Fabelle 6. Winkel innerhalb einer	Joa	latgruppe	
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Atom 1	Atom 2	Atom 3	Winkel(°)	Fehler (°)
O(1)	O(2)	O(3)	63,0	0,3
O(2)	O(1)	O(3)	59,5	0,3
O(1)	O(3)	O(2)	57,5	0,3
O(1)	J	O(2)	92,8	0,4
O(1)	J	O(3)	102,2	0,3
O(2)	J	O(3)	95,3	0,4

Die Packungsdichte im  $K_2Ge(IO_3)_6$  ist typisch für Jodatstrukturen. Die Raumerfüllung beträgt *ca*. 51 % gegenüber 74 % in einer dichtesten Sauerstoffpackung.

Die für die Steuerung und Auswertung der Diffraktometermessungen notwendigen Programme stellte uns dankenswerterweise Herr Professor Dr G. Ruban zur Verfügung. Die übrigen Rechnungen wurden mit Programmen des Systems X-ray 63 (X-ray Handbook, 1965) am DRZ in Darmstadt durchgeführt.

Herrn Professor Dr K. Plieth danken wir sehr herzlich dafür, dass er uns Messzeit am Vierkreisdiffraktometer des Instituts für Kristallografie (FU Berlin) eingeräumt hat, den Herrn Dr W. Dreissig und Dr P. Luger schulden wir Dank für ihre Unterstützung bei der Durchführung der Messungen und Rechnungen.

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# The Crystal Structure of a Seco Steroid

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The crystal and molecular structure of  $d_il$ -3a,6-dimethyl-6-(*trans*-3-chlorobut-2-ene-1-yl)-2,4,5,6,8,9-hexahydro-3*H*-benz[*e*]indene-3,7-(3a*H*)-dione (C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>Cl), II, has been determined from X-ray diffraction data in order to establish the geometrical isomerism of the molecule. The space group is monoclinic,  $P_{2_1}/c$ , with four molecules in a unit cell of dimensions: a = 10.091 (3), b = 11.515 (3), c = 14.709 (4) Å,  $\beta = 92.54$  (4)°. The intensities of 2912 reflections were measured on a four-circle automated diffractometer using Cu K $\alpha$  radiation. The structure was refined by the anisotropic least-squares method to a final *R* value on *F* of 0.081 computed with all of the structure factor data. The results of the crystal structure analysis show that two methyl groups are in the *trans* configuration. The conjugated double bond in the fused ring system confers an approximately coplanar arrangement on nine of the thirteen atoms in the rings.

### Introduction

Compound II was prepared *via* base-induced methylation of dione I (Danishefsky *et al.*, 1972).



The relative stereochemical arrangement of the methyl groups at carbons (3a) and (6) was crucial to the possibility of subsequent use of II in the elaboration of steroids. The crystal structure of II was examined in order to determine whether these methyl groups are *cis* or *trans* with respect to the plane of the fused rings. This, in turn, had further significance with respect to the problem of the stereochemistry of methylation of extended enolates derived from dienones such as I. Another reason for examining the three-dimensional structure of II was the possibility of assessing the conformational effects of the 8,14-diene systems on the steroid system (for convenience in comparing this structure with other steroids, the conventional steroid numbering scheme in Table 1 will be adopted in the subsequent discussion).

Table 1. Crystal data for seco steroid, C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>Cl



 $C_{19}H_{23}O_2Cl$  M.W. = 318.847 m.p. = 132.5-133.5°C

Monoclinic, space group  $P2_1/c$  from systematic absences: h0l absent for l odd; 0k0 absent for k odd.

а	=	10·091 (3) Å		$\lambda(Cu K\alpha) = 1.5418 \text{ Å}$
b	=	11.515 (3)	measured	$\lambda(\operatorname{Cu} K\alpha_1) = 1.54051$
с	=	14.709 (4)	at 24°C	$\lambda(Cu K\alpha_2) = 1.5443$
ß	=	92·54 (4)°		$\mu(Cu K\alpha) = 20.17 \text{ cm}^{-1}$
V	=1'	707•5 Å3		F(000) = 680
Ζ	=	4		
$d_x$		1.240 g.cm-3		
$d_n$	, =	1.237 g.cm-3	measured by flo	otation method in aqueous
			potassium iodi	de solution at 23°C

#### Experimental

The crystals of II, which were supplied by Professor S. Danishefsky and Dr P. Solomon, are colorless, acicular in habit, and elongated in the direction of the unique axis. The space group was determined from oscillation and Weissenberg photographs. The unitcell dimensions were deduced from manual  $2\theta$  scans of the observable axial reflections using a Picker automatic diffractometer equipped with a scintillation counter. The crystal was mounted such that its *b* axis coincided with the  $\varphi$  axis of the full-circle crystal orienter. Ni-filtered Cu  $K\alpha$  radiation was used throughout the analysis. Table 1 contains the crystal data.

The integrated intensity measurements were made by scanning reflections in the  $\theta:2\theta$  mode at a rate of 2°/min over a  $2\theta$  range of 2°. At both limits of this range, stationary 10 sec background counts were taken. Seven reflections were chosen as standards, and at least a pair of these were monitored at intervals of approximately two hours. Examination of the standards during the data collection revealed a gradual decrease of 7% in the diffraction intensity. Scale factors based on the seven standards compensate to a large extent for the time-dependent decrease.

In total, 2912 reflections were collected; of these 728 were less than 3  $\sigma(I)$ , where  $\sigma(I)$  is given by

 $ATN[(10S+5)+9\{(10B_1+5)+(10B_2+5)\}]^{1/2}$ 

S is the total number of decacounts accumulated during the scan, and ATN is the attenuator factor.  $B_1$  and  $B_2$  are the accumulated background in decacounts. The intensities were corrected in the usual manner by the Lorentz and polarization factors, but they were not corrected for absorption.

### Structure determination and refinement

An initial set of structure amplitudes  $(|F_a|)$  were calculated from the 2912 independent reflections. The X-ray 70 system of programs (Stewart, Kundell & Baldwin, 1970) was used to compute both a scale and an overall temperature factor from a Wilson (1942) plot, to convert the observed structure factor amplitudes to normal E values, and to determine the signs of 332 reflections,  $E \ge 1.50$ , by the direct method (programs SIGMA 2) and *PHASE*). The coordinates of 17 atoms were obtained readily from an E map computed with the 332 normalized structure factors. The remaining 5 atoms, exclusive of the hydrogens, were located in a difference Fourier synthesis which followed a single cycle of isotropic full-matrix least-squares refinement of the partial structure. The parameters of the 22 atoms were then refined anisotropically by the full-matrix leastsquares method. The Hughes (1941) weighting scheme was employed with  $\sigma = F/11.3$  if F > 11.3 and with  $\sigma =$ 1 if  $F \le 11.3$ . The function minimized was  $\sum w(|F_a| K[F_c])^2$  where K is a single scale factor. Atomic scattering factors for chlorine, oxygen, and carbon were taken from the International Tables for X-ray Crystallography (1962), while those for hydrogen were taken from Stewart, Davidson & Simpson (1965). The hydrogen coordinates were obtained from a difference synthesis calculated when the R value had been reduced to 0.12 for ali reflections. These were included as variables in subsequent cycles of refinement. However, hydrogen thermal parameters were not refined but were set equal to those of the atoms to which the hydrogens are bonded. The final reliability index was 0.081 for all 2912 independent reflections and 0.064 for the 2184 observed reflections. The structure amplitudes of all reflections are listed in Table 2. The atomic coordinates and thermal parameters with their e.s.d.'s are given in Table 3.

Other computer programs used in this analysis are the Shiono (1965) version of ORFLS (Busing, Martin & Levy, 1962), a modification of the Zalkin Fourier Synthesis (Shiono, 1967), the ORTEP program (Johnson, 1965), and a number of those listed in the University of Pittsburgh Crystallography Laboratory Technical Reports (Shiono, 1963–1968).

### Discussion of the structure

The molecular shape and the thermal ellipsoids of the atoms are depicted in Fig. 1. The least-squares planes through some regions of the *B*, *C* and *D* rings and the distances of various atoms from these planes are given in Table 4. Planes 1 and 2 show that the conventional chair or boat description does not apply to the six-membered rings, *B* and *C*, because of the presence of unsaturation at C(8)-C(9). Ring *D* has a distorted envelope conformation as indicated by plane 3 and by torsion angle C(13)-C(14)-C(15)-C(16) which is 4.2°. As expected for a conjugated diene system, atoms C(7), C(8), C(9), C(10), C(11), C(13), C(14)

### Table 2. Observed and calulated structure factors

The columns within each group in order from left to right are the running index l,  $10|F_o|$  and  $10|F_o|$ . Asterisks indicate unobserved reflections.

# Table 2 (cont.)

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	26 134 278 137	-14 30 -12 120 -10 269 -8 144	33 41 179 3	38 162 8*	1	41 50 32 29	47 51 33 33	10	921 921	69 1092 156 870		28 10 28	7 33 8 8• 9 22 10 7•	11 2 H= 6 48	7 42 51	14	41 238 29 19	51 239 93 23	6 7 8 9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	405 28 467 732 152	-6 398 -4 29 -2 455 0 761 2 132	66 22 18 6 17	62 24 8* 8* 7*	70789	50 32 58	90 56 30 39	12	228 265 38 36 327	243 255 38 36 308	5 4 7 8	4 10 10 32 33 35	-9 70 -8 33 -7 24 -6 36	21 65 59 14	22 61 54 8*	-13 -12 -11 -10	13 91 52 23 23	24 93 71 23 26	10 11 12 13
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	444 122 32 110	6 441 6 128 10 27 12 110	10 46 21	70 45 28 49	10 -9 -8 -7	34 10 15 11 79	33 8. 8.	-15 -14 -13 -12 -11	80 7 180 13 2	79 80 169 90	10 11 12 13	109 62 36	-5 61 -6 109 -3 31 -2 31 -1 23	40 53 40 27 76	30 55 37 32 76	-0 -7 -6	24 3 16 15	20 -2 70 19	-16 -15
$\begin{array}{c} -2 & -2 & -2 & -2 & -2 & -2 & -2 & -2 $	+8 23 H= 5 36	14 54 16 8* 7* 0 -16 32	5 68 24 29	71 89 90		78 105 36 18	80 1C3 30 26	-10 -9 -8 -7	42 42 41 3	24 45 74	14	76	0 8* 1 79 2 8* 3 8*	136 49 248 46	151 42 251 38	-4	98 195 53	89 289 62	-14 -13 -12 -11
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1 106 97 275	-12 8* -10 99 -8 96 -6 282	113 42 50	110 87 32	-1 0 1 2	29 113 83 54	31 115 80 49	-5 -4 -3 -2	30 37 31	32 32 31	-15 -14 -17 -12	41	5 8• 6 42 7 7• 8 7•	41 151 (15	51 155 118 185	123	305 64 141 50	296 64 159 57	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	244 217 603 529	4 263 -2 221 0 640 2 548 4 109	5 13 31 25 7	8* 8* 27 7*	3 4 5 6 7	67 31 116 5	05 38 118 7•	0	0 206 206	8* 60 200 79	-11 -10 -9 -8 -7	1= 1! 0 66 19 28	-6 7 -5 68 -4 7 -3 27	32	49 36 64	07 8 9	08 243 295 211 517	244 297 231 513	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	76	6 79 8 37 10 56 12 90	1 • 11 8 29	7. -1 H 6. 29	-7	102 115 27 81	95 102 33 69	4 7 6 7 R	203 195 323 586 125	204 213 318 580	-6 -5 -4 -3 -7	48 28 40 1 21	-2 50 -1 28 0 39 1 7* 2 23	10 37 83	94 36 80 44 43	10	47 226 67 3 79	220 67 150	01234
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	31 128	-14 27 -12 118 -10 42	17 43 32 4	7. 55 39 7.	-4 -7 -7 -1	136 34 102 36	135 35 93 28	0 10 11 12	400 216 180 384	419 224 186 391	-1	25 13 10 (= 0	3 29 5 70 8 -1 1	H= 7 39 56 63 70	K= -2 39 50 58 76	-14 -13 -12	67 112 134 61 94	65 104 131 60 95	56789
15 39 34 -5 57 63 -11 52 45 9 22 20 -11 125 129 7 0 4 136 145 16 74 4 -4 39 33 -10 107 103 10 125 127 -10 31 2 583 616 6 90 98	21 224 14 306	-6 21 -4 23 -2 7 0 305	57 0 17 22	57 75 72	1234	12 12 23	7. -1 7.	-14	320	328 443 26 190		37 70 37 39	-16 34 -15 65 -14 43 -13 33	50 46 29 66	44 49 33 68	-10 -9 -8 -7	90 101 10 114	97 103 9. 105	10 11 12 13
R= -2 H= 4 -3 144 140 -9 18 8 11 41 38 -9 264 258 4 277 302 8 113 120   -16 63 60 -2 31 34 -8 100 88 12 64 60 -8 52 40 6 544 546 10 22 11	145 98 120 11	4 136 6 90 8 113 10 22	0 616 302 546	583 277 544	2	129 31 258 46	125 37 764 52	-11 -10 -9 -8	20 127 38 60	22 125 41 64	9 10 11 12	45 103 88	-11 52 -10 107 -9 18 -8 106	63 33 140 34	57 39 144 31		34 • • •	39 7 2 63	15
-14, 22, 23, -0, 457, 44, -4, 17, 166, 15, 94, 16, -2, 27, 11, 8, 142, 159, 14, 110, 109, 157, 151, 151, 154, 154, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 154, 155, 155	109 52 H- 7 32 77	12 110 14 44 8- 0 -14 25 -12 76	159 367 59 23 11	142 348 62 28 7•	1C 12 14 16	109 87 85 80	1C7 85 87 68	-0 -3	22	8* 23	14 15 15	104 458 520 1794	-6 119 -5 417 -4 484 -3 1588	67 87 69	57 59 96 84	0	23	22 163 45 47	-14 -13 -12 -11
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	42 110 125 113 43	-10 34 -8 105 -6 129 -4 232 -2 35	50 16 75 88	60 80 80 84	-16 -14 -12 -10	96 77 93 44 97	103 78 95 59 103	-2 -1 0 2 2	56 29 24 182 17	27 27 175 29	-16 -15 -14 -23 -12	+81 15 16	-1 434 K1 4 -17 70 -10 24	168 43 111 52	168 40 126 50	5 6 7 8	37 349 72 130	29 334 86 151	-9 -8 -7 -6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	150 103 94 71	0 148 2 115 4 84 6 77 8 85	4R 114 1212 138 26	58 114 1173 121	-8 -6 -4 -2 0	28 113 49 3 78	29 109 43 9• 79	3 4 5 6 7	22 167 51 85 216	35 171 48 97 225	-11 -10 -9 -8 -7	11 61 55 2 127	-15 8• -14 63 -13 50 -12 8• -11 132	23 6 11 22 9	25 8• 8• 22 7•	10	183 22 106 26 29	205 28 118 93 37	
0 2400 174 6 - 2 M 8 8 - 10 132 123 - 6 10 27 8 28 28 28 2 422 456 0 9 10 9 10 9 10 12 125 123 0 5 10 9 10 9 10 12 125 123 0 12 12 12 12 12 12 12 12 12 12 12 12 12	19 22 84 49 204	10 9* 12 25 8* 0 -12 42 -10 205	45C 869 116 2 94	422 764 117 74 76	24	28 110 21 21	28 1C7 26 9•	9 10 11	27 49 31 344 170	30 43 25 361 191	****	123 68 95 801 227	-10 132 -9 19 -8 99 -7 806 -6 217	4 8 32 49 8 100	42 99	-13 -12 -11 -10	176 176 25 21 148	240 167 30 74 120	01234
5 807 72 -9 47 38 -5 689 716 -1 91 95 13 16* 1 12 270 262 722 75   151 125 -75 -75 -76 -72 -76 -72 75   164 164 -75 -72 -74 -74 -76 -72 75   174 164 164 -75 -71 -75	75 40 40	-6 72	242	229 42 • 0 H	12 14 16	1 112 21	107 107 70	-13	95 273 181 386 824	91 252 195 404 803	-1	716 914 204 247 929	-5 689 -4 880 -3 214 -2 241 -1 913	38 19 122 49 33	47 22 114 50 46	-9 -8 -7 -6 -5	72 125 140 48 84	87 151 146 51 86	56789
10 103 100 -** 57 60° 0 396 605 6 310 301 -12 6 31 41 -13 60° 106 2 156 184 11 95 90 -2 9° 5 1 71 95 5 151 154 -91 67 41 -12 168 175 4 6 2 156 184 13 96 57 -7 123 125 2 79 95 6 70 15 -9 8 15 -10 116 115 4 6 24 15 14 90 25 6 19 10 116 125 2 8 2 8 10 116 112 8 2 8 10 116 112 8 8 8 8 10 116 115 115 115 115 115 115 115 115 115	164 55 19	2 158 4 62 6 24 8 8	106 175 112 274	97 168 114 260	-14 -12 -10	41	47	-1C -9 -8 -7	301 154 15 151	310 134 7. 153	4 5 6 7 4	406 82 85 210	0 396 1 71 2 79 3 221	60 5 125 2	57 123	-4 -3 -2 -1 0	100 90 57	103 95 60 80	10
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	H= 9 51 47	12 7+ K= 0 -10 40 -8 59	642 422 272 281	1018 1343 287 1196	1202	47 60 ° 61	50 47 66		182 73 87 48	175 70 89 43	10	254 192 84 14	5 234 6 202 7 69 8 19 9 172	27 96 58 18	34 100 68 25	12345	33 18 5 18 49 19	32 -2 17 52 20	-15 -15 -14 -13
-12 01 01 0 0 01 22 10 71 100 14 15 15 10 13 10 13 17 0 03 17 1 0 03 10 10 10 10 10 10 10 10 10 10 10 10 10	80 21 151 136	-4 74 -2 33 0 135 2 135	244 424 116 156	215 413 115 162	6 8 10 17	73 22 3	63 35 22	0123	38	)8 7• • -1 77	14 15 -15	85 85 34	10 71 11 85 12 61 13 40	22	94 107 27 43 25	6 7 8 9	61 80 154 66	61 76 143 57 21	-12 -11 -10 -9
-7 192 195 11 27 28 15 8 1 13 13 15 16 80 13 1 1 15 15 16 10 15 16 10 10 10 10 10 10 10 10 10 10 10 10 10	94 50 40 H= 10	6 80 8 58 10 76	11 3 38 76	80 61 78	16 - 16 - 14	18 50 91 25	26	5 6 7 8	60 93 36 1	58 94 35 8•	-13	13 39 • ~ ~	15 8• 16 32 17 7• K• -L H	26 10 62	25 74 10 25 74 74 78	-11	195 44 113 55 14	192 63 116 70 7•	
-72 112 113 -49 76 72 -16 79 73 -6 79 73 -6 79 73 -6 79 73 -16 73 74 74 75 74 74 74 74 74 74 74 74 74 74 74 74 74	102	-6 110 -4 196 -2 117 0 42	60 7 80 284	62 29 70 331	-10	21 × 23 °	35 35 • -1 •	10	35	28	- 7 - 6 - 7	23 96 51 61	16 8* 15 89 14 51 13 57	72 41 39 98	74 43 31 96	-9 -8 -7 -5	113 310 144 144 225	112 319 205 137 258	-10-12
1 132 134 44 33 33 - 11 - 11 53 45 - 72 53 45 - 72 54 45 - 72 54 45 - 72 54 45 - 72 54 54 54 54 54 54 54 54 54 54 54 54 54	67 31 30 14	2 70 6 22 8 25	230 72 900 21	218 62 994 70	10240	10		-10	64 141 62	03 303 67		49 54 169 150	11 53 10 43 -9 155 -8 338 -7 360	33 110 62 32	33 103 63 35 87	-1 -1 0	134 100 91 35	132 99 19 100 35	3 4 5 6 7
	12 47 47	-2 65 0 63 2 20	200	183	10	74	71 +3	11777	218 20 129	239 239 78 132	23456	157 448 66 52 87	-6 175 -5 449 -4 63 -3 50 -2 91	9 69 4] 11 54	68 45 31 48	12.74	149 2 96 31 47	133 90 98 93	8 9 10 11 12

Table 3 (cont.)

### Fractional coordinates $\times 10^3$

	x	У	Z
H1(C1)	113 (3)	176 (3)	158 (2)
H2(C1)	-017(4)	097 (3)	164(2)
H(C2)	116 (3)	-073(3)	135 (2)
H1(C4)	234 (8)	-142(5)	020 (4)
H2(C4)	244 (5)	-089(4)	-062(3)
H3(C4)	367 (6)	-081(4)	010 (3)
H1(C6)	017 (3)	-159(3)	396 (2)
H2(C6)	091 (3)	-046(3)	431 (2)
H1(C7)	262 (3)	-171(3)	423 (2)
H2(C7)	215 (3)	-176(3)	320 (2)
H1(C11)	282 (3)	249 (3)	302 (2)
H2(C11)	327 (3)	183 (3)	217(3)
HI(C12)	447 (3)	197 (2)	391 (2)
H2(C12)	515 (3)	253 (3)	319 (2)
H(C15)	479 (3)	-171(2)	432 (2)
H1(C16)	689 (3)	-075(3)	470 (2)
H2(C16)	722 (3)	-118(3)	385 (2)
H1(C18)	487 (3)	031 (3)	187 (2)
H2(C18)	611 (3)	112 (3)	202 (2)
H3(C18)	616 (3)	-025(3)	217(2)
H1(C19)	044 (3)	165 (3)	394 (3)
H2(C19)	076 (3)	251 (3)	314(2)
H3(C19)	-067 (3)	186 (3)	320 (2)

C(15) and C(16) are approximately coplanar, although significant deviations are apparent, especially in the cases of C(11), C(13) and C(16). If these atoms in plane 4 were strictly coplanar, then the B/C and C/Djunctions would lie in a common plane, and torsion angle C(9)-C(8)-C(14)-C(15) would equal 180°. However, its observed value is 167°. Other torsion angles about the B/C and C/D junctions are listed in Table 5. Significantly, C(6) and C(12) are displaced in the same direction from plane 4. Therefore, rings B and C are in an extended boat conformat.on. CH<sub>3</sub>(19) lies on the same side of plane 4 as C(6) and C(12) whereas the chlorobutenyl side chain and CH<sub>3</sub>(18) lie on the oppo-

Table 3. Atomic parameters and their estimated standard deviations

	Fractio	onal coordinate	es × 104	Thermal	parameters	$\times 10^4$ in the	form exp [	$(h^2\beta_{11}+\cdots$	$\cdot 2k[\beta_{23})]$
	x	У	Z	$\beta_{11}$	$\beta_{22}$	β33	B12	B13	B22
Cl	2558 (2)	1415 (1)	105 (1)	424 (3)	121 (1)	84 (1)	-49(1)	69 (1)	20 (1)
C(1)	737 (4)	977 (3)	1762 (2)	123 (4)	112 (3)	73 (2)	11(3)	-9(2)	7 (2)
C(2)	1326 (3)	23 (3)	1220 (2)	188 (4)	94 (3)	50 (1)	-25(3)	- (2)	1 (1)
C(3)	2079 (4)	84 (3)	526 (2)	206 (5)	102 (3)	48(1)	-24(3)	2(2)	5 (2)
C(4)	2668 (8)	- 887 (5)	27 (4)	394 (12)	129 (5)	57 (2)	-25(7)	50(4)	-14(3)
C(5)	200 (3)	-276 (3)	3093 (2)	99 (3)	100 (3)	64(2)	-10(2)	21(2)	-21(2)
C(6)	817 (3)	-947 (3)	3869 (2)	137 (4)	104 (3)	63 (2)	-43(3)	18(2)	21(2)
C(7)	2217 (3)	-1283 (3)	3645 (2)	135 (3)	76 (2)	62 (2)	-22(2)	3 (2)	$\frac{2}{6}(2)$
C(8)	3010 (3)	-243 (2)	3384 (2)	109 (3)	69 (2)	42 (l)	-10(2)	11 (1)	-2(1)
C(9)	2434 (3)	721 (2)	3036 (2)	104 (3)	72 (2)	45 (1)	-4(2)	17 (1)	-2(1)
C(10)	958 (3)	796 (2)	2800 (2)	107 (3)	83 (2)	59 (l)	$6(\bar{2})$	13 (2)	-6(1)
$C(\Pi)$	3243 (3)	1785 (3)	2817 (2)	124 (3)	72 (2)	64 (2)	-3(2)	15 (2)	12 (2)
C(12)	4602 (3)	1831 (2)	3296 (2)	118 (3)	69 (2)	62 (2)	-16(2)	25(2)	-3(2)
C(13)	5305 (3)	673 (2)	3202 (2)	106 (3)	78 (2)	45 (l)	-11(2)	18(2)	-4(1)
C(14)	4451 (3)	- 292 (2)	3549 (2)	110 (3)	68 (2)	42 (1)	-5(2)	13 (2)	-6(1)
C(15)	5187 (3)	- 1069 (3)	4028 (2)	127 (3)	86 (2)	49 (1)	6 (2)	8 (2)	4(2)
C(10)	6594 (3)	- 709 (3)	4133 (2)	120 (4)	117 (3)	53 (2)	14 (3)	-0 (l)	-8(2)
C(17)	6546 (3)	0521 (3)	3813 (2)	102 (3)	102 (3)	54 (2)	-8(2)	21 (2)	-15(2)
C(10)	5677 (3)	0455 (3)	2217 (2)	160 (4)	118 (3)	54 (2)	-10(3)	35 (2)	-6(2)
	312 (3)	1817 (3)	3304 (3)	139 (4)	95 (3)	98 (3)	12 (3)	37 (3)	-10(2)
O(1)	-84/(3)	- 552 (3)	2727 (2)	100 (3)	129 (3)	96 (2)	-12(2)	9 (2)	-21(2)
0(2)	7342 (3)	12/8 (3)	4007 <b>(2)</b>	123 (3)	127 (3)	90 (2)	-27 (3)	9 (2)	- 19 (Ž)

site side. Accordingly, methyl groups CH<sub>3</sub>(18) and CH<sub>3</sub>(19) are in the trans configuration. The keto oxygen atom, O(1), lies -0.390 Å out of plane 1 while the other keto oxygen, O(2), lies 0.886 Å out of plane 3. The torsion angles around the C(1)-C(10) bond connecting the side chain are:

 $C(2)-C(1)-C(10)-C(19) = -179 \cdot 7^{\circ}; C(2)-C(1)-C(10)-C(10)$  $C(5) = -65.8^{\circ}$ ; and  $C(2)-C(1)-C(10)-C(9) = 58.4^{\circ}$ . The Cl atom is *cis* relative to C(1).

The bond distances and valency angles with their associated standard deviations, exclusive of those involving hydrogen atoms, are shown in Fig. 2. The C-H bond distances lie in the range between 0.75 and 1.06 Å. The single bonds to C(10) are longer than expected, even though the experimental bond distances in Fig. 2 are probably underestimated because of the thermal motion of the molecule. Bonds C(9)-C(10)and C(5)-C(10) exceed 1.505 Å, the normally quoted

Table 4. Some	e least-squares	planes t	hrough	i groups of atom	S
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Coefficients  $\times 10^4$  in Ax + By + Cz - D = 0, referred to the crystallographic axes (x, y, z in Å).

Plane	No.	A	В	С	D
C(7) C(8) C(9) C(10)	1	-1682	3775	9172	39721
C(8) C(9) C(11) C(14)	2	- 1459	3465	9322	40957
C(13) C(14) C(15) C(16)	3	-2197	5224	8329	31629
C(7) to C(16), C(12) omitted	4	-1662	4082	9041	39178

Plane No.

Displacement from the plane (Å  $\times 10^3$ )

- C(7) 11, C(8) 24, C(9) 24, C(10) 11, C(5) 47, C(6) 698, O(1) 390.
- C(8) 4, C(9) -4, C(11) 2, C(14) -2, C(12) 478, C(13) -218 2
- 3 C(13) - 12, C(14) 22, C(15) - 22, C(16) 12, C(17) 370, O(2) 8864
  - C(7) 46, C(8) 37, C(9) 50, C(10) 20, C(11) 124, C(13) 233, C(14) 83, C(15) 66, C(16) 140, Cl 3542, C(1) 1239, C(2) 2507, C(3) 3528, C(4) 4747, C(5) 32, C(6) 646, C(12) 555, C(17) 300, C(18) 1708, C(19) 1278, O(1) - 409, O(2) 780



Fig. 1. A thermal ellipsoid plot (Johnson, 1965), at the 50 % probability level, of one molecule showing the numbering system of the atoms.

distance for an  $sp^2-sp^3$  single bond between carbon atoms (Bartell & Bonham, 1960) by 2.8 and 4.8 $\sigma$  respectively. Bonds C(1)-C(10) and C(19)-C(10) are 1.8 and  $1.6\sigma$  greater than 1.54 Å, the  $sp^3-sp^3$  distance. On the other hand, endocyclic bonds C(15)–C(16), C(16)–C(17), C(12)–C(13), C(11)–C(12), C(5)–C(6) and C(6)–

## Table 5. Torsion angles in the rings and at the B/C and C/D junctions

 $\Phi$  in Part I is the torsion angle about the specified bond. The other two atoms required to define the angle are attached to the ends of the bond and are in the ring in question.

The sign convention for the torsion angle is that of Klyne & Prelog (1960). The torsion angles in the other enantiomorph are opposite in sign.



Fig.2. Interatomic distances (Å) and angles (°) for the molecule. The estimated standard deviations are given in parentheses following the listed values.

C(7) are shorter by 6.3, 3.0, 5.5, 6.3, 3.5 and 6.3 $\sigma$  respectively, than their expectation values. Bonds C(2)–C(3) and C(3)–C(4) in the chlorobutenyl side chain are fore-shortened by 6.8 and 4.1 $\sigma$ , seemingly due to thermal disorder.

The projections of the structure along the b and c axes, illustrating the packing of the molecules, are shown in Figs. 3 and 4. The intermolecular contacts between nonhydrogen atoms which are less than 4 Å are listed in Table 6. The distances between neighboring molecules correspond to normal van der Waals interactions.

Table 6.	Intermolecular	distances	less	than	4 Å	between
	nonh	vdrogen at	toms			

		- 0	
<b>C</b> (1)	)C(6'	')	3.967 Å
<b>C</b> (1)	1)0(1'	Ú.	3.964
C(12	2)–Cl'		3.987
C(19	9)–O(1	')	3.441
C(19	9)–C(5′	Ċ)	3.950
C(19	9)–Cl″	-	3.971
	Symm	etry coo	le:
'	-x	$\frac{1}{2} + y$	$\frac{1}{2} - z$
*	х,	$\frac{\overline{1}}{2}-y$ ,	$\frac{1}{2} + z$

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Fig. 3. Projection of one unit cell along the b axis.



Fig. 4. Projection of one unit cell along the c axis.

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