

**trans-4a-Acetoxy-8a-chloro-1,4,4a,5,8,8a-hexahydronaphthalene**

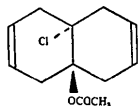
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**Abstract.** Crystals of  $C_{12}O_2H_{15}Cl$  are orthorhombic, with  $a = 11.006$  (5),  $b = 14.190$  (9),  $c = 7.359$  (3) Å, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $D_c = 1.22$  g cm $^{-3}$ . Full-matrix least-squares refinement gave a final  $R$  of 4.4%. C-Cl is 1.823 (4) Å, a value surprisingly long in view of the unreactivity of this tertiary chloride with hot alcoholic silver nitrate. Other structural features are typical.

**Introduction.** Starting with naphthalene Roberts (1971), using the reaction sequence of HCl addition to the 4a,8a-epoxide of isotetralin and acetylation, prepared what was presumed to be the title compound (I).



(I)

The end product, however, was found not to react with hot alcoholic silver nitrate, a result unexpected for a tertiary chloride. An X-ray diffraction study was therefore carried out to determine whether the assigned structure was correct, and, if so, whether any unusual structural features consistent with the unanticipated chemical reactivity were present.

One nearly spherical crystal of diameter *ca* 0.3 mm was available in this study. Precession photography showed it to be orthorhombic, with the space group uniquely indicated as  $P2_12_12_1$ . The crystal was then transferred to a Picker Nuclear FACS-I automatic diffractometer. Least-squares treatment of the spacings of 12 reflections with  $2\theta \geq 50^\circ$  gave the lattice constants. Intensity data were collected on the diffractometer in the range  $10^\circ < 2\theta < 125^\circ$  using monochromatized Cu  $K\alpha$  radiation and the  $\theta$ - $2\theta$  scan technique with a scan rate of  $1^\circ$  min $^{-1}$ , a base width of  $2^\circ$  and a background time of 20 s. Periodic monitoring of three standard reflections gave no indication of arc slippage or crystal decay. Based on the criterion that an observed reflection is one where  $I \geq 2.33\sigma(I)$ , the set of 1094 reflections contained 86 which were taken as unobserved.

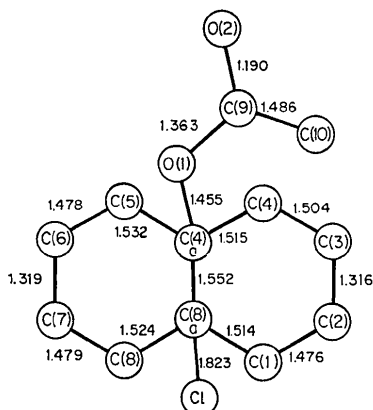
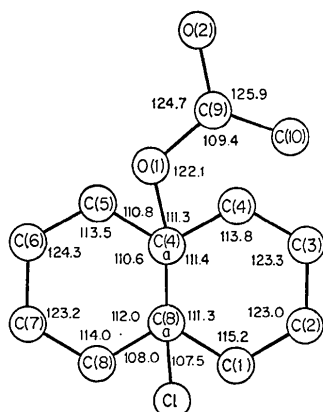
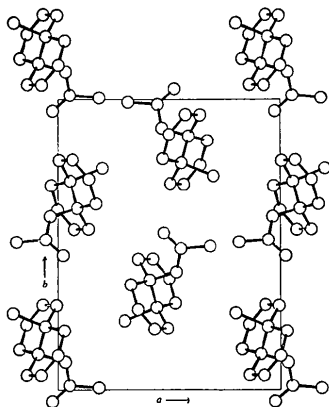
The intensity data were reduced in the usual way, and placed on an approximate scale by use of a Wilson

plot. The accompanying temperature factor was then used to calculate normalized structure factors. A set of 123  $E$  values greater than 1.50 were then used in the direct methods program of Main, Woolfson & Germain (1971). An  $E$  map calculated from the best solution clearly revealed the positions of all 15 heavy atoms which were then refined by full-matrix least squares, allowing, eventually, for anisotropic thermal motion and the positions of the H atoms, all of which were located at an intermediate stage in a difference map. From an initial value of 35%,  $R$  was reduced to 4.4% finally. The weighting scheme used was  $w = \sigma^{-1}(F_o)$ , where  $\sigma(F_o) = [ |F_o|^2 + \sigma(I_o) ]^{1/2} - |F_o|$ ,  $\sigma(I_o)$  being determined from counting statistics. The final posi-

Table 1. Final positional parameters and their estimated standard deviations for  $C_{12}O_2ClH_{15}$ Parameters for C, O, and Cl are  $\times 10^4$ , parameters for H are  $\times 10^3$ .

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	4940 (5)	2104 (3)	3911 (7)
C(2)	4334 (5)	2080 (3)	5699 (7)
C(3)	3601 (4)	2750 (4)	6270 (6)
C(4)	3284 (4)	3603 (3)	5152 (6)
C(4a)	4126 (3)	3762 (2)	3552 (5)
C(5)	3614 (4)	4477 (3)	2192 (7)
C(6)	4266 (5)	4488 (3)	437 (7)
C(7)	5007 (4)	3817 (3)	-119 (7)
C(8)	5289 (4)	2970 (3)	972 (6)
C(8a)	4440 (3)	2822 (2)	2584 (5)
C(9)	5531 (4)	4844 (3)	5122 (5)
C(10)	6845 (5)	4924 (4)	5559 (8)
O(1)	5334 (2)	4040 (2)	4153 (4)
O(2)	4761 (3)	5389 (2)	5551 (6)
Cl	3004 (1)	2364.5 (7)	1720 (2)
H(1)	576 (4)	222 (3)	417 (6)
H'(1)	481 (4)	143 (4)	324 (7)
H(2)	465 (5)	168 (4)	669 (8)
H(3)	325 (4)	269 (3)	745 (7)
H(4)	239 (5)	356 (3)	459 (7)
H'(4)	325 (4)	406 (3)	595 (7)
H(5)	268 (4)	435 (3)	195 (6)
H'(5)	363 (4)	508 (3)	299 (7)
H(6)	419 (5)	505 (4)	-60 (9)
H(7)	538 (4)	384 (3)	-130 (6)
H(8)	616 (3)	300 (2)	143 (5)
H'(8)	516 (4)	243 (4)	5 (7)
H(10)	707 (7)	440 (6)	647 (11)
H'(10)	714 (5)	515 (4)	468 (9)
H''(10)	708 (6)	544 (5)	707 (10)

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Fig. 1. Bond lengths (Å) in  $C_{12}O_2ClH_{15}$ .Fig. 2. Bond angles ( $^{\circ}$ ) in  $C_{12}O_2ClH_{15}$ .Fig. 3. Projection of the structure down the  $c$  axis.

tional parameters and their e.s.d.'s are shown in Table 1.\*

**Discussion.** The bond lengths are shown in Fig. 1, the bond angles in Fig. 2; the respective standard errors are 0.007 Å, or less, and 0.5°, or less. The bond lengths

\* The lists of thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31683 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

are not unexpected. Pasternak (1951) found the ethylenic C-C bond in pentachlorocyclohexene to be 1.22 Å, but the C atoms in that study could, of course, be located only with very low precision. In a different cyclohexene derivative Hwang, Donohue & Tsai (1972) found an ethylenic bond of length 1.304 (7) Å, similar to the values of 1.316 (7) and 1.319 (7) Å found here. All of these are shorter than the value of 1.335 (5) Å in various ethylenes (Sutton, 1965). The bond angles in the C=C-C groups average to 123.5 (6)°; this value is significantly larger than the value of 120° predicted by the customary  $sp^2$  hybridization picture of the double bond. The bond lengths in the acetate group do not differ significantly from those reported by O'Gorman, Shand & Schomaker (1950) for gaseous methyl acetate.

The two cyclohexene rings have the expected half-chair conformation. The best plane through the eight peripheral C atoms gives an average deviation of only 0.009 Å of these atoms from that plane, while C(4a) and C(8a) are 0.34 Å away from it, in opposite directions.

Structural features involving the H atoms are not shown in Figs. 1 and 2. The averages are: bond distance C-H = 1.02 (13) Å, bond angles C=C-H = 118 (5), and C-C-H = 109 (5)°.

The C-Cl distance of 1.823 (4) Å is large when compared with the value 1.767 (2) Å observed in paraffinic chlorides, but is essentially equal to the distance of 1.828 Å found by Momany, Bonham & Druelinger (1963) in an electron diffraction study of gaseous t-butyl chloride. Bowen, Gilchrist & Sutton (1955) observed that the length of a C-halogen bond varied inversely with the strength of the bond. The present example seems to be an exception to this rule, and we have not found any structural features which explain the lack of reactivity of this molecule toward silver nitrate.

The packing of the molecules in the unit cell is illustrated in Fig. 3.

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