conformations of the two crystallographically independent steroid molecules are very similar. The *A* and *C* rings of both molecules have normal chair conformations, and both *D* rings have 13β-envelope conformations. The *B*-ring conformations differ slightly with molecule (1) having an 8β,9α half-chair and molecule (2) a conformation intermediate between a half chair and sofa. The conformation about the C(17)—C(20) bond, which defines the orientation of the phenyl ring with respect to the steroid nucleus, is illustrated in Fig. 2.

There are four crystallographically independent hydrogen bonds, and all available hydroxyls serve as hydrogen donors. The hydrogen bonds (donor → acceptor) and their distances are: O(3*B*) → O(3*B*′) 2·72, O(17*B*) → O(3*B*) 2·81, O(3*B*′) → O(17*B*′) 2·76, O(17*B*′) → O(17*B*) 2·91 Å.

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Dihydrophotoaldrin Acetate,* $C_{14}H_{12}Cl_6O_2$

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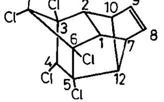
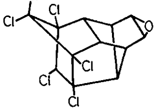
Abstract. M_r = 425·0, monoclinic, $P2_1/c$, a = 9·399 (4), b = 11·090 (5), c = 15·920 (8) Å, β = 91·48 (4)°, V = 1659 Å^3, Z = 4, D_m = 1·70, D_x = 1·701 Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 1·03 mm^{-1}, F(000) = 856, T = 298 K. Final R = 0·049 for 2067 observed reflections. The title compound is one of three isomeric acetates formed by the addition of acetic acid to photoaldrin. This structure determination has confirmed the configuration suggested from chemical evidence for the acetate and analogous photoaldrin derivatives.

Introduction. Photoaldrin (I) and photodieldrin (II) are more active biologically as insecticides than their respective precursors, aldrin and dieldrin, from which they are formed to some extent *in vivo*. Bieniek & Korte (1969) suggested that the structure of one of the dieldrin metabolites is the ketone (III) but gave no evidence that would exclude the isomeric ketone (IV). The title compound, dihydrophotoaldrin acetate (V), is one of three isomeric acetates formed either by the regioselective reaction in the photocyclization of *exo*-dihydroaldrinol acetate or by the addition of acetic acid to photoaldrin (Bird & Khan, 1980). The structure of the acetate (V) was determined to resolve this ambiguity existing between (III) and (IV) with which (V) is related by chemical interconversion.



(I)



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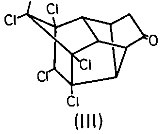

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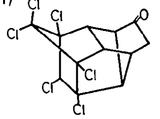

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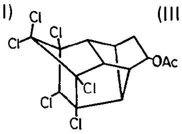

(V)

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* IUPAC name: 2,3,3,4-*exo*,5,6-hexachloropentacyclo[6.4.0.0^{2,6}.0^{4,12}.0^{7,11}]dodec-9-*exo*-yl acetate.

0108-2701/83/121701-03$01.50

Experimental. Crystals grown from isopropyl alcohol as blocky pseudo-hexagonal prisms, 0·30 × 0·30 × 0·12 mm. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator. 14 reflections used for measuring lattice parameters. No corrections for absorption or extinction. $2\theta_{\rm max} = 50^\circ$. Range of *hkl*: ±11, 13, 18. Standards with overall variation: 600 (0·2%); 020 (2·7%); 006 (0·4%). Of 2981 unique reflections 2067 considered observed with $I > 2{\cdot}5\sigma(I)$. Structure solution by multisolution $\sum_2$ sign-expansion direct methods of *SHELX*76 (Sheldrick, 1976). Least-squares refinement (F's) with anisotropic thermal parameters on all non-H atoms gave $R = 0{\cdot}049$ (unit weights). H atoms located in a difference Fourier synthesis, included at fixed positions with their isotropic U values set invariant at 0·05 Å^2. $(\Delta/\sigma)_{\rm max} = 3{\cdot}0$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}73$. Max. peak in final difference Fourier map 0·23 e Å^{-3} above background of 0·15 e Å^{-3}. Scattering factors from Cromer & Mann (1968) (non-H), Stewart, Davidson & Simpson (1965) (H), while Cl atoms corrected for anomalous dispersion (Cromer & Liberman, 1970).

Discussion. Atomic positional parameters are listed in Table 1* while bond distances and angles are given in Table 2.

This structure determination has confirmed the configuration proposed by Bird & Kahn (1980) (Fig. 1), and allows the assignment of the structure of the corresponding photoaldrin ketone metabolite to be (III) rather than (IV). This isomer is best described as the one having the ketone group on the same side of the molecule as the bridge, *i.e.* if C(5) is bonded to C(12), then the ketone group is at C(8). The acetate group is *exo* to the photoaldrin ring system (towards the molecular bridge) with the methyl group also directed

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^3)

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

	x	y	z	$U_{\rm eq}$
Cl(1)	−145 (2)	8517 (2)	1526 (2)	54 (1)
Cl(2)	199 (2)	6505 (2)	460 (2)	55 (1)
Cl(3)	−1686 (3)	9088 (2)	−362 (2)	57 (1)
Cl(4)	−2221 (3)	6124 (2)	−861 (1)	53 (1)
Cl(5)	−3502 (2)	4676 (2)	694 (1)	43 (1)
Cl(6)	−1473 (2)	5635 (2)	2136 (1)	47 (1)
C(1)	−3030 (7)	7721 (7)	1850 (4)	32 (4)
C(2)	−3313 (7)	8520 (6)	1034 (4)	31 (4)
C(3)	−2267 (8)	7990 (7)	359 (4)	36 (4)
C(4)	−3075 (8)	6935 (6)	−48 (4)	32 (4)
C(5)	−3398 (8)	6269 (6)	776 (4)	29 (4)
C(6)	−2178 (7)	6719 (6)	1443 (4)	31 (4)
C(7)	−4450 (8)	7125 (8)	2027 (4)	30 (4)
C(8)	−5517 (8)	8074 (7)	2295 (4)	39 (4)
C(9)	−5841 (8)	8776 (7)	1467 (5)	40 (4)
C(10)	−4866 (7)	8182 (6)	827 (4)	32 (4)
C(11)	−1093 (7)	7429 (7)	921 (4)	34 (4)
C(12)	−4783 (8)	6826 (7)	1110 (4)	30 (4)
C(81)	−6923 (8)	7074 (7)	3317 (4)	36 (4)
C(82)	−8347 (9)	6765 (9)	3543 (6)	60 (5)
O(8)	−6861 (5)	7564 (5)	2544 (3)	38 (3)
O(81)	−5862 (7)	6939 (6)	3757 (3)	49 (3)

Table 2. *Bond distances* (Å) *and angles* (°) *for dihydrophotoaldrin acetate* (V) *compared with photoaldrin* (I) (*Khan, Baur & Khan,* 1972)

	(V)	(I)		(V)	(I)		(V)	(I)
C(1)–C(2)	1·589 (10)	1·607 (10)	C(4)–Cl(4)	1·784 (7)	1·779 (4)	C(8)–O(8)	1·448 (9)	
C(1)–C(6)	1·524 (10)	1·514 (6)	C(5)–C(6)	1·621 (10)	1·620 (5)	C(9)–C(10)	1·536 (10)	1·513 (7)
C(1)–C(7)	1·522 (11)	1·569 (6)	C(5)–C(12)	1·547 (10)	1·563 (6)	C(10)–C(12)	1·571 (10)	1·583 (6)
C(2)–C(3)	1·588 (10)	1·601 (6)	C(5)–Cl(5)	1·774 (7)	1·764 (4)	C(11)–Cl(1)	1·770 (7)	1·756 (4)
C(2)–C(10)	1·534 (10)	1·580 (6)	C(6)–C(11)	1·547 (10)	1·546 (6)	C(11)–Cl(2)	1·763 (7)	1·805 (4)
C(3)–C(4)	1·530 (9)	1·541 (5)	C(6)–Cl(6)	1·750 (7)	1·760 (4)	O(8)–C(81)	1·348 (9)	
C(3)–C(11)	1·534 (10)	1·543 (6)	C(7)–C(8)	1·522 (11)	1·518 (6)	C(81)–O(81)	1·213 (9)	
C(3)–Cl(3)	1·769 (7)	1·764 (4)	C(7)–C(12)	1·522 (10)	1·543 (6)	C(81)–C(82)	1·436 (10)	
C(4)–C(5)	1·542 (10)	1·572 (6)	C(8)–C(9)	1·554 (10)	1·361 (7)			
C(2)–C(1)–C(6)	97·9 (5)	98·1 (3)	C(4)–C(5)–Cl(5)	115·2 (5)	114·8 (3)	C(9)–C(10)–C(2)	109·5 (6)	107·2 (3)
C(2)–C(1)–C(7)	105·3 (5)	104·9 (3)	C(6)–C(5)–C(12)	103·8 (5)	103·7 (3)	C(9)–C(10)–C(12)	104·3 (6)	101·6 (3)
C(6)–C(1)–C(7)	103·6 (6)	104·2 (3)	C(6)–C(5)–Cl(5)	113·0 (5)	115·1 (3)	C(2)–C(10)–C(12)	97·6 (5)	96·7 (3)
C(1)–C(2)–C(3)	104·7 (5)	104·4 (3)	C(12)–C(5)–Cl(5)	112·2 (5)	112·5 (3)	C(3)–C(11)–C(6)	92·6 (5)	93·1 (3)
C(1)–C(2)–C(10)	100·2 (5)	100·4 (3)	C(5)–C(6)–C(1)	97·6 (5)	98·9 (3)	C(3)–C(11)–Cl(1)	112·7 (5)	111·4 (3)
C(3)–C(2)–C(10)	111·5 (5)	110·6 (3)	C(5)–C(6)–C(11)	105·6 (5)	105·7 (3)	C(3)–C(11)–Cl(2)	119·1 (6)	118·7 (3)
C(2)–C(3)–C(4)	105·1 (6)	105·6 (3)	C(5)–C(6)–Cl(6)	116·8 (5)	116·3 (3)	C(6)–C(11)–Cl(1)	112·6 (5)	112·0 (3)
C(2)–C(3)–C(11)	101·8 (5)	101·5 (3)	C(1)–C(6)–C(11)	102·6 (6)	103·3 (3)	C(6)–C(11)–Cl(2)	113·5 (5)	115·9 (3)
C(2)–C(3)–Cl(3)	113·0 (5)	113·5 (3)	C(1)–C(6)–Cl(6)	115·3 (6)	115·3 (3)	Cl(1)–C(11)–Cl(2)	106·3 (4)	105·7 (2)
C(4)–C(3)–Cl(3)	114·2 (5)	113·6 (3)	C(11)–C(6)–Cl(6)	116·4 (5)	115·3 (3)	C(5)–C(12)–C(7)	105·2 (6)	105·6 (3)
C(4)–C(3)–C(11)	106·2 (6)	105·2 (3)	C(1)–C(7)–C(8)	109·8 (7)	109·7 (3)	C(5)–C(12)–C(10)	108·6 (6)	110·2 (3)
C(11)–C(3)–Cl(3)	115·3 (6)	116·2 (3)	C(1)–C(7)–C(12)	94·4 (5)	93·0 (3)	C(7)–C(12)–C(10)	94·2 (6)	94·7 (3)
C(3)–C(4)–C(5)	96·5 (5)	96·6 (3)	C(8)–C(7)–C(12)	107·4 (6)	103·2 (4)	C(8)–O(8)–C(81)	117·7 (6)	
C(3)–C(4)–Cl(4)	117·7 (5)	117·6 (3)	C(7)–C(8)–C(9)	103·0 (6)	107·2 (4)	O(8)–C(81)–C(82)	112·8 (7)	
C(5)–C(4)–Cl(4)	118·5 (5)	118·4 (3)	C(7)–C(8)–O(8)	113·1 (6)		O(8)–C(81)–O(81)	121·5 (7)	
C(4)–C(5)–C(6)	105·0 (5)	104·5 (3)	C(9)–C(8)–O(8)	105·9 (6)		O(81)–C(81)–C(82)	125·7 (7)	
C(4)–C(5)–C(12)	106·7 (5)	105·2 (3)	C(8)–C(9)–C(10)	103·9 (6)	108·9 (4)			

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38768 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

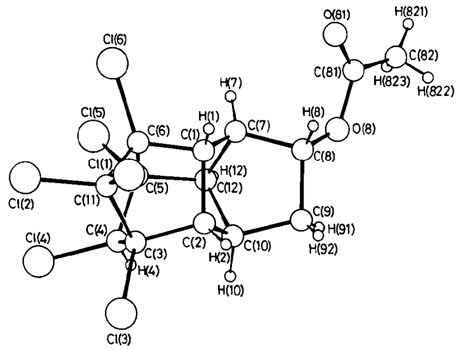

Fig. 1. Molecular configuration and atom-numbering scheme for (V).

away from the molecule. Torsion angles associated with the acetate side chain are −169·3 (7)° for C(9)—C(8)—O(8)—C(81) and +171·1 (9)° for C(8)—O(8)—C(81)—C(82).

The changes in the distance and angular parameters which result from the conversion of the unsaturated hexachloro-8,9,10-trinorbornene nucleus [with C(4)=C(5)] to the saturated bridged cyclopentane ring are largely in the distortion of the molecular cage framework. Although the intra-ring angles at C(11) [92·6 (5)], C(3) [106·2 (6)] and C(6) [105·6 (5)°] are comparable with the mean of those found equivalent in the ring for the cyclodiene series of insecticides (Smith, 1978), the difference in the angles at C(4) [96·5 (5)] and C(5) [105·0 (5)°] reflects the constraints imposed by the bridge between C(5) and C(12). Other distances and angles are similar to those of the parent compound aldrin (DeLacy & Kennard, 1972), its stereoisomer isodrin (Kennard, Smith & Hovmöller, 1979) and other 'cyclodiene' analogues (Smith, 1978).

Packing in the unit cell emphasizes the non-associated nature of the molecules, a common feature among this series of compounds. No intermolecular contacts shorter than 3 Å exist.

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(1*S*,5*R*,9*R*)-2-Cyclopropylmethyl-2′-hydroxy-5,9-dimethyl-8-oxo-6,7-benzomorphan Hydrochloride Monohydrate (Ketazocine),* $\mathrm{C_{18}H_{23}NO_2.HCl.H_2O}$†

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Abstract. $M_r = 339{\cdot}86$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}367\,(5)$, $b = 13{\cdot}673\,(4)$, $c = 8{\cdot}941\,(3)$ Å, $V = 1756\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}28$, $D_x = 1{\cdot}285$ Mg m^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 0{\cdot}236$ mm^{-1}, $F(000) = 728$, room temperature. The structure was determined by Patterson synthesis and direct methods and refined to $R = 0{\cdot}049$ for 2347 observed reflections. The cyclopropylmethyl side chain adopts the same conformation as in gemazocine.

Introduction. As part of a structure–activity study on 6,7-benzomorphans, the structure of ketazocine was

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* *Chemical Abstracts* name: 3-cyclopropylmethyl-3,4,5,6-tetrahydro-8-hydroxy-2,6-methano-6,11-dimethyl-3-benzazocin-1(2*H*)-one hydrochloride monohydrate.

† Structural Studies of Substituted 6,7-Benzomorphan Compounds. VII. Part VI: Peeters, De Ranter & Blaton (1982).

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