Apparent carbon–carbon bond cleavage in an epoxide. 2,3,4,5,6-Hexachloro-12oxopentacyclo[5.4.1.1.^{8,11}.0^{3,10}.0^{5,9}]tridecane; a minor product from the acid treatment of endrin^{1,4,5}

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JOHN W. APSIMON, KAZU YAMASAKI, ALAIN FRUCHIER, ALFRED S. CHAU, and CAROL P. HUBER. Can. J. Chem. **60**, 501 (1982). The treatment of *endrin* (1) with sulfuric acid produces ketoendrin 2 and from 6 to 8% of another product that we show to be 2,3,4,4,5,6-hexachloro-12-oxapentacyclo[5.4.1.1.^{8,11}.0.^{3,10}.0.^{5,9}]tridecane 3, based initially on spectral evidence and confirmed by a single crystal X-ray diffraction study. The formation of 3 involves an apparent and unusual carbon–carbon single bond cleavage in an epoxide accompanied by cycloaddition to a proximate carbon–carbon double bond. This transformation probably proceeds by the route outlined in ref. 1. Some of the observed nmr parameters of 3 are discussed in the light of its structure and a comparison is made with the observed spectra for endrin (1).

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L'endrine (1) réagit dans l'acide sulfurique en produisant la cétoendrine (2) ainsi que 6 à 8% d'hexachloro-2,3,4,4,5,6 oxa-12 pentacyclo[$5.4.1.1.^{8,11}.0^{5,10}.0^{5,9}$]-tridécane (3) dont la structure avait été proposée initialement sur la base de données spectrales et que nous avons confirmée par diffraction de rayons X sur un monocristal. La formation du composé 3 implique apparemment un clivage inusité d'une liaison simple carbone–carbone d'un epoxyde accompagné d'une cycloaddition avec la double liaison carbone–carbone à proximité. Cette transformation se fait probablement selon la voie suggérée dans la référence 1. On discute, à la lumière de sa structure, de quelques paramètres observés en rmn et on établit des comparaisons avec les spectres observés dans l'endrine (1).

⁵The numbering system used for 3 in this article varies in order to aid the reader. Thus, the IUPAC derived numbering system is shown in 3a while the numbering system used in the nmr spectral discussion in the text is shown in 3b. This choice is made since it is essential to our arguments that comparison be made to endrin 1. This comparison is best appreciated if the two numbering systems correspond. The crystallographic work unfortunately uses another set of numbers to locate the atoms in the two independent molecules found in the unit cell. This system is indicated in Fig. 1.



During a study of the nuclear magnetic resonance spectral properties of the rearrangement products of polychlorocyclodiene insecticides, we have systematically examined the transformation products of endrin 1. Thus, with sulfuric acid, endrin 1 yields ketoendrin 2 (2) together with a minor product (6–8%) to which we have previously assigned structure 3 (1) based on spectral evidence.^{6,7} We now report confirmation of this proposal based on further nmr studies and a single crystal X-ray diffraction study.

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¹For a preliminary communication see ref. 1.

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⁴NRCC No. 19793.

⁶The assignments for H-12a and H-12s in Table 1 of this reference should be reversed as should the attributions to C-3/C-6 and C-2/C-7 in Table 2. This is amplified in the later discussion.

⁷A referee has correctly pointed out that the formation of 3 does not really involve C—C bond cleavage in an epoxide. Rather, if our proposed mechanism for the formation of 3 from 1 is correct (1), then the C—C bond cleavage occurs after epoxide C—O bond cleavage. The final product appears only as the net effect of C—C bond cleavage.

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FIG. 1. ORTEP views of the two crystallographically independent molecules of **3**. The thermal ellipsoids enclose 50% probability (5).

X-ray structural studies

The results indicated that two independent molecules exist per asymmetric unit in the crystal of **3**. Views of these as established by the X-ray analysis are shown in Fig. 1. Final atomic parameters are listed in Table 1, and bond lengths and bond angles are given in Table 2. The C—H bond distances vary from 0.89 to 1.04 Å with mean 0.96 Å, and the bond angles involving hydrogen atoms vary from 103 to 122°, with mean 112°. The angles involving hydrogens are expected to be larger than 109° in compensation for the small angles formed by the heavier atoms in five-membered rings.

As in other related structures (endrin (3), aldrin



(3), and dieldrin (4)), the molecules have essentially mirror symmetry with the mirror planes here defined by C(1), O(1), and C(12) and by C(21), O(21), and C(32). Agreement is reasonably good between chemically related bonds and angles in individual molecules as well as between corresponding values in the two molecules. Allowing for differences in the molecular structures, agreement between bond lengths and angles in the present structure and equivalent values in endrin, aldrin, and dieldrin is satisfactory.

The five-membered rings are all in envelope conformation and the six-membered ring is in the boat form. Because of the formation of bonds between the hexachloro system and what was the epoxide ring in endrin, the present molecule is more nearly spherical and more compact than endrin or dieldrin. The distances $Cl(3)\cdots Cl(6)$, $Cl(2)\cdots C(12)$, and $O(1)\cdots Cl(1)$ in this structure are 5.51, 5.98, and 5.82 Å respectively, while the corresponding $Cl\cdots Cl$ and $Cl\cdots$ epoxide oxygen distances in endrin and dieldrin are 5.47 and 5.52 ($Cl\cdots Cl$) and 6.78 and 7.36 Å ($Cl\cdots O$).

A parallel study of the nmr spectra of 3 was undertaken and some data are presented here. Using the computer program LACX (6) we have examined the eight spin system of 3 taking into account the inherent symmetry of the molecules. This calculation involved about 1000 observable transitions and provides the first complete analysis of this type of compound. Figure 2 shows the experimental 250 MHz proton nmr spectrum compared to the calculated spectrum after iteration. The signal for the 12s proton in the experimental

TABLE 1. Final fractional coordinates and their estimated standard deviations (which refer to the least significant digit). The hydrogen coordinates have been multiplied by 10^3 , the x and y coordinates of the other atoms by 10^4 and z by 10^5

	x	У	z
Molecule 1			
Cl(1)	3908(1)	-631(1)	4804(5)
Cl(1)	3866(1)	-2673(1)	13461(5)
Cl(2)	5429(1)	601(1)	18513(5)
Cl(3)	J429(1) 4029(1)	-650(1)	24953(4)
Cl(4)	4029(1) 1746(1)	-0.00(1) -1.780(1)	16475(6)
	1/40(1)	-1/69(1)	104/3(0)
	1550(1)	-1441(2)	3433(3)
	2091(2)	2117(4)	192/3(11) 10477(15)
C(1)	3528(3)	-757(4)	104/(15)
C(2)	4008(3)	555(4)	14855(15)
C(3)	3401(3)	480(4)	18657(15)
C(4)	2232(3)	-118(5)	14223(16)
C(5)	2347(3)	-268(4)	8/23(15)
C(6)	2330(3)	1456(5)	7091(15)
C(7)	3487(3)	2045(4)	11366(17)
C(8)	3267(3)	3211(5)	15234(18)
C(9)	3182(3)	2169(5)	19932(16)
C(10)	1536(3)	1366(5)	13882(17)
C(11)	1557(3)	2351(5)	8937(16)
C(12)	2152(3)	3876(5)	11384(18)
H(6)	221(3)	158(5)	30(2)
H(7)	402(3)	252(5)	99(2)
H(8)	380(3)	394(5)	168(2)
H(9)	362(3)	255(5)	238(2)
H(10)	86(3)	107(5)	134(2)
H(11)	93(3)	245(5)	59(2)
H(12)	220(3)	448(5)	87(2)
H(13)	180(3)	447(5)	131(2)
Molecule 2			
Cl(21)	8459(1)	2672(1)	20461(5)
Cl(22)	8460(1)	2229(1)	9532(5)
Cl(23)	6024(1)	3366(2)	9033(6)
Cl(24)	6762(1)	4745(1)	-303(4)
Cl(25)	9223(1)	5549(1)	5107(4)
Cl(26)	10380(1)	4777(1)	18567(4)
O(21)	7526(2)	8273(3)	6260(12)
C(21)	8269(3)	3623(5)	14023(15)
C(22)	7193(3)	4521(5)	11286(17)
C(23)	7286(3)	5558(5)	6616(15)
C(24)	8544(3)	5972(4)	9375(15)
C(25)	8979(3)	5100(5)	15222(15)
C(26)	8543(3)	6188(5)	18423(15)
C(27)	7312(3)	5790(5)	15754(17)
C(28)	6751(3)	7291(6)	12601(19)
C(20)	6776(3)	7163(5)	6680(18)
C(2)	8534(3)	7753(5)	10/07(17)
C(31)	8586(3)	7896(5)	16621(17)
C(32)	7515(4)	8575(6)	16049(21)
H(26)	886(4)	603(6)	226(2)
H(27)	716(5)	549(7)	189(2)
H(28)	600(4)	725(6)	125(2)
H(29)	611(3)	725(5)	35(2)
H(30)	911(3)	831(5)	<u>00(2)</u>
H(31)	925(3)	841(5)	193(2)
$\mathbf{U}(22)$	733(5)	041(3)	133(2) 142(2)
H(32)	133(3) 755(A)	730(1) 800(2)	142(2)
n(33)	155(4)	000(0)	199(2)

spectrum is broader compared to the simulated version where we did not introduce any small nonmeasurable long-range couplings. This accounts also for the difference in resolution between the signals for H_4 and H_5 in the two spectra since irradiation indicates these couplings to be present. Table 3 presents the chemical shifts and coupling constants for 3 and compares these data with those reported for endrin 1 (7).

The availability of the X-ray data for 3 and 1 (3) enables us to make the following comments comparing the nmr spectra of both compounds.

1. The value of $J_{12s,12a}$ is larger in 3 than in endrin (absolute value). In the former, it is close to the cyclohexane value (-12.6 Hz). The X-ray data show clearly that in 3 the H_{12s} —C— H_{12a} angle is 108° (i.e. close to the tetrahedral angle), whereas in endrin (1) this angle is 123°. The relief of strain on formation of the five-membered tetrahydrofuran ring in 3 is evident here.

2. The value of $J_{3,4}$ is larger in 3 than in endrin (1) (8.6 Hz vs. 0.9 Hz). These values are unexceptional when the dihedral angles $H_4 - C_4 - C_3 - H_3$ are examined $(8.5^{\circ} \text{ in } 3a \text{ and } 51^{\circ} \text{ in endrin})$. The same Karplus-type agreement can be seen for $J_{2,3}$ (5.1 Hz in 3a and 2.5 Hz in endrin) where the dihedral angles are 22.5° and 65° respectively.

3. The modified geometry of **3** resulting from the epoxide C-C bond opening and the consequent relief of strain is further demonstrated by the observed coupling constants for $J_{3,12a}$ and $J_{3,12s}$ as follows. In **3** the H_{12a} — C_{12} — C_{3} — H_{3} dihedral angle is 50° with a $J_{3,12}$ being 3.7 Hz and in endrin the corresponding angle is 71° reflected by a coupling constant of 1.3 Hz. The H_{12s}-C₁₂-H₃ dihedral angle in 3a is 70° with $J_{3,12s}$ being 1.3 Hz; in endrin this angle becomes 61° and $J_{3,12s}$ is 2.0 Hz.

4. The unambiguous assignment of the H_{12a} and H_{12s} signals can be made by a shift reagent study (8) for endrin (1) and 3. The results obtained are outlined in Table 4. Assuming the oxygen atom is involved as the major complexation site with $Eu(fod)_3$, the assignments are self evident.

5. It is to be noted that the signal for H_{12a} is more sensitive to the transformation of endrin (1) to 3 than that for H_{12s} , even though this proton is more proximate to the site of chemical change (0.50 ppm)and 0.16 ppm downfield shifts respectively). One interpretation of these results is that the major contribution to the shielding of H_{12} is the epoxidegroup ring-current which is destroyed on conversion of endrin (1) to 3; whereas for H_{12s} the major shielding contribution arises from the proximate oxvgen atom.

It is apparent from the above observations that 3

Molecule 1		Molecule 2	Molecule 2		
Bond lengths					
Cl(1) - C(1)	1.765(4) Å	Cl(21)—C(21)	1.722(4) Å		
Cl(2)—C(1)	1.780(4)	Cl(22)—C(21)	1.761(4)		
Cl(3)—C(2)	1.754(4)	Cl(23)—C(22)	1.749(5)		
Cl(4) - C(3)	1.765(4)	Cl(24) - C(23)	1.762(4)		
Cl(5) - C(4)	1.761(4)	Cl(25) - C(24)	1.764(4)		
C(6) = C(5)	1.760(4)	C(26) = C(25)	1.749(4)		
O(1) = C(9)	1.427(0) 1.422(5)	O(21) - C(29) O(21) - C(30)	1.435(6)		
C(1) = C(10)	1.422(5) 1.524(5)	C(21) = C(30)	1.532(6)		
C(1) - C(5)	1.534(6)	C(21) - C(25)	1.537(6)		
C(2) - C(3)	1.543(6)	C(22) - C(23)	1.549(6)		
C(2)—C(7)	1.543(5)	C(22)—C(27)	1.541(6)		
C(3)—C(4)	1.588(6)	C(23)—C(24)	1.590(6)		
C(3)—C(9)	1.535(6)	C(23)—C(29)	1.537(6)		
C(4) - C(5)	1.534(6)	C(24) - C(25)	1.557(5)		
C(4) = C(10)	1.556(6)	C(24) = C(30)	1.546(6)		
C(5) = C(6)	1.525(6)	C(25) = C(26)	1.529(6)		
C(6) = C(11)	1.570(0)	C(26) = C(27)	1.555(7)		
C(7) - C(8)	1.532(6)	C(20) - C(28)	1.532(7)		
C(8) - C(9)	1.553(6)	C(28) - C(29)	1.557(6)		
C(8)—C(12)	1.524(6)	C(28) - C(32)	1.510(7)		
C(10)—C(11)	1.544(6)	C(30)—C(31)	1.565(6)		
C(11)—C(12)	1.518(6)	C(31)—C(32)	1.522(8)		
C(6)—H(6)	1.01(4)	C(26)—H(26)	0.98(5)		
C(7) - H(7)	1.04(5)	C(27) - H(27)	0.95(6)		
C(8) - H(8)	0.91(4)	C(28) = H(28)	1.01(6)		
C(9) = H(9) C(10) = H(10)	0.98(4) 0.91(4)	C(29) - H(29) C(30) - H(30)	0.93(4) 0.98(5)		
C(11) - H(11)	0.91(4) 0.89(5)	C(31) - H(31)	0.98(5)		
C(12) - H(12)	0.90(4)	C(32) - H(32)	0.94(6)		
C(12)—H(13)	0.93(4)	C(32)—H(33)	1.00(5)		
	Bor	nd angles			
C(9)—O(1)—C(10)	102.5(3)°	C(29)	102.9(3)°		
Cl(1) - C(1) - Cl(2)	107.7(2)	Cl(21)—C(21)—Cl(22)	108.4(2)		
Cl(1) - C(1) - C(2)	113.0(3)	Cl(21)-C(21)-C(22)	112.6(3)		
Cl(1) - C(1) - C(5)	112.9(3)	Cl(21) - C(21) - C(25)	111.2(3)		
Cl(2) = C(1) = C(2)	113.6(3)	Cl(22) = C(21) = C(22)	114.7(3)		
C(2) = C(1) = C(3)	114.8(3) 94.6(3)	C(22) = C(21) = C(25)	113.0(3)		
C(2) = C(1) = C(3)	116 0(3)	C(22) = C(21) = C(23) C(23) = C(22) = C(21)	115 4(3)		
$C_{1}(3) - C_{2}(2) - C_{3}(3)$	115.6(3)	C(23) - C(22) - C(23)	115.6(3)		
Cl(3) - C(2) - C(7)	114.9(3)	Cl(23) - C(22) - C(27)	115.3(3)		
C(1) - C(2) - C(3)	105.6(3)	C(21) - C(22) - C(23)	105.0(3)		
C(1)—C(2)—C(7)	103.0(3)	C(21)—C(22)—C(27)	103.6(3)		
C(3) - C(2) - C(7)	99.8(3)	C(23)—C(22)—C(27)	99.9(3)		
Cl(4) - C(3) - C(2)	115.8(3)	Cl(24) - C(23) - C(22)	116.0(3)		
CI(4) = C(3) = C(4)	114.6(3)	C(24) = C(23) = C(24)	115.4(3)		
C(2) = C(3) = C(9)	111-9(3)	C(24) = C(23) = C(29) C(22) = C(23) = C(24)	112.0(3) 102.3(3)		
C(2) = C(3) = C(4)	102.3(3) 108.0(3)	C(22) = C(23) = C(24) C(22) = C(23) = C(29)	102.3(3)		
C(4) - C(3) - C(9)	102.9(3)	C(24) - C(23) - C(29)	101.9(3)		
Cl(5) - C(4) - C(3)	115.9(3)	Cl(25)—C(24)—C(23)	115.7(3)		
Cl(5) - C(4) - C(5)	116.2(3)	Cl(25)—C(24)—C(25)	115.6(3)		
Cl(5)—C(4)—C(10)	112.1(3)	Cl(25)—C(24)—C(30)	111.6(3)		
C(3) - C(4) - C(5)	102.3(3)	C(23) - C(24) - C(25)	102.4(3)		
C(3) - C(4) - C(10)	100.8(3)	C(23) - C(24) - C(30)	101.9(3)		
C(5) = C(4) = C(10)	108.0(3)	C(25) = C(24) = C(30)	108.3(3)		
$C_{1}(0) = C_{1}(0) = C_{1}(0)$	115.7(3)	CI(20) - C(23) - C(21) CI(26) - C(25) - C(24)	115.0(3)		
$C_{1}(0) = C_{1}(0) = C_{1}(0)$	110.0(0)	$C_{1}(20) = C(23) = C(27)$	110.0(0)		

TABLE 2. Bond lengths and bond angles for both molecules of 3 observed in the crystal

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TABLE 2 (Concluded)

Molecule 1		Molecule 2	Molecule 2		
Cl(6) - C(5) - C(6)	114.6(3)	$C_{26} - C_{25} - C_{26}$	115.4(3)		
C(1) - C(5) - C(4)	105.6(3)	C(21) - C(25) - C(24)	104.6(3)		
C(1) - C(5) - C(6)	103.4(3)	C(21) - C(25) - C(26)	104.1(3)		
C(4) - C(5) - C(6)	100.8(3)	C(24) - C(25) - C(26)	99.6(3)		
C(5) - C(6) - C(7)	102.8(3)	C(25) - C(26) - C(27)	103.2(3)		
C(5) - C(6) - C(11)	108.7(3)	C(25) - C(26) - C(31)	109.4(3)		
C(7) - C(6) - C(11)	103.9(3)	C(27) - C(26) - C(31)	104.4(3)		
C(2) - C(7) - C(6)	102.7(3)	C(22) - C(27) - C(26)	103.2(3)		
C(2) - C(7) - C(8)	108.7(3)	C(22) - C(27) - C(28)	108.5(4)		
C(6) - C(7) - C(8)	104.3(3)	C(26) - C(27) - C(28)	104.5(4)		
C(7) - C(8) - C(9)	104.4(3)	C(27) - C(28) - C(29)	104.4(4)		
C(7) - C(8) - C(12)	103.7(3)	C(27) - C(28) - C(32)	103.3(4)		
C(9) - C(8) - C(12)	109.4(4)	C(29) - C(28) - C(32)	109.3(4)		
O(1) - C(9) - C(3)	103.7(3)	O(21)—C(29)—C(23)	104.0(3)		
O(1) - C(9) - C(8)	110.8(3)	O(21)—C(29)—C(28)	110.6(4)		
C(3) - C(9) - C(8)	106.1(3)	C(23)—C(29)—C(28)	106.1(4)		
O(1) - C(10) - C(4)	104.2(3)	O(21)—C(30)—C(24)	104.3(3)		
O(1) - C(10) - C(11)	112.3(3)	O(21) - C(30) - C(31)	111.5(3)		
C(4) - C(10) - C(11)	105.7(3)	C(24)—C(30)—C(31)	105.5(3)		
C(6) - C(11) - C(10)	104.7(3)	C(26)—C(31)—C(30)	104.2(3)		
C(6) - C(11) - C(12)	103.7(3)	C(26)—C(31)—C(32)	103.1(4)		
C(10) - C(11) - C(12)	108.5(3)	C(30)—C(31)—C(32)	108.2(4)		
C(8) - C(12) - C(11)	99.2(3)	C(28)—C(32)—C(31)	99.9(4)		
C(5)—C(6)—H(6)	112(2)	C(25)—C(26)—H(26)	115(3)		
C(7)—C(6)—H(6)	112(2)	C(27)—C(26)—H(26)	110(3)		
C(11)-C(6)-H(6)	117(2)	C(31)—C(26)—H(26)	114(3)		
C(2)—C(7)—H(7)	108(3)	C(22)—C(27)—H(27)	117(4)		
C(6) - C(7) - H(7)	122(3)	C(26)—C(27)—H(27)	106(4)		
C(8) - C(7) - H(7)	111(3)	C(28)—C(27)—H(27)	116(4)		
C(7) - C(8) - H(8)	113(3)	C(27)—C(28)—H(28)	105(3)		
C(9) - C(8) - H(8)	111(3)	C(29)C(28)H(28)	115(3)		
C(12)-C(8)-H(8)	115(3)	C(32)-C(28)-H(28)	118(3)		
O(1) - C(9) - H(9)	106(3)	O(21)—C(29)—H(29)	110(3)		
C(3) - C(9) - H(9)	116(3)	C(23) - C(29) - H(29)	110(3)		
C(8) - C(9) - H(9)	113(3)	C(28)—C(29)—H(29)	116(3)		
O(1) - C(10) - H(10)	110(3)	O(21) - C(30) - H(30)	108(3)		
C(4) - C(10) - H(10)	110(3)	C(24)-C(30)-H(30)	112(3)		
C(11) - C(10) - H(10)	115(3)	C(31)-C(30)-H(30)	115(3)		
C(6) - C(11) - H(11)	108(3)	C(26) - C(31) - H(31)	111(3)		
C(10) - C(11) - H(11)	116(3)	C(30) - C(31) - H(31)	112(3)		
C(12) - C(11) - H(11)	115(3)	C(32) - C(31) - H(31)	118(3)		
C(8) - C(12) - H(12)	109(3)	C(28) - C(32) - H(32)	112(4)		
C(8) - C(12) - H(13)	117(3)	C(28) - C(32) - H(33)	116(3)		
C(11) - C(12) - H(12)	112(3)	C(31)-C(32)-H(32)	115(4)		
C(11) - C(12) - H(13)	112(3)	C(31)-C(32)-H(33)	111(3)		
H(12)-C(12)-H(13)	108(4)	H(32)-C(32)-H(33)	103(5)		

suffers much less angular strain than the parent endrin (1) and its derivatives.

The formation of 3 is of mechanistic interest but at this stage we can make no further comment to that made in our preliminary communication (1) except to stress that this compound arises only via the acid-catalysed route.

Experimental

Reaction of endrin (1) with sulfuric acid

Endrin (5g) was dissolved with stirring in concentrated sulfuric acid (65 mL) and allowed to stand for 48 h. The resulting clear solution was poured into ice water (300 mL). The crystalline precipitate obtained was filtered and washed with aqueous sodium bicarbonate (saturated) and water. Preparative thin layer chromatography on silica gel plates eluted with benzene/5% acetone provided, after isolation in the usual manner, ketoendrin 2 (4.1g) and 3 (0.34g), mp 286°C. A sample was recrystallized twice from CCl₄ for analysis; M⁺ (mass spectral): 381. Anal. calcd. for $C_{12}H_8OCl_6$: C 37.84, H 2.12, O 4.30, Cl 55.9; found: C 37.93, H 2.12, O 4.20, Cl 55.57. See text for nmr spectral data. All chemical operations were standard. Mass spectra were determined on an AE1 MS 10 spectrometer at Trent University, Peterborough, Ontario. The nmr spectra were originally determined on a Varian T-60 and XL-100 spectrometer at Carleton University. The 250 MHz nmr spectra were recorded on a CAMECA spectrometer at the Faculté de Pharmacie de Marseilles.

Crystal data are:

Monoclinic, space group $P2_1/c$, a = 13.680(1), b, 8.515(2), c =

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	Minor product (LACX analysis)	Endrin (Keith <i>et al</i> . (7))	Difference (MP – Endrin)
$v_2 = v_7$	3.256	3.22	+0.04
$v_3 = v_6$	2.888	2.89	0.0
$v_4 = v_5$	4.810	3.30	+1.51
v_{12a}	1.433 ^a	0.93	+0.50
v_{12s}	1.947^{a}	1.79	+0.16
$J_{2,3} = J_{6,7}$	5.1	2.5	
$J_{24}^{2,5} = J_{57}^{0,7}$	b	0	
$J_{2,5}^{2,7} = J_{4,7}^{2,7}$	0	0	
$J_{2.6} = J_{3.7}$	1.1	1.5	
J _{2.7}	9.7	0 ^c	
$J_{2,128} = J_{7,128}$	b	0	
$J_{2,12a} = J_{7,12a}$	0	0	
$J_{3,4} + J_{5,6}$	8.6	0.9	
$J_{3,5} = J_{4,6}$	0	0.9	
$J_{3.6}$	2.0	0 c	
$J_{3,128} = J_{6,128}$	1.3	2.0	
$J_{3,12a} = J_{6,12a}$	3.7	1.3	
$J_{4,5}$	2.0	0 ^c	
$J_{4,12s} = J_{5,12s}$	b	< 0.5	
$J_{4,12a} = J_{5,12a}$	0	0.5	
J _{128,12a}	-12.3	-10.3	

TABLE 3. Chemical shifts (in ppm/TMS, solvent CDCl₃) and coupling constants (in Hz)

^aSee footnote 6

^b Double irradiation experiments seem to indicate that a small coupling exists which has not been measured. ^c The authors assumed this value to be zero, presumably due to symmetry.

TABLE 4. Shift reagents comparison studies (Eu(fod)₃) on endrin and the title compound, 3. Chemical shifts are present in ppm from internal TMS at 100 MHz

	End	Endrin		Compound 3	
	Chem. shifts	Rel. bound shifts	Chem. shifts	Rel. bound shifts	
H_2 and H_7	3.22	100	3.26	100	
H_3 and H_6	2.89	170	2.89	128	
H_4 and H_5	3.30	421	4.81	397	
H _{12a}	0.93	150	1.43	104	
H _{12s}	1.79	379	1.95	251	

25.963(2) Å, β = 115.71(3)°, V = 2724.9 Å³, $d_x = 1.857$ g cm⁻³, Z = 8 (two independent molecules per asymmetric unit) (λ(Cu-Kα₁) = 1.54051, λ(CuKα₂) = 1.54433 Å), μ(CuKα) = 114.1 cm⁻¹.

The material crystallized from CCl₄ as clear colourless prisms. Data were collected from a specimen with maximum dimensions $0.30 \times 0.15 \times 0.40$ mm, mounted parallel to the elongation direction (along b). Precession photographs showed monoclinic symmetry with systematic absences (0k0) with k odd, and (h0l) with l odd. Intensity data and cell dimensions were measured on a Picker diffractiometer using Ni-filtered Cu radiation. The $\theta/2\theta$ scan mode was employed in measuring intensity data; the (20) scan speed was 2° min⁻¹, scan ranges were 2.0° for $0 < 2\theta < 100^\circ$, 3.0° for $100 < 2\theta \le 130^\circ$, and a 20 s background count was taken at the end of each scan. Of the 4611 independent reflections accessible in this range in two octants (hkl and hkl) of reciprocal space, 3383 were considered "observed" on the basis of having net counts ≥ 15 and at least 10% of the total background count. Lorentz and polarization corrections were applied, and absorption corrections were made using a Gaussian integration formula; maximum and minimum transmission factors were 0.282 and 0.054 respectively.

The structure was solved by the symbolic addition procedure, and refined by block-diagonal least-squares calculations minimizing $\Sigma w(|F_0| - |F_c|)^2$. The nonhydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were refined isotropically. The weighting scheme was w = 1.0 if $|F_0| < 35.0$, otherwise $w = (35.0/F_0)^2$, and six reflections were assigned zero weight in the later least-squares cycles. (Three (-113, -125, and -228) were affected by extinction and three (-206, 110, and 240) seemed to be Renninger reflections.) Scattering factor values for Cl, O, C, and H were taken from International Tables for X-ray Crystallography, Vol. IV (9). The Cl scattering curve was corrected (9) for the real part ($\Delta f' =$ 0.348) of anomalous dispersion. In the last refinement cycle all shifts were less than one-third of their respective estimated standard deviations, and the mean (shift/esd) was 0.05. The final R value for all (3383) observed reflections was 0.039. A difference map calculated from the final structure factors⁸ showed 15 significant peaks (none larger than 0.40 e/Å³), all of which occurred near Cl atom sites, most in locations consistent with lone-pair electron density. Computations were performed with the NRCC set of crystallographic computer programs (10).

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⁸The atomic thermal parameters and the structure amplitudes are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

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