Acta Cryst. (1981). B37, 1620–1622

Structure of a Spirocyclic Chroman: 3′,8-Bis(chloromethoxy)-4′,5,6′,7-tetramethylchroman-2-spiro-1′-cyclohexa-3′,5′-dien-2′-one

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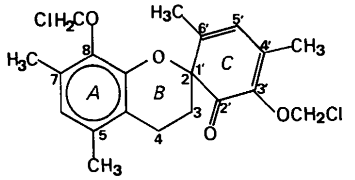
(*Received* 18 *December* 1980; *accepted* 9 *February* 1981)

Abstract. $C_{20}H_{22}Cl_2O_4$, triclinic, $P\bar{1}$, $a = 10{\cdot}241\,(4)$, $b = 9{\cdot}067\,(2)$, $c = 11{\cdot}206\,(3)$ Å, $\alpha = 105{\cdot}57\,(3)$, $\beta = 101{\cdot}00\,(4)$, $\gamma = 91{\cdot}09\,(3)°$, $Z = 2$, $F(000) = 416$, μ(Cu $K\alpha$) = $3{\cdot}03$ mm^{-1}. Final $R = 0{\cdot}071$ for 2681 observed reflections. Ring B is in a half-chair form whereas ring C is envelope. In the latter, there is indication of some conjugation; the two long and two short C—C bonds in the 1,3-diene moiety have mean values 1·451 (7) and 1·340 (6) Å respectively.

Introduction. The title compound (I), a spirocyclic chroman, has resulted from an unexpected reaction between 5-hydroxymethyl-2,4-dimethylspiroepoxy-2,4-cyclohexadienone and chlorotrimethylsilane (Cacioli, Mackay & Reiss, 1980). The reaction was carried out as a means of initiating possible ring-expansion, ring-opening and/or rearrangement processes, and forms part of an investigation of reactions of spiro-epoxycyclohexadienones with nucleophiles (Baldwin, Cacioli & Reiss, 1980).



(I)

Weissenberg photographs showed that the yellow plate-like crystals grown from *n*-hexane were triclinic. Intensities were measured with Cu $K\alpha$ radiation (graphite-crystal monochromator, $\bar{\lambda} = 1{\cdot}5418$ Å) from a crystal *ca* 0·35 × 0·05 × 0·30 mm aligned with **a** approximately parallel to the φ axis of a Rigaku-AFC four-circle diffractometer. Of the 3487 non-equivalent terms ($2\theta_{\max} = 129°$) recorded by an ω–2θ scan of 2° min^{-1} and with 10 s stationary background counts, the 2681 for which $|F_o| > 3\sigma|F_o|$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The scattering factors for Cl, O and C were from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion corrections were made for the non-H atoms (Cromer & Liberman, 1970).

The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976). The H atoms were located on a difference map after full-matrix least-squares refinement with anisotropic temperature factors for Cl, O and C. The H coordinates were refined and the methyl and non-methyl H atoms given refined isotropic temperature factors $U = 0{\cdot}064\,(4)$ and $0{\cdot}114\,(7)$ Å^2 respectively. Final refinement converged to give $R = 0{\cdot}071$ and $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2} = 0{\cdot}087$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the terms weighted according to $(\sigma^2|F_o| + 0{\cdot}0013\,|F_o|^2)^{-1}$. The final difference map contained no residual maxima $>0{\cdot}3$ e Å^{-3}, apart from one of $0{\cdot}7$ e Å^{-3} near a Cl atom. Final atomic coordinates are given in Tables 1 and 2.† Figs. 1 and 2 have been prepared with *ORTEP* (Johnson, 1965).

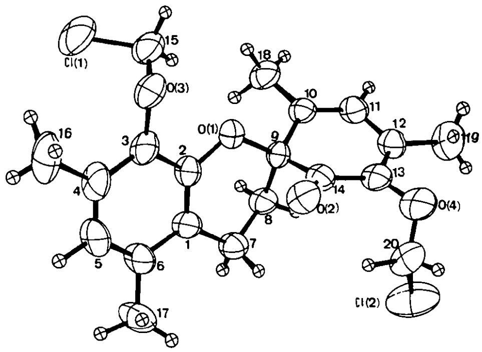


Fig. 1. Perspective view of the molecule with thermal ellipsoids scaled to 50% probability. The H atoms are represented by spheres of arbitrary radius. The C atoms are denoted by numerals only.

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35943 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/081620-03$01.00

Table 1. *Final atomic parameters of the non-*H *atoms* (×10^4) *and equivalent isotropic temperature factors with e.s.d.'s in parentheses*

$B_{eq} = 8\pi^2 U_{eq}$, where $U_{eq} = (U_1 U_2 U_3)^{1/3}$.

	x	y	z	B_{eq} (Å^2)
Cl(1)	6735 (1)	6481 (2)	−2128 (1)	6·7 (1)
Cl(2)	−1449 (2)	8185 (2)	2177 (2)	7·9 (1)
O(1)	3613 (3)	7348 (3)	61 (2)	3·7 (2)
O(2)	1530 (3)	5939 (3)	574 (3)	4·6 (2)
O(3)	4747 (3)	5178 (3)	−1467 (3)	4·4 (2)
O(4)	715 (3)	6891 (4)	2913 (3)	4·9 (2)
C(1)	1809 (4)	7460 (5)	−1677 (4)	3·7 (2)
C(2)	2995 (4)	6909 (4)	−1199 (3)	3·4 (2)
C(3)	3637 (4)	5840 (5)	−1985 (4)	3·9 (2)
C(4)	3136 (5)	5301 (5)	−3272 (4)	4·3 (3)
C(5)	1953 (5)	5905 (6)	−3748 (4)	4·4 (3)
C(6)	1297 (5)	6948 (5)	−2981 (4)	4·1 (2)
C(7)	1098 (4)	8529 (6)	−792 (4)	4·1 (2)
C(8)	2050 (4)	9357 (5)	425 (4)	3·9 (2)
C(9)	2926 (4)	8233 (5)	975 (3)	3·3 (2)
C(10)	3940 (4)	9196 (5)	2088 (4)	3·4 (2)
C(11)	3635 (5)	9497 (6)	3229 (4)	4·2 (2)
C(12)	2472 (4)	8813 (5)	3501 (4)	4·2 (2)
C(13)	1688 (4)	7701 (5)	2582 (4)	3·8 (2)
C(14)	1998 (4)	7158 (5)	1335 (4)	3·7 (2)
C(15)	5903 (5)	6134 (6)	−944 (5)	4·9 (3)
C(16)	3786 (8)	4089 (8)	−4108 (6)	6·2 (3)
C(17)	−18 (6)	7490 (7)	−3541 (5)	5·6 (3)
C(18)	5175 (5)	9887 (7)	1836 (5)	4·9 (3)
C(19)	2223 (7)	9322 (9)	4812 (5)	6·8 (4)
C(20)	−505 (5)	6532 (5)	2087 (5)	4·8 (3)

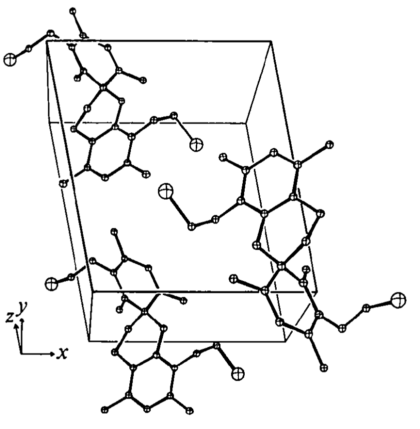

Fig. 2. Crystal packing.

Discussion. For the molecular structure illustrated in Fig. 1, a different numbering for the atoms is used from that for systematic nomenclature given in (I). Bond lengths and angles involving the non-H atoms, and some torsion angles in the pyranspirocyclohexadienone moiety are given in Tables 3 and 4 respectively, while selected least-squares planes and atom deviations are given in Table 5.

Ring *B* is in a half-chair form with C(9) +0·059 (5) and C(8) −0·154 (5) Å from the plane of the other four atoms which are coplanar within ±0·014 Å. Ring *C* is

Table 2. *Refined hydrogen coordinates* (×10^3) *with e.s.d.'s in parentheses*

The atoms are given the same numbers as the C atom to which they are bonded.

	x	y	z
H(5)	163 (5)	561 (5)	−468 (5)
H(7*A*)	27 (5)	796 (5)	−64 (4)
H(7*B*)	65 (5)	941 (5)	−111 (4)
H(8*A*)	160 (5)	992 (5)	108 (5)
H(8*B*)	264 (5)	1004 (5)	23 (4)
H(11)	416 (5)	1014 (5)	394 (5)
H(15*A*)	652 (5)	574 (5)	−35 (4)
H(15*B*)	566 (5)	714 (6)	−43 (4)
H(16*A*)	479 (8)	437 (8)	−401 (6)
H(16*B*)	372 (7)	318 (9)	−397 (6)
H(16*C*)	355 (7)	407 (8)	−488 (7)
H(17*A*)	−17 (7)	700 (7)	−447 (6)
H(17*B*)	−77 (7)	726 (7)	−312 (6)
H(17*C*)	−3 (7)	863 (9)	−335 (6)
H(18*A*)	489 (7)	1026 (7)	105 (6)
H(18*B*)	576 (7)	903 (8)	155 (6)
H(18*C*)	563 (7)	1068 (8)	261 (7)
H(19*A*)	144 (8)	914 (9)	486 (7)
H(19*B*)	282 (7)	863 (8)	521 (7)
H(19*C*)	238 (7)	1024 (9)	522 (7)
H(20*A*)	−41 (5)	611 (5)	118 (5)
H(20*B*)	−97 (5)	600 (6)	244 (4)

Table 3. *Bond lengths* (Å) *and angles* (°) *involving the non-*H *atoms with e.s.d.'s in parentheses*

Cl(1)–C(15)	1·797 (5)	C(6)–C(1)	1·400 (6)
Cl(2)–C(20)	1·789 (5)	C(1)–C(7)	1·496 (6)
O(1)–C(2)	1·379 (4)	C(7)–C(8)	1·513 (6)
O(1)–C(9)	1·429 (5)	C(8)–C(9)	1·544 (6)
O(2)–C(14)	1·223 (5)	C(9)–C(10)	1·511 (6)
O(3)–C(3)	1·397 (5)	C(10)–C(11)	1·332 (6)
O(3)–C(15)	1·386 (6)	C(11)–C(12)	1·452 (7)
O(4)–C(13)	1·389 (6)	C(12)–C(13)	1·348 (6)
O(4)–C(20)	1·380 (6)	C(13)–C(14)	1·450 (6)
C(1)–C(2)	1·389 (6)	C(14)–C(9)	1·529 (6)
C(2)–C(3)	1·391 (6)	C(4)–C(16)	1·497 (9)
C(3)–C(4)	1·383 (6)	C(6)–C(17)	1·522 (8)
C(4)–C(5)	1·410 (7)	C(10)–C(18)	1·508 (7)
C(5)–C(6)	1·376 (7)	C(12)–C(19)	1·490 (7)

C(2)–C(1)–C(6)	118·2 (4)	C(8)–C(9)–C(10)	106·9 (3)
C(6)–C(1)–C(7)	122·1 (4)	C(8)–C(9)–C(14)	107·3 (3)
C(2)–C(1)–C(7)	119·6 (4)	C(10)–C(9)–C(14)	113·5 (3)
C(1)–C(2)–C(3)	121·1 (4)	C(9)–C(10)–C(11)	117·8 (4)
C(1)–C(2)–O(1)	123·7 (3)	C(9)–C(10)–C(18)	118·5 (4)
O(1)–C(2)–C(3)	115·2 (3)	C(11)–C(10)–C(18)	123·5 (4)
C(2)–C(3)–C(4)	121·6 (4)	C(10)–C(11)–C(12)	124·4 (5)
C(2)–C(3)–O(3)	120·1 (4)	C(11)–C(12)–C(13)	119·3 (4)
O(3)–C(3)–C(4)	118·1 (4)	C(11)–C(12)–C(19)	118·4 (5)
C(3)–C(4)–C(5)	116·6 (4)	C(13)–C(12)–C(19)	122·2 (5)
C(3)–C(4)–C(16)	121·6 (5)	C(12)–C(13)–C(14)	121·2 (4)
C(5)–C(4)–C(16)	121·7 (5)	C(12)–C(13)–O(4)	118·3 (4)
C(4)–C(5)–C(6)	122·5 (5)	C(14)–C(13)–O(4)	119·5 (4)
C(1)–C(6)–C(5)	120·0 (4)	C(9)–C(14)–C(13)	116·2 (4)
C(1)–C(6)–C(17)	120·0 (4)	C(9)–C(14)–O(2)	120·1 (4)
C(5)–C(6)–C(17)	120·0 (5)	C(13)–C(14)–O(2)	123·6 (4)
C(1)–C(7)–C(8)	110·0 (4)	O(3)–C(15)–Cl(1)	112·3 (4)
C(7)–C(8)–C(9)	111·5 (4)	O(4)–C(20)–Cl(2)	111·1 (4)
O(1)–C(9)–C(8)	111·0 (3)	C(2)–O(1)–C(9)	119·4 (4)
O(1)–C(9)–C(10)	108·9 (3)	C(3)–O(3)–C(15)	116·4 (4)
O(1)–C(9)–C(14)	109·3 (3)	C(13)–O(4)–C(20)	117·3 (4)

Table 4. *Selected torsion angles* (°) *in the pyranspirocyclohexadienone moiety*

E.s.d.'s range from 0·5 to 0·7°.

C(1)–C(2)–O(1)–C(9)	−9·9	C(13)–C(14)–C(9)–C(10)	−31·9
C(2)–O(1)–C(9)–C(8)	35·1	C(14)–C(9)–C(10)–C(11)	26·0
O(1)–C(9)–C(8)–C(7)	−54·7	C(2)–O(1)–C(9)–C(10)	152·4
C(9)–C(8)–C(7)–C(1)	48·2	C(2)–O(1)–C(9)–C(14)	−83·1
C(8)–C(7)–C(1)–C(2)	−23·5	C(7)–C(8)–C(9)–C(10)	−173·3
C(7)–C(1)–C(2)–O(1)	3·4	C(7)–C(8)–C(9)–C(14)	64·6
C(9)–C(10)–C(11)–C(12)	−7·9	C(11)–C(10)–C(9)–C(8)	−92·1
C(10)–C(11)–C(12)–C(13)	−5·8	C(11)–C(10)–C(9)–O(1)	148·0
C(11)–C(12)–C(13)–C(14)	−1·1	C(13)–C(14)–C(9)–O(1)	−153·6
C(12)–C(13)–C(14)–C(9)	20·3	C(13)–C(14)–C(9)–C(8)	86·0

Table 5. *Selected least-squares planes and atom deviations* (Å × 10^3)

The plane equations are in the form $pX + qY + rZ + s = 0$, with X,Y,Z expressed in Å referred to orthogonal axes. Conversion from triclinic to orthogonal coordinates is given by

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & cP \\ 0 & 0 & cQ \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

where $P = (\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$
$Q = (1 - \cos^2\beta - P^2)^{1/2}$.

	p (× 10^4)	q (× 10^4)	r (× 10^4)	s (× 10^4)
Plane *A*	5549	8194	−1440	−73818
Plane *B*	5200	8439	−1318	−74418
Plane *C*	−5525	7873	−2737	−35265

C(1)	−11 (5)	C(7)	−6 (5)	C(10)	37 (5)
C(2)	10 (4)	C(1)	13 (5)	C(11)	−43 (5)
C(3)	0 (5)	C(2)	−14 (4)	C(12)	9 (5)
C(4)	−10 (5)	O(1)	7 (3)	C(13)	26 (5)
C(5)	9 (5)	C(8)*	509 (5)	C(14)	−29 (5)
C(6)	2 (5)	C(9)*	−154 (5)	C(9)*	372 (4)
O(1)*	27 (3)			C(18)*	−59 (6)
O(3)*	−124 (3)			C(19)*	−21 (8)
C(16)*	−94 (8)			O(4)*	−145 (4)
C(17)*	−57 (6)			O(2)*	−333 (3)
C(7)*	−92 (5)				

* Atom omitted from the plane calculation.

envelope; five of the atoms form a plane with a r.m.s. deviation of 0·03 Å and C(9) is +0·372 (4) Å out of the plane. The exocyclic ketonic and ether atoms, O(2) and O(4), deviate from the latter by −0·333 (3) and −0·145 (4) Å respectively, so that the torsion angle O(4)–C(13)–C(14)–O(2) is 6·4 (4)°. All five atoms associated with ring *A* are displaced from the ring plane. Apart from O(1), which is displaced by only +0·027 (3) Å, the other four atoms are displaced by values ranging from −0·057 (6) to −0·124 (3) Å, with the exocyclic O(3) showing the maximum deviation.

The bond lengths and angles are in good agreement with accepted values. Dimensions of ring *C* from C(10) through to C(14) indicate that there is some conjugation. Although the mean value 1·340 (6) Å for the two shorter C—C bonds agrees with the double-bond value of Lide (1962) and Stoicheff (1962), the mean value 1·451 (7) Å for the two longer bonds is significantly shorter than the values 1·47–1·48 Å reported by these authors for the single $C(sp^2)$—$C(sp^2)$ bond. All distances and angles involving H atoms are normal. The C—H distances for the methyl groups range from 0·82 (8) to 1·04 (8) Å, while the other C—H bonds have values which range from 0·88 (5) to 1·04 (5) Å.

The crystal packing illustrated in Fig. 2 is stabilized by van der Waals interactions. The molecules form layers parallel to [010]. Each layer contains molecules of one chirality stacked alternately with layers of molecules of the opposite chirality. There are no unusually short intermolecular contacts. The closest involve O atoms, and the distances, O(2)···Cl(1) 3·468 (3), C(15)···O(2) 3·287 (6), O(3)···O(3) 3·333 (4) and C(15)···O(3) 3·397 (6) Å, are between atoms of molecules related by the inversion centre at $[\frac{1}{2}\frac{1}{2}0]$. The shortest contact, C(20)···O(2) 3·185 (6) Å, is between atoms of molecules related by the inversion centre at $[0\frac{1}{2}0]$.

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