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Structure of Dimethyl 1,2,3,4,7,7-Hexachloro-5-*endo*-methoxybicyclo[2.2.1]hept-2-ene-5-*exo*,6-*endo*-dicarboxylate

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Abstract. $C_{12}H_{10}Cl_6O_5$, $M_r = 446{\cdot}93$, monoclinic, $P2_1/c$, $a = 16{\cdot}458\ (4)$, $b = 12{\cdot}651\ (3)$, $c = 16{\cdot}863\ (4)$ Å, $\beta = 96{\cdot}83\ (3)$°, $V = 3486\ (2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}703$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 9{\cdot}42$ mm^{-1}, $F(000) = 1792$, $T = 293$ K, final $R = 0{\cdot}077$ for 3948 observed reflections. There are two crystallographically independent molecules. The bridgehead C—C—C angles are 93·4 (5) and 92·7 (5)°. The ranges of the C(sp^3)—Cl and C(sp^2)—Cl bond lengths are 1·741 (7)–1·775 (7) and 1·684 (7)–1·702 (7) Å, respectively. The angles between the mean planes through non-H atoms of the ester groups are 61·6 (4) and 50·1 (3)°. One of the molecules shows slight disorder at the terminal methoxy C atom.

Introduction. The title compound was obtained from the reaction between dimethyl 1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate and methanolic KOH (Vančik, Sunko & Lovrić, 1985). The X-ray structure determination was undertaken because of the general importance of the norbornene ring system. It is interesting to compare characteristic bond lengths and angles of such a highly substituted norbornene derivative with those already reported for related compounds.

Experimental. Intensity data collected from a crystal of dimensions 0·05 × 0·21 × 0·31 mm with crystal faces ±(100), ±(010), ±(001). D_m not measured. Philips PW 1100 four-circle diffractometer, θ–2θ scanning technique, scan width 1·20°, scan rate 0·06 s^{-1}. Unit-cell parameters obtained from least-squares analysis of 20 reflections with 2θ values ranging from 24 to 36°. Absent reflections $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ confirmed space group $P2_1/c$. Out of 5430 reflections scanned within a quadrant $\pm h,k,l$ (h 19,–20; k 15; l 20) up to $\sin\theta/\lambda \leq 0{\cdot}61$ Å^{-1}, 4343 unique reflections classified as observed. Corrections applied for Lorentz and polarization effects and for absorption; transmission factors from 0·06 to 0·42. Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Of 46 non-H atoms in two crystallographically independent molecules (labeled *A* and *B*) only six C atoms were not obtained from the *E* map calculated with the 384 largest *E* values ($E \geq 1{\cdot}59$). Subsequent calculations performed mainly with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) using 3948 reflections with $I > 3\sigma(I)$. A difference map revealed two maxima near the expected position for the methoxy C atom in molecule *A*, representing two disordered atoms at an apparent separation of 0·98 (3) Å. Because the ratio of the maxima was 0·71/0·29, the corresponding population parameters of the atoms designated as C(53*A*) and C(54*A*) and of H atoms attached to them were assumed to be 0·71 and 0·29. All H atoms were located from the difference map and theoretical calculations. In block-diagonal least-squares refinement of *F*, positional and anisotropic thermal parameters of non-H atoms were varied separately in subsequent cycles (143 and 284 parameters refined, respectively); parameters of H atoms kept fixed with isotropic temperature factors 10% greater than those of bonded C atoms; *R* and *wR* 0·077 and 0·091 respectively; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 0{\cdot}131/\sigma^2(F_o)$ giving $S = 0{\cdot}95$. Max. and mean $\Delta/\sigma < 0{\cdot}3$ and 0·1 respectively. Final difference map revealed no residuals greater than 0·66 e Å^{-3}. In an attempt to reduce the absorption effect, 1979 intensity data up to $\sin\theta/\lambda \leq 0{\cdot}61$ Å^{-1} were collected from another crystal using Mo $K\alpha$ radiation (corrections applied for Lorentz and polarization effects

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and for absorption; transmission factors from 0·25 to 0·55). This set of data also revealed the same disorder of the C(53*A*) atom as described above. Block-diagonal refinement on F for 1715 reflections with $I > 3\sigma(I)$ gave only a slightly lower R (0·070), while the σ's of the atom coordinates were unsatisfactorily high, almost twice those in the analogous refinement with Cu $K\alpha$ intensity data. For this reason the results presented here are given on the basis of the calculations with the Cu $K\alpha$ intensity data. No correction for secondary extinction. Scattering factors of Cromer & Mann (1968) for non-H and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). All calculations performed on a Univac 1110 computer at the University Computing Centre in Zagreb.

Discussion. The final atomic parameters are listed in Table 1* and intramolecular bond lengths and angles in Table 2. Fig. 1 shows a perspective view of a molecule with the atomic numbering.

Bond lengths and angles in the hexachloronorbornene part of the molecules are essentially in agreement with weighted means of the corresponding values of some other compounds containing this moiety. The comparison, performed in a similar way as in the tables of Smith, Kennard & Shields (1977) and Smith & Kennard (1977), is presented in Table 3.

The C(sp^3)—C(sp^3) bond lengths in the part of the norbornene ring system near the ester groups are lengthened, especially those involving C(5) atoms carrying both methoxy and ester groups. The longest of these

Table 1. *Fractional positional parameters* (×10⁴) *and equivalent isotropic temperature factors* (×10²) *for non*-H *atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å²)
Cl(1*A*)	5035 (2)	−4071 (2)	6056 (1)	6·88 (9)
Cl(2*A*)	4660 (1)	−1563 (2)	6321 (1)	6·53 (8)
Cl(3*A*)	6074 (1)	−79 (1)	5509 (1)	5·20 (6)
Cl(4*A*)	7465 (1)	−1678 (2)	4961 (1)	5·45 (7)
Cl(71*A*)	6867 (1)	−4298 (2)	5206 (1)	6·05 (7)
Cl(72*A*)	6918 (1)	−2952 (2)	6567 (1)	6·63 (8)
O(51*A*)	6998 (3)	−2669 (5)	3394 (3)	6·7 (2)
O(52*A*)	6081 (3)	−3963 (4)	3386 (3)	4·8 (2)
O(53*A*)	5562 (3)	−1570 (4)	3914 (3)	5·3 (2)
O(61*A*)	3966 (3)	−2429 (5)	4636 (3)	7·6 (3)
O(62*A*)	4228 (3)	−3341 (5)	3568 (3)	6·8 (2)
C(1*A*)	5495 (4)	−3114 (5)	5509 (4)	4·5 (3)
C(2*A*)	5383 (4)	−1973 (6)	5747 (4)	4·3 (2)
C(3*A*)	5948 (4)	−1403 (5)	5465 (4)	3·7 (2)
C(4*A*)	6487 (3)	−2163 (5)	5046 (4)	3·7 (2)
C(5*A*)	5929 (3)	−2498 (5)	4238 (4)	3·2 (2)
C(6*A*)	5291 (4)	−3226 (5)	4592 (4)	3·6 (2)
C(7*A*)	6438 (4)	−3139 (5)	5580 (4)	4·3 (2)
C(51*A*)	6416 (4)	−3045 (5)	3630 (4)	3·9 (2)
C(52*A*)	6524 (6)	−4544 (7)	2823 (5)	7·0 (4)
C(53*A*)*	5422 (9)	−1361 (9)	3131 (7)	7·1 (5)
C(54*A*)*	5930 (18)	−1003 (21)	3349 (17)	6·3 (12)
C(61*A*)	4409 (4)	−2934 (6)	4288 (4)	4·5 (3)
C(62*A*)	3416 (5)	−3099 (10)	3183 (6)	10·7 (5)
Cl(1*B*)	992 (2)	−4589 (2)	5770 (1)	6·59 (8)
Cl(2*B*)	2670 (1)	−3129 (2)	5861 (1)	6·86 (9)
Cl(3*B*)	2203 (1)	−597 (2)	6239 (1)	7·09 (9)
Cl(4*B*)	227 (2)	−384 (2)	6078 (2)	7·74 (9)
Cl(71*B*)	−664 (1)	−2907 (2)	5862 (1)	7·37 (9)
Cl(72*B*)	442 (2)	−2320 (2)	4760 (1)	7·61 (9)
O(51*B*)	−567 (4)	−1071 (5)	7474 (4)	9·6 (3)
O(52*B*)	−469 (3)	−2739 (4)	7877 (3)	5·6 (2)
O(53*B*)	1247 (3)	−1683 (4)	7757 (3)	4·9 (2)
O(61*B*)	2172 (3)	−3877 (4)	7505 (3)	5·9 (2)
O(62*B*)	1231 (3)	−3878 (4)	8350 (3)	4·6 (2)
C(1*B*)	1004 (4)	−3328 (5)	6184 (4)	4·2 (3)
C(2*B*)	1777 (4)	−2658 (6)	6107 (4)	4·5 (3)
C(3*B*)	1575 (4)	−1668 (6)	6219 (4)	4·7 (3)
C(4*B*)	672 (4)	−1622 (5)	6334 (4)	4·5 (2)
C(5*B*)	609 (4)	−2090 (5)	7189 (4)	4·2 (2)
C(6*B*)	818 (3)	−3269 (5)	7058 (4)	3·5 (2)
C(7*B*)	350 (4)	−2516 (6)	5778 (4)	5·2 (3)
C(51*B*)	−220 (4)	−1900 (6)	7515 (5)	5·5 (3)
C(52*B*)	−1234 (5)	−2640 (8)	8195 (5)	7·3 (4)
C(53*B*)	1170 (7)	−636 (7)	8093 (6)	8·5 (4)
C(61*B*)	1498 (4)	−3701 (5)	7657 (4)	3·9 (2)
C(62*B*)	1821 (5)	−4348 (7)	8953 (5)	7·0 (3)

* Population parameters of C(53*A*) and C(54*A*) are 0·71 and 0·29, respectively.

Table 2. *Intramolecular bond lengths* (Å) *and angles* (°) *of non*-H *atoms in molecules A and B*

	A	*B*		*A*	*B*		*A*	*B*		*A*	*B*
C(1)–Cl(1)	1·749 (7)	1·741 (7)	C(3)–C(4)	1·535 (9)	1·524 (10)	C(5)–C(51)	1·539 (9)	1·549 (10)	C(52)–O(52)	1·462 (10)	1·432 (10)
C(1)–C(2)	1·515 (10)	1·548 (9)	C(4)–Cl(4)	1·745 (6)	1·760 (7)	C(6)–C(61)	1·527 (8)	1·517 (8)	C(53)–O(53)	1·339 (12)	1·451 (10)
C(1)–C(6)	1·548 (9)	1·542 (10)	C(4)–C(5)	1·607 (8)	1·573 (10)	C(7)–Cl(71)	1·775 (7)	1·762 (7)	C(54)–O(53)	1·388 (30)	
C(1)–C(7)	1·544 (10)	1·583 (10)	C(4)–C(7)	1·536 (9)	1·523 (10)	C(7)–Cl(72)	1·771 (7)	1·759 (8)	C(61)–O(61)	1·177 (9)	1·189 (8)
C(2)–Cl(2)	1·702 (7)	1·684 (7)	C(5)–O(53)	1·401 (8)	1·430 (8)	C(51)–O(51)	1·180 (8)	1·193 (10)	C(61)–O(62)	1·321 (9)	1·316 (8)
C(2)–C(3)	1·310 (10)	1·315 (10)	C(5)–C(6)	1·566 (9)	1·553 (9)	C(51)–O(52)	1·330 (8)	1·313 (9)	C(62)–O(62)	1·447 (10)	1·447 (9)
C(3)–Cl(3)	1·689 (7)	1·701 (7)									

	A	*B*		*A*	*B*		*A*	*B*
Cl(1)–C(1)–C(2)	116·5 (5)	116·0 (5)	C(3)–C(4)–C(5)	104·6 (4)	105·9 (5)	Cl(71)–C(7)–C(4)	113·9 (5)	115·0 (5)
Cl(1)–C(1)–C(6)	114·1 (5)	115·7 (5)	C(3)–C(4)–C(7)	99·3 (5)	99·6 (6)	Cl(72)–C(7)–C(1)	113·7 (5)	112·4 (5)
Cl(1)–C(1)–C(7)	116·0 (5)	116·5 (5)	C(5)–C(4)–C(7)	102·8 (5)	103·2 (6)	Cl(72)–C(7)–C(4)	113·3 (5)	115·6 (5)
C(2)–C(1)–C(6)	109·4 (5)	108·2 (5)	O(53)–C(5)–C(4)	106·6 (5)	110·9 (5)	C(1)–C(7)–C(4)	93·4 (5)	92·7 (5)
C(2)–C(1)–C(7)	98·7 (5)	97·6 (5)	O(53)–C(5)–C(6)	111·4 (5)	106·5 (5)	O(51)–C(51)–O(52)	124·7 (6)	124·3 (7)
C(6)–C(1)–C(7)	99·9 (5)	100·4 (5)	O(53)–C(5)–C(51)	110·5 (5)	108·2 (5)	O(51)–C(51)–C(5)	123·5 (6)	123·5 (7)
Cl(2)–C(2)–C(1)	123·8 (5)	125·3 (5)	C(4)–C(5)–C(6)	100·0 (5)	101·1 (5)	O(52)–C(51)–C(5)	111·7 (5)	112·1 (6)
Cl(2)–C(2)–C(3)	127·8 (6)	128·0 (6)	C(4)–C(5)–C(51)	113·1 (5)	115·0 (5)	O(61)–C(61)–O(62)	125·8 (6)	125·3 (6)
C(1)–C(2)–C(3)	108·3 (6)	106·6 (6)	C(6)–C(5)–C(51)	114·5 (5)	114·7 (5)	O(61)–C(61)–C(6)	125·8 (6)	123·8 (6)
Cl(3)–C(3)–C(2)	128·3 (6)	126·7 (6)	C(1)–C(6)–C(5)	104·6 (5)	104·7 (5)	O(62)–C(61)–C(6)	108·4 (6)	110·8 (5)
Cl(3)–C(3)–C(4)	124·5 (5)	124·5 (5)	C(1)–C(6)–C(61)	113·4 (6)	113·9 (5)	C(51)–O(52)–C(52)	114·8 (6)	116·2 (6)
C(2)–C(3)–C(4)	107·2 (6)	108·8 (6)	C(5)–C(6)–C(61)	112·5 (5)	114·2 (5)	C(5)–O(53)–C(53)	124·4 (7)	120·0 (6)
Cl(4)–C(4)–C(3)	114·0 (4)	112·7 (5)	Cl(71)–C(7)–Cl(72)	107·0 (4)	108·0 (4)	C(5)–O(53)–C(54)	119·9 (12)	
Cl(4)–C(4)–C(5)	117·6 (4)	119·3 (5)	Cl(71)–C(7)–C(1)	115·4 (5)	112·6 (5)	C(61)–O(62)–C(62)	115·2 (6)	115·3 (5)
Cl(4)–C(4)–C(7)	116·4 (4)	113·9 (5)						

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42296 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are C(4*A*)—C(5*A*) 1·607 (8) and C(4*B*)—C(5*B*) 1·573 (10) Å. Such long bonds between highly substituted C atoms are not uncommon. They have been found to occur in two carboxylate derivatives of norbornenone (Balasubrahmanyam, Usha & Venkatesan, 1981).

As expected, strain within the norbornene ring system is manifested by a decrease in all C—C—C bond angles. This is especially pronounced for the bridge angles which are 93·4 (5) and 92·7 (5)°. C(1), C(2), C(3) and C(4) deviate from their mean planes within ±0·011 (7) and ±0·015 (7) Å (for molecules *A* and *B*, respectively). The opposite side of the system, containing C(1), C(6), C(5) and C(4) has deviations within ±0·039 (6) and ±0·014 (6) Å, respectively. The angles between these two planes are 112·6 (3) and 112·9 (4)°, respectively. These angles are in a good agreement with the value of 112·1° found in a norbornyl derivative (Newton, Pantaleo, Kirbawy & Allinger, 1978). The plane through C(1), C(7) and C(4) forms with the two planes described above angles of 125·4 (4) and 122·0 (4)° for molecule *A* and 124·1 (4) and 123·0 (4)° for molecule *B*.

The C(1), C(2), C(3), C(4), C(5), C(6) six-membered rings show $^{1,4}B$ boat conformations. The corresponding puckering parameters (Cremer & Pople, 1975) for molecules *A* and *B* are: $Q = 0{\cdot}960$ (7) and 0·951 (6) Å, $\theta = 93{\cdot}6$ (4) and 91·6 (4)°, $\varphi = 2{\cdot}6$ (4) and 1·0 (4)°. The five-membered rings show envelope conformations. The puckering parameters for the C(7), C(1), C(2), C(3), C(4) rings of molecules *A* and *B* are: $Q = 0{\cdot}573$ (7) and 0·593 (7) Å, $\varphi = 1{\cdot}47$ (7) and 2·61 (7)°; the parameters for the C(7), C(1), C(6), C(5), C(4) rings are: $Q = 0{\cdot}616$ (7) and 0·609 (7) Å, $\varphi = -175{\cdot}0$ (6) and $-178{\cdot}5$ (6)°.

The dihedral angle formed by mean planes through the non-H atoms of the ester groups is 61·6 (4)° in molecule *A* and 50·1 (3)° in molecule *B*. These planes form with the mean planes through C(4), C(5), C(6), C(1) angles within the range 47·6 (3) to 64·4 (4)°.

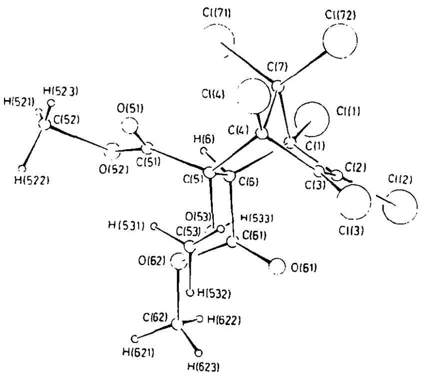

Fig. 1. A perspective view of a molecule along **b** showing the atomic numbering.

Table 3. *Ranges of bond lengths* (Å) *and angles* (°) *within the hexachloronorbornene moiety compared with the corresponding weighted means evaluated from six published structures of compounds containing this moiety*

	Range (this work)	Mean*
Bridgehead C(*sp*^{3})–Cl	1·759 (8) –1·775 (7)	1·773 (3)
Bridgehead C(*sp*^{3})–C(*sp*^{3})	1·523 (10)–1·583 (10)	1·554 (4)
Bridge angle C–C–C	93·4 (5), 92·7 (5)	92·7 (3)
Bridge angle Cl–C–Cl	107·0 (4), 108·0 (4)	107·5 (3)
Peripheral C(*sp*^{3})–Cl	1·741 (7) –1·760 (7)	1·757 (3)
C(*sp*^{2})–Cl	1·684 (7) –1·702 (7)	1·702 (3)
C(*sp*^{3})–C(*sp*^{2})	1·515 (10)–1·548 (9)	1·510 (4)
C(*sp*^{2})–C(*sp*^{2})	1·310 (10), 1·315 (10)	1·324 (6)

* Endrin, aldrin (DeLacy & Kennard, 1972); heptachlor (Shields & Kennard, 1973); endosulfan (Smith, Kennard & Shields, 1977); isobenzan (Smith & Kennard, 1977); heptachlor epoxide (Hovmöller, Smith & Kennard, 1978).

Two Cl···O intermolecular contacts are near to the sum of the van der Waals radii (3·20 Å): Cl(3*A*)···O(61*A*$^{\rm i}$) = 3·182 (7) and Cl(72*A*)···O(51*A*$^{\rm ii}$) = 3·166 (6) Å, where the symmetry operations are (i) $1 - x, -y, 1 - z$ and (ii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$.

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