relationships for parinol and other 3-pyridine alcohols and alkanes have been reported (Brown, Whaley, Taylor & Van Heynigen, 1967; Whaley & Taylor, 1970). Parinol possesses structural features in common with the insecticide *p,p'*-DDT (DeLacy & Kennard, 1972), the central trichloroethane moiety being replaced by the 3-pyridylmethanol group. Loss in insecticidal activity results when bulky groups are introduced into the 2-position of the ethyl group in *p,p'*-DDT, *e.g.* chlorine [1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)-ethane (Hovmöller, Smith & Kennard, 1978)] or hydroxyl [1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (dicofol) (Smith, Kennard & White, 1978)]. The structure was determined in order to compare the effect of both the pyridyl and hydroxyl groups on the relative conformational aspects of the *p*-chlorophenyl groups and to observe the effects hydrogen-bonding associations may have on the mode of packing of the molecules in the solid state. This work is part of a structural study of DDT-like compounds. The previous structure in this series was 1,1-bis(*p*-methoxyphenyl)-2,2-dimethylpropane (Smith, Kennard & Palm, 1980).

Colourless crystals, m.p. 452–453 K, were grown from a mixture of hexane and acetone. Preliminary X-ray data (*0kl*, $k + l$ = odd; *h0l*, h = odd) were consistent for either space group *Pnam* or $Pna2_1$, the latter being confirmed by successful structure solution and refinement. 1305 reflections with $I > 2{\cdot}5\sigma(I)$ were considered observed out of 1475 unique reflections collected from one crystal (0·05 × 0·28 × 0·18 mm) mounted along the *a* axis in the counter aperture of a Philips PW 1100 four-circle diffractometer ($2\theta_{max}$ = 134°; graphite-monochromatized Cu $K\alpha$ radiation) using an $\omega/2\theta$ scanning mode with a fixed scan width of 1·6°. The data were corrected for absorption but not for extinction.

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The structure was solved by the heavy-atom and Fourier methods and refined by full-matrix least squares to a final residual R $(=\sum||F_o| - |F_c||/\sum|F_o|)$ of 0·053 and Rw $[=(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$ of 0·059. Reflections were given the weights $w = 1{\cdot}00/[\sigma^2(F_o) + 0{\cdot}0004(F_o)^2]$. H positions were found in a difference Fourier synthesis and included in the refinement at fixed positions with their isotropic U set invariant at 0·05 Å^2. A final difference Fourier map revealed no electron density greater than 0·13 e Å^{-3}. Positional parameters are given in Table 1.* Bond distances and angles are in Table 2. The molecular conformation and labelling scheme are given in Fig. 1. All computations were completed using the *SHELX* program set (Sheldrick, 1976) on the Cyber 76 computer of the CSIRO computing system.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36097 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic positional parameters* (×10^4) *and equivalent isotropic thermal parameters* (×10^3) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq} (Å^2)
Cl(4)	−9 (2)	241 (2)	0	62 (1)
Cl(10)	3972 (2)	2002 (2)	−8904 (3)	75 (1)
C(1)	840 (5)	2578 (3)	−3021 (6)	35 (3)
C(2)	−165 (5)	2033 (4)	−3180 (6)	41 (3)
C(3)	−443 (5)	1275 (4)	−2254 (6)	42 (3)
C(4)	322 (5)	1124 (4)	−1183 (6)	43 (3)
C(5)	1349 (6)	1635 (4)	−1012 (5)	46 (3)
C(6)	1594 (6)	2356 (5)	−1937 (6)	45 (3)
C(7)	1780 (5)	3064 (4)	−5277 (7)	39 (3)
C(8)	1552 (6)	2190 (5)	−5904 (7)	50 (4)
C(9)	2195 (7)	1864 (5)	−7026 (8)	59 (5)
C(10)	3116 (6)	2411 (5)	−7497 (8)	50 (4)
C(11)	3358 (6)	3297 (5)	−6897 (8)	51 (4)
C(12)	2689 (6)	3599 (4)	−5793 (7)	47 (4)
C(13)	1107 (5)	3423 (4)	−3989 (7)	38 (3)
O(13)	1843 (3)	4083 (3)	−3313 (5)	42 (2)
C(14)	−8 (3)	3962 (3)	−4409 (5)	39 (4)
C(15)	−838 (5)	4142 (5)	−3416 (7)	48 (4)
C(16)	−1766 (5)	4741 (5)	−3703 (6)	53 (4)
C(17)	−1804 (4)	5185 (4)	−5018 (7)	57 (4)
N(18)	−1007 (5)	5012 (5)	−5994 (6)	55 (5)
C(19)	−113 (4)	4388 (5)	−5663 (6)	50 (4)
H(2)	−964	2190	−3935	
H(3)	−1199	936	−2308	
H(5)	1809	1648	−171	
H(6)	2289	2720	−1632	
H(8)	769	1842	−5721	
H(9)	2016	1120	−7362	
H(11)	3896	4025	−7486	
H(12)	2934	4181	−5354	
H(15)	−802	3805	−2503	
H(16)	−2572	4731	−3106	
H(17)	−2572	5679	−5031	
H(19)	499	4157	−6599	
H(O13)	2000	4678	−3591	

Discussion. The *p*-chlorophenyl rings of the parinol molecules adopt a symmetrical conformation about the C(13)–C(14) bond with respect to the pyridine ring, the torsion angles C(7)–C(13)–C(14)–C(15) and C(1)–C(13)–C(14)–C(19) being +14·4 (3) and −32·1 (3)° respectively. This has also been found for one of the two molecules of dicofol in the asymmetric unit which does not participate in hydrogen bonding *via* the hydroxyl O (Smith *et al.*, 1978). With parinol,

Table 2. *Bond distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

C(1)–C(2)	1·397 (3)	C(10)–Cl(10)	1·775 (2)
C(2)–C(3)	1·422 (3)	C(10)–C(11)	1·394 (4)
C(3)–C(4)	1·376 (3)	C(11)–C(12)	1·382 (4)
C(4)–Cl(4)	1·723 (2)	C(12)–C(7)	1·383 (3)
C(4)–C(5)	1·394 (3)	C(13)–C(7)	1·550 (3)
C(5)–C(6)	1·376 (3)	C(13)–C(14)	1·547 (3)
C(6)–C(1)	1·396 (3)	C(14)–C(19)	1·354 (3)
C(1)–C(13)	1·536 (3)	C(14)–C(15)	1·379 (3)
C(13)–O(13)	1·413 (3)	C(15)–C(16)	1·388 (3)
C(7)–C(8)	1·387 (3)	C(16)–C(17)	1·413 (3)
C(8)–C(9)	1·390 (4)	C(17)–N(18)	1·339 (3)
C(9)–C(10)	1·388 (4)	N(18)–C(19)	1·389 (3)

C(1)–C(2)–C(3)	121·6 (2)	C(7)–C(8)–C(9)	121·8 (3)
C(2)–C(3)–C(4)	116·1 (2)	C(8)–C(9)–C(10)	119·0 (3)
C(3)–C(4)–C(5)	123·9 (2)	C(9)–C(10)–C(11)	120·5 (2)
C(3)–C(4)–Cl(4)	117·7 (1)	C(9)–C(10)–Cl(10)	120·1 (1)
C(4)–C(5)–C(6)	118·2 (2)	C(10)–C(11)–C(12)	118·6 (2)
C(5)–C(6)–C(1)	121·4 (2)	C(11)–C(12)–C(7)	122·5 (2)
C(5)–C(4)–Cl(4)	118·4 (1)	C(11)–C(10)–Cl(10)	119·4 (1)
C(6)–C(1)–C(2)	118·7 (2)	C(12)–C(7)–C(8)	117·5 (2)
C(6)–C(1)–C(13)	120·1 (2)	C(12)–C(7)–C(13)	122·7 (2)
C(2)–C(1)–C(13)	121·3 (2)	C(13)–C(14)–C(15)	119·0 (2)
C(1)–C(13)–C(7)	109·9 (2)	C(14)–C(15)–C(16)	120·6 (2)
C(1)–C(13)–C(14)	111·4 (2)	C(15)–C(16)–C(17)	117·8 (2)
C(1)–C(13)–O(13)	109·9 (2)	C(16)–C(17)–N(18)	122·2 (3)
C(7)–C(13)–O(13)	106·2 (2)	C(17)–N(18)–C(19)	117·5 (3)
C(7)–C(13)–C(14)	111·4 (2)	N(18)–C(19)–C(14)	123·3 (2)
C(13)–C(7)–C(8)	119·7 (2)	C(19)–C(14)–C(15)	118·7 (2)
C(13)–C(7)–C(12)	122·7 (2)	C(19)–C(14)–C(13)	121·5 (2)

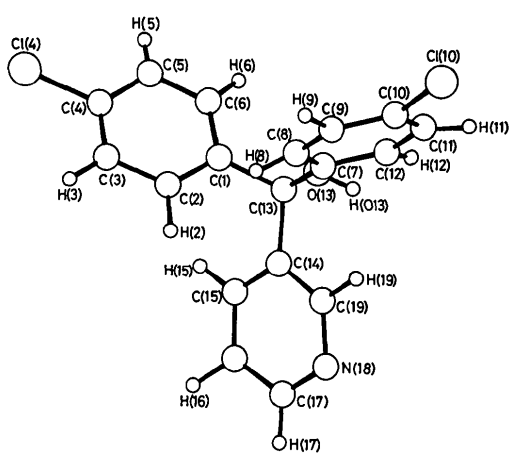

Fig. 1. Molecular conformation and labelling scheme for parinol viewed perpendicular to the plane of C(1), C(13), C(14).

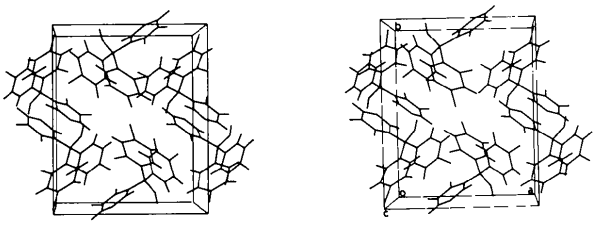

Fig. 2. Stereoscopic view of the packing in the cell viewed perpendicular to the *ab* plane.

however, there is one intermolecular hydrogen-bonding interaction involving a hydroxyl H and a pyridine N (O···N, 2·746 Å) (Fig. 2). The presence of the hydroxyl group has an effect on the conformation of the three rings about C(13). The *p*-chlorophenyl rings of parinol are rotated with respect to the plane of C(1)–C(13)–C(7), making dihedral angles with the least-squares planes of the rings C(1) to C(6) and C(7) to C(12) of 94·6 and 42·0° respectively. The ring-to-ring angle is 80·7°.

Torsion angles down the C(13)–C(7) and C(13)–C(1) vectors corresponding to the angles τ_1 [C(8–7–13–14)] and τ_2 [C(2–1–13–14)] as defined by Hovmöller, Norrestam & Palm (1976) are +87·0 (3) and −38·7 (3)° respectively. These compare with the corresponding angles in: *p,p'*-DDT (+87, −14°); dicofol, molecule *A* (hydrogen bonding *via* OH) (+78, −1°); dicofol, molecule *B* (no hydrogen bonding) (+90, −39°); and 1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)ethane (+85, −25°).

Bond distances and angles are similar to those found for other analogous DDT compounds except that no significant distortion of the *exo* C(1) and C(7) angles is present. This is a feature of a number of members of this series.

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Structure of the 1:2 Complex of 2,5-Piperazinedione and Formic Acid

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Abstract. $C_4H_6N_2O_2.2CH_2O_2$, triclinic, $P\bar{1}$, a = 6·852 (2), b = 7·078 (2), c = 6·253 (2) Å, α = 109·76 (2), β = 122·12 (2), γ = 95·28 (3)°, Z = 1. The structure was solved by direct methods and refined by the block-diagonal least-squares method to an R of 0·057 from a set of 902 observed reflections. The piperazinedione ring is almost exactly planar.

Introduction. 2,5-Piperazinedione (DKP) is present in a number of molecules with important biological activity. Some cyclic dipeptides also exhibit strong denaturing action on globular proteins, weakening the secondary structure by competing with their interchain hydrogen bonds (Cresenzi, Cesaro & Russo, 1973). In view of the fact that DKP can interact strongly with other molecules, we examined the crystal structures of some DKP complexes and here we report on the results for the DKP–formic acid complex.

DKP dissolves in formic acid and crystals of the complex grow very quickly. The crystal chosen for data

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