The Crystal and Molecular Structures of two Cyclobuta-Steroids: 4',4'-Dichloro-2β,3β-dihydrocyclobuta[2,3]-5α-cholestan-3'(4'H)-one (I) and 3',3'-Dichloro-2β,3β-dihydrocyclobuta[2,3]-5α-cholestan-4'(3'H)-one (II)

By L. R. Nassimbeni,* A. G. Orpen, G. M. Sheldrick† and J. C. van Niekerk

Department of Physical Chemistry, University of Cape Town, South Africa

and G. M. L. Cragg

Department of Organic Chemistry, University of Cape Town, South Africa

The title steroids, $C_{27}H_{42}OCl_2$, are both monoclinic. (I) has $a = 45.02$ (2), $b = 6.147$ (5), $c = 10.285$ (5) Å, $\beta = 95.4$ (2)°, $Z = 4$, space group C2. (II) has $a = 15.627$ (5), $b = 7.669$ (5), $c = 12.095$ (5) Å, $\beta = 106.6$ (2)°, $Z = 2$, space group $P2_1$. The puckered cyclobutanone ring in (II) has become flattened due to strong steric interaction. In both structures the steroid rings are all *trans*-fused to one another and the side chains are in extended conformations.

Introduction

Dichloroketene reacts with inactivated alkenes in a stereospecifically *cis* manner to give 1:1 cycloadducts (Brady, 1971). As part of a study of the reaction with steroid alkenes, the reaction of 5α-cholest-2-ene with dichloroketene has been investigated (Cragg, 1970). Two cycloadducts, 4',4'-dichloro-2β,3β-dihydrocyclobuta[2,3]-5α-cholestan-3'(4'H)-one (I), and 3',3'-dichloro-2β,3β-dihydrocyclobuta[2,3]-5α-cholestan-4'(3'H)-one (II), were formed and their structures assigned on the basis of spectroscopic evidence. NMR and circular-dichroism evidence indicated a flattening of the cyclobutanone ring of (II), the flattening being attributed to steric interaction between the 5α proton and the quasi-axial Cl atom. It was therefore considered of interest to determine the conformations of (I) and (II) by X-ray analysis.

(I)　　　　　(II)
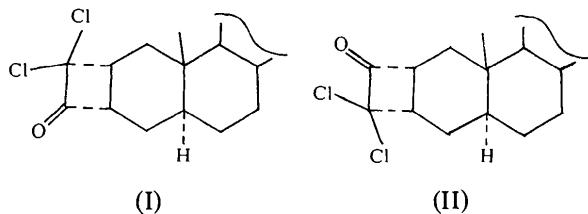
Experimental

(I) and (II) were formed in 52% and 4% yields respectively by reaction of 5α-cholest-2-ene with dichloro-

ketene generated *in situ* by dehalogenation of trichloroacetyl bromide with Zn (Cragg, 1970).

Microanalysis yielded the following results.

	C	H	Cl
Found for (I)	72.30%	9.65%	14.7%
Calculated for (I)	72.35	9.65	14.7
Found for (II)	72.45	9.70	14.3
Calculated for (II)	72.35	9.65	14.7.

Both sets of crystals were colourless needles elongated along **b**.

Preliminary data were obtained from oscillation and Weissenberg photographs (Cu $K\alpha$ radiation, $\lambda = 1.542$

Table 1. *Crystal data*

	(I)	(II)
Molecular formula	$C_{27}H_{42}OCl_2$	$C_{27}H_{42}OCl_2$
M_r	453.5	453.5
Space group	C2	$P2_1$
a	45.02 (2) Å	15.627 (5) Å
b	6.147 (5)	7.669 (5)
c	10.285 (5)	12.095 (5)
β	95.4 (2)°	106.6 (2)°
V	2833.6 Å³	1389.13 Å³
D_m	1.10 g cm⁻³	1.09 g cm⁻³
D_c	1.06 (for $Z = 4$)	1.08 (for $Z = 2$)
μ	2.08 cm⁻¹	2.12 cm⁻¹
$F(000)$	1048	524
Range of reflexions	3° $< \theta < 22$°	3° $< \theta < 22$°
Number of unique reflexions	1907	1790
Scan width	0.9° (θ)	0.9° (θ)
Scan speed	0.03° (θ) s⁻¹	0.03° (θ) s⁻¹
Observed reflexion criteria	I (rel.) $> 2\sigma I$ (rel.)	I (rel.) $> 2\sigma I$ (rel.)
Number of reflexions observed	1612	886

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* Author to whom correspondence should be addressed.
† Visiting Scholar at the University of Cape Town; permanent address: University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

Å). (I) had systematic absences hkl, $h + k = 2n + 1$; $h0l$, $h = 2n + 1$; and $0k0$, $k = 2n + 1$, indicating space group $C2$. (II) had systematic absences $0k0$, $k = 2n + 1$, indicating space group $P2_1$. Crystal data are listed in Table 1.

The cell parameters were obtained by least squares from the settings of 25 reflexions measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, graphite-monochromated). The $\omega-2\theta$ scan technique was used. The background was counted on both sides of the peak for half the peak scan time. The intensities of three standard reflexions measured every hour remained constant to within 1.1 and 3.1% of their mean values for (I) and (II) respectively. Lorentz–polarization but no absorption corrections were applied.

Solution and refinement

Both structures were solved by a multisolution tangent-refinement program, originally written for the NOVA and ECLIPSE minicomputers with 32 K 16-bit word core storage and subsequently adapted to an IBM 370/165 computer. For structure (I), 256 permutations were generated.

The best solution, according to the criteria of the negative quartet test, $NQEST = -0.224$ (De Titta, Edmonds, Langs & Hauptmann, 1975) and $R(\alpha) = 0.086$ (Roberts, Petterson, Sheldrick, Isaacs & Kennard, 1973), yielded an E map with 20 correct atoms out of the top 24 peaks. The two strongest peaks corresponded to the Cl positions. The remaining atoms were found in a subsequent difference map.

Table 2. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *for* (I)

	x	y	z		x	y	z
Cl(1)	2474 (0)	5240	7790 (2)	H(61)	130	280	804
Cl(2)	2743 (0)	−1071 (5)	6624 (2)	H(62)	117	114	671
O(1)	2018 (1)	−2871 (11)	5350 (5)	H(71)	104	−172	821
C(1)	2039 (1)	−1420 (11)	8923 (5)	H(72)	87	72	863
C(2)	2255 (1)	−388 (10)	8020 (5)	H(8)	126	136	1037
C(3)	2088 (1)	464 (12)	6726 (5)	H(9)	151	−290	948
C(3')	2151 (2)	−1718 (14)	6143 (6)	H(111)	176	−28	1180
C(4)	1770 (1)	1329 (13)	6723 (6)	H(112)	189	−278	1126
C(4')	2403 (1)	−2081 (11)	7169 (6)	H(121)	160	−321	1317
C(5)	1588 (1)	114 (13)	7686 (5)	H(122)	144	−465	1178
C(6)	1283 (1)	1148 (14)	7699 (6)	H(14)	105	−308	1031
C(7)	1088 (1)	−114 (16)	8600 (6)	H(151)	73	91	1121
C(8)	1243 (1)	−266 (11)	9986 (5)	H(152)	59	−117	1017
C(9)	1552 (1)	−1351 (11)	9951 (5)	H(161)	49	−336	1192
C(10)	1758 (1)	−88 (11)	9075 (5)	H(162)	56	−105	1292
C(11)	1702 (1)	−1823 (11)	11343 (5)	H(17)	96	−488	1264
C(12)	1493 (1)	−3066 (11)	12199 (5)	H(181)	103	109	1289
C(13)	1197 (1)	−1888 (10)	12280 (5)	H(182)	140	132	1257
C(14)	1057 (1)	−1600 (12)	10871 (5)	H(183)	131	5	1402
C(15)	741 (1)	−811 (17)	11032 (6)	H(191)	164	307	977
C(16)	655 (1)	−2135 (16)	12233 (7)	H(192)	198	306	903
C(17)	942 (1)	−3194 (12)	12868 (6)	H(193)	197	199	1061
C(18)	1248 (2)	308 (13)	13001 (7)	H(20)	91	−171	1474
C(19)	1847 (2)	2181 (10)	9672 (6)	H(211)	140	−306	1482
C(20)	943 (1)	−3352 (13)	14377 (6)	H(212)	130	−583	1487
C(21)	1238 (1)	−4205 (13)	15056 (6)	H(213)	119	−402	1607
C(22)	684 (1)	−4877 (17)	14684 (6)	H(221)	74	−652	1445
C(23)	615 (2)	−4772 (18)	16110 (7)	H(222)	48	−439	1407
C(24)	361 (2)	−6347 (20)	16374 (7)	H(231)	81	−521	1672
C(25)	247 (3)	−6436 (30)	17623 (10)	H(232)	55	−312	1634
C(26)	20 (3)	−8127 (25)	17762 (11)	H(241)	43	−794	1613
C(27)	337 (4)	−5129 (33)	18638 (13)	H(242)	17	−587	1570
H(11)	215	−161	987	H(25)	47	−682	1802
H(12)	197	−298	852	H(261)	−5	−894	1688
H(2)	238	65	870	H(262)	−14	−710	1811
H(3)	214	195	626	H(263)	9	−930	1849
H(41)	177	303	698	H(271)	52	−398	1870
H(42)	165	114	575	H(272)	35	−613	1949
H(5)	155	−153	735	H(273)	12	−423	1856

Table 3. *Fractional atomic coordinates* $(\times 10^3)$ *for* (II)

	x	y	z		x	y	z
Cl(1)	280 (0)	723	230 (0)	H(61)	305	1106	622
Cl(2)	466 (0)	698 (1)	241 (0)	H(62)	253	1181	481
O(1)	396 (0)	354 (1)	354 (1)	H(71)	111	1040	484
C(1)	300 (1)	585 (2)	523 (1)	H(72)	147	1184	602
C(2)	392 (1)	591 (2)	493 (1)	H(8)	215	940	728
C(3)	413 (1)	758 (2)	441 (1)	H(9)	143	721	518
C(3')	387 (1)	673 (2)	318 (1)	H(111)	227	596	759
C(4)	368 (1)	931 (2)	465 (1)	H(112)	188	469	633
C(4')	389 (1)	506 (2)	385 (1)	H(121)	37	547	617
C(5)	280 (0)	905 (2)	492 (1)	H(122)	88	468	757
C(6)	255 (1)	1077 (2)	542 (1)	H(14)	31	875	575
C(7)	162 (1)	1064 (2)	564 (1)	H(151)	82	1112	778
C(8)	165 (1)	914 (2)	648 (1)	H(152)	4	1143	642
C(9)	190 (1)	744 (2)	602 (1)	H(161)	−34	1011	847
C(10)	284 (0)	755 (2)	583 (1)	H(162)	−108	1013	706
C(11)	178 (1)	586 (2)	676 (1)	H(17)	−75	704	675
C(12)	87 (1)	573 (2)	698 (1)	H(181)	188	734	861
C(13)	62 (0)	748 (2)	750 (1)	H(182)	107	688	932
C(14)	69 (1)	897 (2)	664 (1)	H(183)	130	906	903
C(15)	31 (1)	1050 (2)	710 (1)	H(191)	344	897	735
C(16)	−44 (1)	971 (2)	758 (1)	H(192)	424	793	678
C(17)	−34 (0)	770 (2)	751 (1)	H(193)	358	669	746
C(18)	125 (1)	774 (2)	871 (1)	H(20)	−29	728	928
C(19)	359 (1)	781 (2)	692 (1)	H(211)	13	456	866
C(20)	−68 (0)	681 (2)	845 (1)	H(212)	−86	442	754
C(21)	−56 (1)	481 (2)	843 (1)	H(213)	−85	408	899
C(22)	−165 (1)	728 (3)	831 (1)	H(221)	−207	663	756
C(23)	−198 (1)	677 (2)	933 (1)	H(222)	−173	867	820
C(24)	−292 (1)	727 (4)	916 (1)	H(231)	−157	742	1009
C(25)	−337 (1)	653 (3)	1008 (1)	H(232)	−191	538	945
C(26)	−310 (2)	779 (4)	1092 (2)	H(241)	−296	867	918
C(27)	−429 (2)	636 (5)	967 (3)	H(242)	−330	680	832
H(11)	301	477	580	H(25)	−318	521	1037
H(12)	247	568	444	H(261)	−242	824	1128
H(2)	434	547	575	H(262)	−330	704	1156
H(3)	477	819	472	H(263)	−354	890	1067
H(41)	356	1014	390	H(271)	−478	585	892
H(42)	414	996	537	H(272)	−449	765	987
H(5)	230	868	413	H(273)	−423	551	1040

(II) was solved by a similar procedure, with 128 permutations. The E map ranked 13th on the negative quartet test and 4th on $R(\alpha)$ yielded 20 of the 32 atoms, and the remaining atoms were found in a subsequent difference map. The Cl atoms had similar peak heights to C in the E map, probably due to thermal motion.

(I) was refined with all non-H atoms treated anisotropically. A difference map revealed the positions of 42 of the 46 H atoms, giving an R of 0·077. Finally, with constrained least-squares refinement (Sheldrick, 1977), R converged to 0·048 with unit weights.

For (II) only the Cl atoms were treated aniso-tropically. All other non-H atoms were treated iso-tropically since attempts to treat all atoms aniso-tropically gave many non-positive-definite atoms. A difference map revealed the positions of 38 of the 46 H atoms, giving an R of 0·110. The final constrained least-squares refinement with unit weights converged to $R = 0·078$. As checks for the correctness of the structures, difference maps were computed. These had

no peaks $>0·09$ e $Å^{-3}$ for (I) and none $>0·14$ e $Å^{-3}$ for (II). Tables 2 and 3 show the final atomic coordinates. Tables 4 and 5 give the bond lengths and angles.*

Description of the structures and discussion

Perspective views of the molecules are shown in Figs. 1 and 2, the former showing atomic nomenclature. The conformations of the steroid nuclei for both structures are fairly similar, as is shown by their asymmetry parameters (Duax & Norton, 1975; Table 7) and torsion angles (Table 6). The A rings have distorted chair conformations, mirror symmetry about the planes through C(3) and C(10) prevailing. All the steroid

nucleus rings are *trans*-fused to one another. The *B* rings in (I) and (II) both have highly symmetrical chair conformations, all their asymmetry parameters falling below 2·5 and 2·9° respectively. Ring *C* in (I) has a symmetrical chair conformation, mirror symmetry through C(9) and C(13) being dominant. Similarly ring *C* in (II) has a symmetrical chair conformation, but mirror symmetry through C(11) and C(14) prevails in this case. The *D* ring in (I) has the common conformation intermediate between a 13β,14α half-chair and a 13β envelope, whereas in (II) the *D* ring approaches the ideal 13β-envelope conformation (Duax & Norton, 1975). Their pseudorotation parameters (Altona, Geise & Romers, 1968) are shown in Table 7.

Of special interest in these two structures are the cyclobutanone rings. A Dreiding model of (II) with ring *A* in a distorted chair conformation reveals a strong steric interaction between the 5α proton and the quasi-axial Cl atom. It had been suggested (Cragg, 1970) that this interaction may be relieved by flattening of the puckered cyclobutanone ring. In (I), however, model building shows no steric hindrances and one can expect

no change in conformation of the cyclobutanone ring. These predictions, which have been supported by NMR and circular-dichroism evidence (Cragg, 1970), have been borne out by the crystal structures. This is evident

Table 5. *Bond angles* (°)

Compound I		Compound II	
C(2)–C(1)–C(10)	114·6 (5)	C(2) C(1) C(10)	111 (1)
C(1)–C(2)–C(4')	113·1 (5)	C(1)–C(2)- C(4')	113 (1)
C(3)–C(2)–C(1)	111·9 (5)	C(3)–C(2)–C(1)	116 (2)
C(3)–C(2)–C(4')	86·7 (5)	C(3)–C(2)–C(4')	88 (2)
C(2)–C(3)–C(3')	87·0 (5)	C(2)–C(3)–C(3')	91 (1)
C(4)–C(3)–C(2)	119·7 (5)	C(4)–C(3)–C(2)	119 (2)
C(4)–C(3)–C(3')	121·3 (6)	C(4)–C(3)–C(3')	122 (1)
C(3)–C(3')–O(1)	134·2 (7)	Cl(2)–C(3')–Cl(1)	110 (1)
C(3)–C(3')–C(4')	90·6 (5)	C(3)–C(3')–Cl(1)	115 (1)
C(4')–C(3')–O(1)	133·8 (8)	C(3)–C(3')–Cl(2)	116 (1)
C(5)–C(4)–C(3)	112·7 (6)	C(3)–C(3')–C(4')	83 (1)
Cl(2)–C(4')–Cl(1)	107·7 (4)	C(4')–C(3')–Cl(1)	112 (1)
C(2)–C(4')–Cl(1)	119·3 (5)	C(4')–C(3')–Cl(2)	118 (1)
C(2)–C(4')–Cl(2)	111·7 (5)	C(5)–C(4)–C(3)	114 (2)
C(2)–C(4')–C(3')	87·7 (5)	C(2)–C(4')–O(1)	136 (2)
C(3')–C(4')–Cl(1)	119·3 (5)	C(2)–C(4')–C(3')	95 (2)
C(3')–C(4')–Cl(2)	110·1 (5)	C(3')–C(4')–O(1)	129 (2)
C(4)–C(5)–C(10)	112·7 (5)	C(4)–C(5)–C(10)	113 (1)
C(6)–C(5)–C(4)	109·9 (6)	C(6)–C(5)–C(4)	108 (1)
C(6)–C(5)–C(10)	113·0 (5)	C(6)–C(5)–C(10)	109 (1)
C(7)–C(6)–C(5)	111·2 (6)	C(7)–C(6)–C(5)	112 (2)
C(8)–C(7)–C(6)	110·7 (5)	C(8)–C(7)–C(6)	108 (1)
C(9)–C(8)–C(7)	109·8 (5)	C(9)–C(8)–C(7)	112 (2)
C(14)–C(8)–C(7)	111·0 (5)	C(14)–C(8)–C(7)	107 (1)
C(14)–C(8)–C(9)	109·1 (5)	C(14)–C(8)- C(9)	109 (1)
C(8)–C(9)–C(10)	112·5 (5)	C(8)–C(9)–C(10)	111 (2)
C(11)–C(9)–C(8)	111·9 (5)	C(11)–C(9)· C(8)	112 (2)
C(11)–C(9)–C(10)	113·4 (4)	C(11)–C(9)–C(10)	114 (2)
C(5)–C(10)–C(1)	106·7 (5)	C(5)–C(10) ·C(1)	106 (1)
C(9)–C(10)–C(1)	109·6 (5)	C(9)- C(10)–C(1)	108 (1)
C(9)–C(10)–C(5)	107·7 (5)	C(9)- C(10)–C(5)	107 (1)
C(19)–C(10)–C(1)	109·5 (5)	C(19)–C(10) ·C(1)	110 (1)
C(19)–C(10)–C(5)	112·0 (5)	C(19)–C(10)· C(5)	113 (1)
C(19)–C(10)–C(9)	111·3 (5)	C(19)- C(10)–C(9)	113 (1)
C(12)–C(11)–C(9)	112·5 (5)	C(12)–C(11)–C(9)	115 (2)
C(11)–C(12)–C(13)	112·1 (5)	C(11)- C(12)–C(13)	111 (1)
C(14)–C(13)–C(12)	106·7 (5)	C(14)–C(13)–C(12)	106 (1)
C(17)–C(13)–C(12)	117·0 (5)	C(17)–C(13)–C(12)	117 (1)
C(17)–C(13)–C(14)	99·8 (4)	C(17)· C(13)- C(14)	100 (1)
C(18)–C(13)–C(12)	110·6 (5)	C(18)–C(13)–C(12)	109 (1)
C(18)–C(13)–C(14)	112·4 (5)	C(18)–C(13)–C(14)	114 (2)
C(18)–C(13)–C(17)	110·0 (5)	C(18)–C(13) ·C(17)	110 (1)
C(8)–C(14)–C(13)	115·0 (5)	C(8)· C(14)–C(13)	113 (1)
C(15)–C(14)–C(8)	117·5 (6)	C(15)- C(14)–C(8)	118 (2)
C(15)–C(14)–C(13)	103·8 (5)	C(15)- C(14)· C(13)	103 (2)
C(16)–C(15)–C(14)	102·8 (6)	C(16)- C(15)–C(14)	105 (2)
C(17)–C(16)–C(15)	107·4 (5)	C(17)- C(16)–C(15)	105 (2)
C(16)–C(17)–C(13)	103·7 (5)	C(16)- C(17)- C(13)	103 (1)
C(20)–C(17)–C(13)	118·8 (5)	C(20)–C(17)–C(13)	120 (1)
C(20)- C(17)–C(16)	112·1 (5)	C(20) ·C(17)- C(16)	110 (2)
C(21)–C(20)- C(17)	113·5 (5)	C(21)–C(20) ·C(17)	111 (2)
C(21)–C(20)–C(22)	109·7 (6)	C(21) C(20)–C(22)	111 (2)
C(22)–C(20)–C(17)	107·9 (5)	C(22) -C(20) C(17)	111 (1)
C(23)–C(22)–C(20)	113·1 (6)	C(23)- C(22)· ·C(20)	114 (1)
C(24)–C(23)–C(22)	111·2 (7)	C(24)- C(23) C(22)	112 (2)
C(25)–C(24)–C(23)	121·1 (9)	C(25)- C(24) C(23)	116 (2)
C(26)- C(25)·· C(24)	115 (1)	C(26)- C(25) C(24)	99 (2)
C(27)–C(25)–C(24)	125 (1)	C(27) C(25)- C(24)	113 (2)
C(27)··C(25)–C(26)	120 (1)	C(27)- C(25) C(26)	114 (3)

Table 4. *Bond lengths* (Å)

Compound I		Compound II	
C(4')–Cl(1)	1·783 (7)	C(3')–Cl(1)	1·76 (2)
C(4')–Cl(2)	1·790 (7)	C(3')–Cl(2)	1·75 (2)
C(3')–O(1)	1·199 (9)	C(4')–O(1)	1·24 (3)
C(2)–C(1)	1·542 (8)	C(2)–C(1)	1·58 (3)
C(3)–C(2)	1·557 (8)	C(3)–C(2)	1·51 (3)
C(4)–C(3)	1·53 (1)	C(4)–C(3)	1·57 (3)
C(3)–C(3')	1·51 (1)	C(3)–C(3')	1·57 (2)
C(5)–C(4)	1·535 (9)	C(4')–C(3')	1·52 (3)
C(2)–C(4')	1·551 (9)	C(5)–C(4)	1·52 (3)
C(3')–C(4')	1·493 (9)	C(2)–C(4')	1·45 (3)
C(6)–C(5)	1·51 (1)	C(6)–C(5)	1·54 (3)
C(7)–C(6)	1·55 (1)	C(7)–C(6)	1·56 (3)
C(8)–C(7)	1·531 (8)	C(8)–C(7)	1·52 (3)
C(9)–C(8)	1·546 (8)	C(9)–C(8)	1·51 (3)
C(14)–C(8)	1·531 (9)	C(14)–C(8)	1·57 (3)
C(11)–C(9)	1·551 (7)	C(11)–C(9)	1·55 (3)
C(1)–C(10)	1·530 (8)	C(1)–C(10)	1·54 (3)
C(5)–C(10)	1·560 (7)	C(5)–C(10)	1·57 (2)
C(9)–C(10)	1·558 (8)	C(9)–C(10)	1·57 (2)
C(19)–C(10)	1·561 (9)	C(19)–C(10)	1·57 (2)
C(12)–C(11)	1·549 (9)	C(12)–C(11)	1·51 (2)
C(12)–C(13)	1·524 (8)	C(12)–C(13)	1·51 (3)
C(14)–C(13)	1·536 (7)	C(14)–C(13)	1·57 (3)
C(17)–C(13)	1·569 (9)	C(17)–C(13)	1·55 (2)
C(18)–C(13)	1·55 (1)	C(18)–C(13)	1·52 (2)
C(15)–C(14)	1·528 (9)	C(15)–C(14)	1·49 (3)
C(16)–C(15)	1·56 (1)	C(16)–C(15)	1·60 (3)
C(17)–C(16)	1·534 (9)	C(17)–C(16)	1·55 (3)
C(20)–C(17)	1·555 (8)	C(20)–C(17)	1·54 (3)
C(21)–C(20)	1·531 (9)	C(21)–C(20)	1·55 (3)
C(22)–C(20)	1·55 (1)	C(22)–C(20)	1·53 (2)
C(23)–C(22)	1·53 (1)	C(23)–C(22)	1·51 (3)
C(24)–C(23)	1·54 (1)	C(24)–C(23)	1·48 (3)
C(25)–C(24)	1·43 (1)	C(25)–C(24)	1·59 (4)
C(26)–C(25)	1·48 (2)	C(26)–C(25)	1·38 (4)
C(27)–C(25)	1·35 (2)	C(27)–C(25)	1·38 (4)

from the torsion angles of the four-membered rings (extra-nuclear torsion angles, Table 6): in (I) they are fairly large, of the order of 20°, whereas in (II) they are reduced to approximately 12°, showing clearly a

flattening of this ring. This flattening causes the internuclear distance between Cl(1) and H(5) to increase from the model distance of approximately 1·6 Å to 2·78 Å, just within the limits of the sum of the van der Waals radii. Cl(1) of (I) has a close contact of 2·68 Å with H(12) but this is not a sufficiently strong inter-
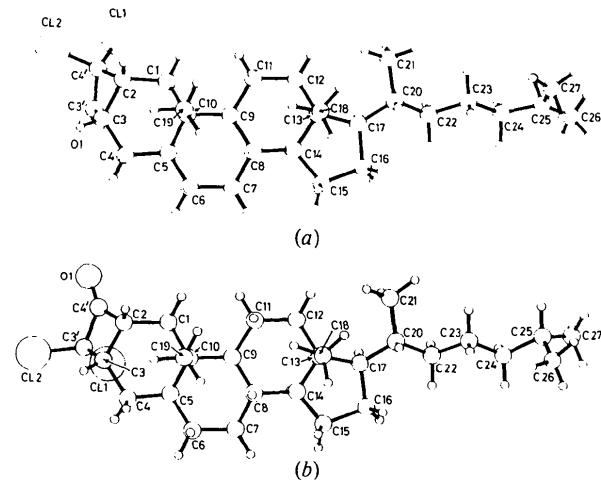
Fig. 1. (a) Perspective view of (I) with atomic nomenclature. (b) Perspective view of (II) with atomic nomenclature.
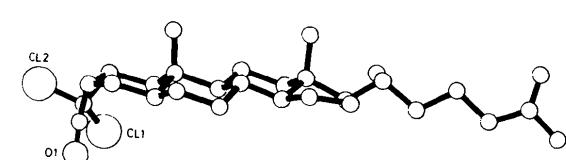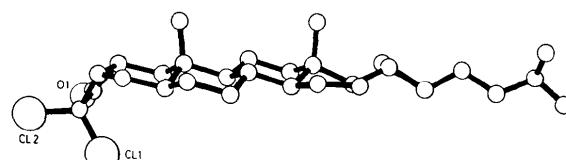
Fig. 2. (a) Perspective side view of (I). (b) Perspective side view of (II).

Table 6. Torsion angles (°)

| Compound I		Compound II	
Ring A		**Ring A**	
C(10) C(1) C(2) C(3)	-46·0	C(10) C(1) C(2) C(3)	-44·2
C(2) C(1) C(10) C(5)	60·9	C(2) C(1) C(10) C(5)	62·4
C(1) C(2) C(3) C(4)	31·9	C(1) C(2) C(3) -C(4)	24·7
C(2) C(3) C(4) C(5)	34·2	C(2) C(3) C(4) C(5)	-25·8
C(3) C(4) C(5) C(10)	49·3	C(3) C(4) C(5) C(10)	46·4
C(4) C(5) C(10) C(1)	62·1	C(4) C(5) C(10) -C(1)	-65·4
Ring B		**Ring B**	
C(10) C(5) C(6) C(7)	56·4	C(10) C(5) C(6) C(7)	-60·9
C(6) C(5) C(10) C(9)	55·0	C(6) C(5) C(10) C(9)	59·6
C(5) C(6) C(7) C(8)	56·6	C(5) C(6) C(7) C(8)	58·0
C(6) C(7) C(8) C(9)	56·9	C(6) C(7) C(8) C(9)	-57·2
C(7) C(8) C(9) C(10)	58·5	C(7) C(8) C(9) C(10)	60·7
C(8) C(9) C(10) C(5)	-55·9	C(8) C(9) C(10) C(5)	60·1
Ring C		**Ring C**	
C(14) C(8) C(9) C(11)	50·7	C(14) C(8) C(9) C(11)	52·0
C(9) C(8) C(14) C(13)	57·8	C(9) C(8) C(14) C(13)	59·5
C(8) C(9) C(11) C(12)	51·1	C(8) C(9) C(11) C(12)	52·0
C(9) C(11) C(12) C(13)	-55·2	C(9) C(11) C(12) -C(13)	-53·8
C(11) C(12) C(13) C(14)	57·0	C(11) C(12) C(13) -C(14)	55·7
C(12) C(13) C(14) C(8)	60·4	C(12) C(13) C(14) -C(8)	-60·0
Ring D		**Ring D**	
C(17) C(13) C(14) C(15)	47·7	C(17) C(13) C(14) C(15)	49·5
C(14) C(13) C(17) C(16)	38·9	C(14) C(13) C(17) C(16)	-43·5
C(13) C(14) C(15) C(16)	37·5	C(13) C(14) C(15) C(16)	-34·9
C(14) C(15) C(16) C(17)	12·2	C(14) C(15) C(16) C(17)	7·7
C(15) C(16) C(17) C(13)	16·8	C(15) C(16) C(17) C(13)	22·8
Extra-nuclear		**Extra-nuclear**	
C(4') C(2) C(3) C(3')	20·8	C(4') C(2) C(3) C(3')	12·3
C(3) C(2) C(4') C(3')	21·0	C(3) C(2) C(4') C(3')	-12·7
C(2) C(3) C(3') C(4')	21·6	C(2) C(3) C(3') C(4')	-11·7
C(3) C(3') C(4') C(2)	21·7	C(3) C(3') C(4') C(2)	12·3

(a)

(b)
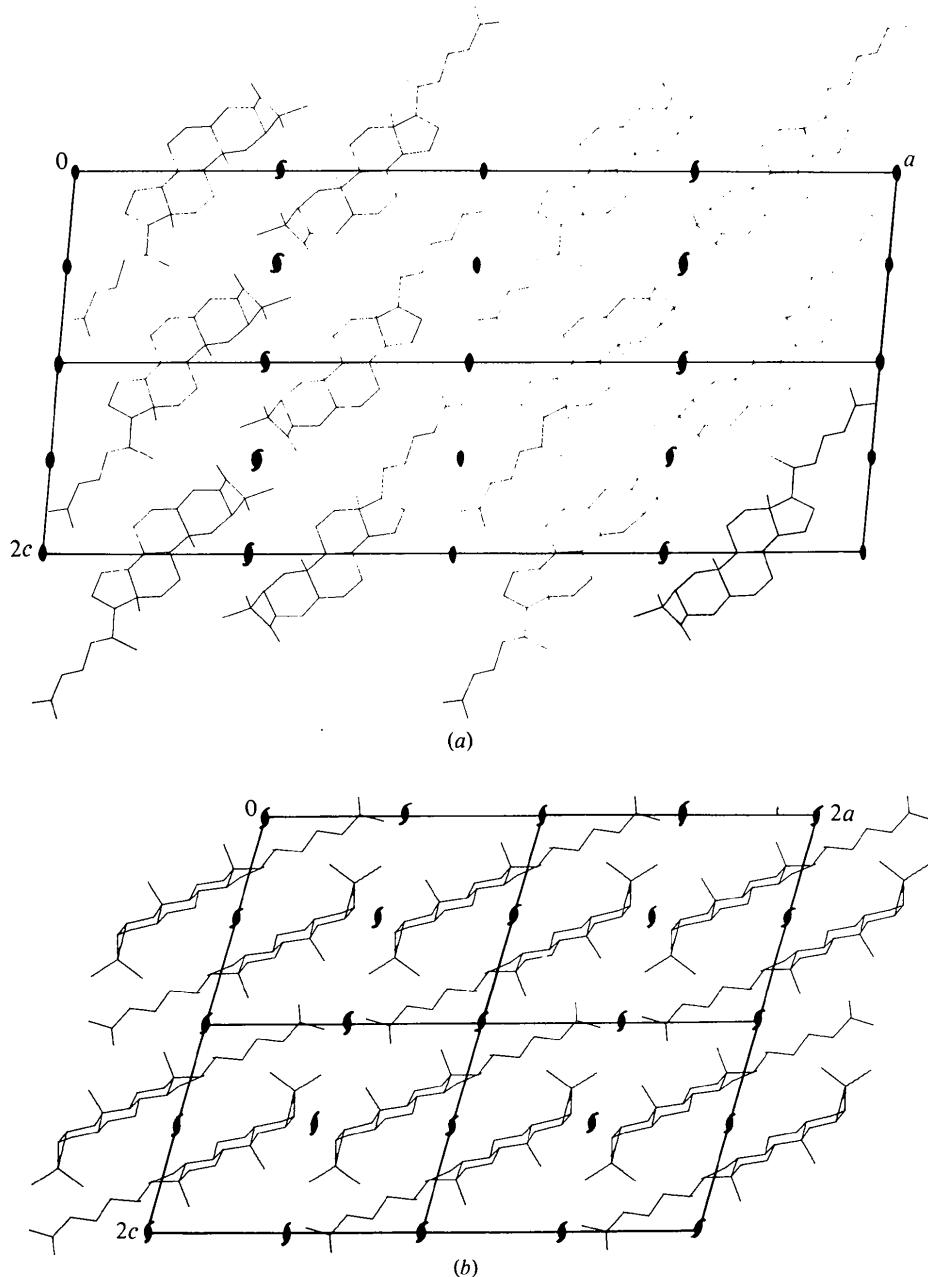
Fig. 3. (a) [010] projection of (I). (b) [010] projection of (II).

action to cause any distortion from the expected conformation.

In both structures the cycloaddition of a dichloroketene occurred on the less hindered α-face of the molecule. However, a structure has been reported (Christensen, 1975) where there is β-face substitution of dichloroethylene on the A ring of androstane. The

resulting compound has a much distorted A ring and the cyclobutyl ring is planar.

Molecular packing of the molecules can be seen in Fig. 3. (I) is packed in a 1 (4) modified Hodgkin notation (Duax & Norton, 1975). It is one molecule thick, the thickness lying parallel to b. The width and length lie in the ac face. (II) is packed with two

Table 7. *Asymmetry parameters and pseudorotation parameters*

	(I)	(II)
Ring A	$\varDelta C_2^3 = 2\cdot39$	$\varDelta C_2^3 = 2\cdot26$
	$\varDelta C_2^{2,3} = 11\cdot75$	$\varDelta C_2^{2,3} = 17\cdot21$
	$\varDelta C_2^{1,2} = 28\cdot41$	$\varDelta C_2^{1,2} = 38\cdot63$
Ring B	$\varDelta C_s^5 = 1\cdot26$	$\varDelta C_s^7 = 0\cdot56$
	$\varDelta C_2^{5,6} = 1\cdot29$	$\varDelta C_2^{5,10} = 1\cdot98$
	$\varDelta C_2^{6,7} = 2\cdot48$	$\varDelta C_2^{5,6} = 2\cdot31$
Ring C	$\varDelta C_s^9 = 2\cdot48$	$\varDelta C_s^{11} = 2\cdot37$
	$\varDelta C_2^{9,11} = 3\cdot24$	$\varDelta C_2^{9,11} = 3\cdot00$
	$\varDelta C_2^{8,14} = 8\cdot01$	$\varDelta C_2^{8,9} = 6\cdot87$
Ring D	$\varDelta = 4\cdot71°$	$\varDelta \quad 17\cdot75°$
	$\varphi_m = 47\cdot71°$	$\varphi_m \quad -50\cdot05°$

molecules per unit cell whereby the length lies parallel to a diagonal of the *ac* face. The width lies approximately in the (111) plane and the thickness in a plane perpendicular to this. There are no significant short intermolecular contacts.

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Structure and Conformation of Amino Acids Containing Sulfur. V. N-Formyl-L-methionine

BY CHENG-SAN CHEN AND R. PARTHASARATHY*

Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, NY 14263, USA

$C_6H_{11}NO_3S$ crystallizes in the orthorhombic space group $P2_12_12_1$ with cell parameters at $22 \pm 3°C$: $a = 7\cdot507$ (2), $b = 14\cdot875$ (1), $c = 7\cdot561$ (1) Å, $Z = 4$, $D_o = 1\cdot39$, $D_c = 1\cdot394$ g cm^{-3}. With diffractometer data to a 2θ limit of 162° for Cu $K\alpha$, the structure was solved and refined by the least-squares method to an R of 0·053 for the correct absolute configuration. The planar carboxyl and acyl groups are inclined to each other at 18·2°. The methionine side chain has the transplanar zigzag extended conformation commonly found for other methionine side chains and aliphatic groups. Short hydrogen bonds (2·555 Å) from the OH of the carboxyl groups to the acyl O atom link the molecules in a head-to-tail fashion in infinite chains along the a axis. The conformations of the side chains of methionine residues are compared and it was found that some correlation exists between the values of χ^1 and χ^2. The preferred values are: $\chi^1 = \pm60, 180$; $\chi^2 = 180$ and $\chi^3 = 180°$.

Introduction

The blocked amino acid N-formyl-L-methionine is the initiator amino acid in the synthesis of proteins in all bacterial systems (Lengyel & Söll, 1969). Protein synthesis in eucaryotic cells is initiated in a manner similar to that of bacteria, but the Met-tRNA initiator is not formylated. The growing polypeptide chain is rapidly deformylated (Adams, 1968) and before the nascent chain is 15 to 20 residues in length, the initiator methionine residue is removed (Wilson & Dintzis, 1970; Jackson & Hunter, 1970). Our interest was to investigate what selective advantage, if any, is conferred by methionine as the initiator amino acid to the protein-synthesizing systems over other amino acids.

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* To whom correspondence should be addressed.