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The Structural Formula and Crystal Structure of Pentachloroethoxycodide, $C_{20}H_{24}NO_3Cl_5$

BY ISABELLA L. KARLE AND JEROME KARLE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C., 20390, *U.S.A.*

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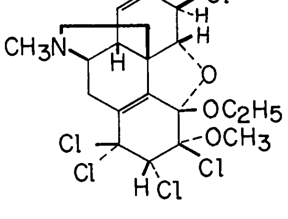
α-Chlorocodide treated with cold SO_2Cl_2 yields the unusual product pentachlorooxycodide. X-ray analysis has established the structural formula of the ethoxy derivative. The four additional Cl atoms have been added to ring I of the codide in equatorial positions on C(1), C(2) and C(3) and in an axial position on C(1), the ethoxy group has been added to C(4) in an axial position *trans* to the methoxy group on C(3). The prismatic crystals are in space group $P2_12_12_1$ with $a = 13{\cdot}38 \pm 0{\cdot}02$, $b = 9{\cdot}50 \pm 0{\cdot}02$ and $c = 17{\cdot}58 \pm 0{\cdot}03$ Å. The symbolic addition procedure was used to obtain the initial phases for the structure determination.

Introduction

An unusual chemical reaction takes place when α-chlorocodide is treated with cold SO_2Cl_2. The end product has a total of five chlorine atoms and an extra oxygen atom. Spectroscopic data show conclusively that the end product no longer contains the aromatic ring present in the codide molecule. The extreme sensitivity of the product to most agents precluded the establishment of the structural formula by chemical means; hence the purpose of this investigation was to elucidate the structure and configuration by an X-ray diffraction analysis. The original product was in the form of thin, silky needles; however, quenching the reaction mixture with cold C_2H_5OH rather than ice produced the ethoxy derivative which forms good prismatic crystals. The molecule is identified to be



A preliminary account of this work has been published (Eisner, Batterham, Weiss & Karle, 1968).

Experimental

Samples of pentachlorooxycodide and the ethoxy analog were prepared by Drs U. Eisner and U. Weiss of the National Institutes of Health. The oxy-compound did not form good crystals whereas the ethoxy analog crystallized into well-shaped stout prisms elongated about the *b* axis with good optical extinctions. The crystals, however, deteriorated fairly rapidly in the X-ray beam. The diffraction spots became fuzzy and lost intensity and the optical extinctions disappeared. For this reason, the data were obtained from several different crystals. Large crystals, ~0·5 × 0·5 × 0·5 mm, were used so as to minimize exposure time to X-rays. Cell parameters listed in Table 1 were determined from precession photographs. The intensity data were collected by the multiple-film equi-inclination Weissenberg technique and estimated visually by comparison with a calibrated film strip. Layers 0–6 about the *b* axis and layers 0–1 about the *c* axis were recorded. Corrections were made for spot size and Lorentz and polarization factors. The data were cross-correlated, put on an absolute scale and corrected for vibrational motion by means of a *K*-curve (Karle & Hauptman, 1953) and normalized structure factor magnitudes $|E|$ were derived.

Table 1. *Physical constants for pentachloroethoxycodide*

Mol. formula	$C_{20}H_{24}NO_3Cl_5$
Mol. wt.	503·70
m.p.	183–184 °C
Habit	Stout prisms
Space group	$P2_12_12_1$
a	13·38 ± 0·02 Å
b	9·50 ± 0·02 Å
c	17·58 ± 0·03 Å
Z	4
Vol.	2234·6 Å^3
ϱcalc	1·497 g.cm^{-3}
Radiation	Cu $K\alpha$ (1·5418 Å)
No. independent reflections	1390
Crystal size	~0·5 × 0·5 × 0·5 mm

Structure analysis

The symbolic addition procedure as applied to noncentrosymmetric crystals (Karle & Karle, 1963; 1966) was used to obtain phases for the initial E-map. The origin was specified by assigning phases to three reflections with large $|E|$ values; 1, 0, 16 (0), 0, 4, 13 (0), and 0, 3, 21 ($+\pi/2$); and the specification of the enantiomorph was effected by assigning $+\pi/2$ to 2, 0, 11. In addition, unknown symbols were assigned to two other reflections; 7, 4, 0 (q) and 9, 5, 0 (s). It is not necessary to assign symbols only to two-dimensional reflections but it is quite convenient to do so where possible, since in this case, the unknowns can have only two values, $\pm\pi/2$. The six reflections whose phases were assigned were used to implement the relationship (Karle & Hauptman, 1950)

$$\varphi_{\mathbf{h}} \simeq \langle \varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}} \rangle_{\mathbf{k}_r} . \tag{1}$$

Fifty phases obtained by the use of (1) were used in the tangent formula (Karle & Hauptman, 1956),

$$\tan \varphi_{\mathbf{h}} \simeq \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \sin (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}}E_{\mathbf{h}-\mathbf{k}}| \cos (\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})} , \tag{2}$$

to obtain phases for a total of 420 reflections with $|E| > 1·1$. There were four possibilities and E-maps were computed for each. In two of the maps some of the largest peaks were too close together. A third map had only one large peak. The fourth map with the unknown symbols given the values $q = -\pi/2$, $s = +\pi/2$, had four large peaks separated by minimum distances of 3 Å.

These four peaks were assumed to represent four of the Cl atoms. Actually they were Cl(1) through Cl(4). The next largest peak in the original E-map proved to be Cl(5). Since this peak was not much stronger than some of the others representing C and O atoms, it was not used as part of the known partial structure. The remainder of the atoms were located in a recycling procedure (Karle, 1968) using phases from the known partial structure in the tangent formula (2) to generate phases for other reflections with $|E| > 1·0$.

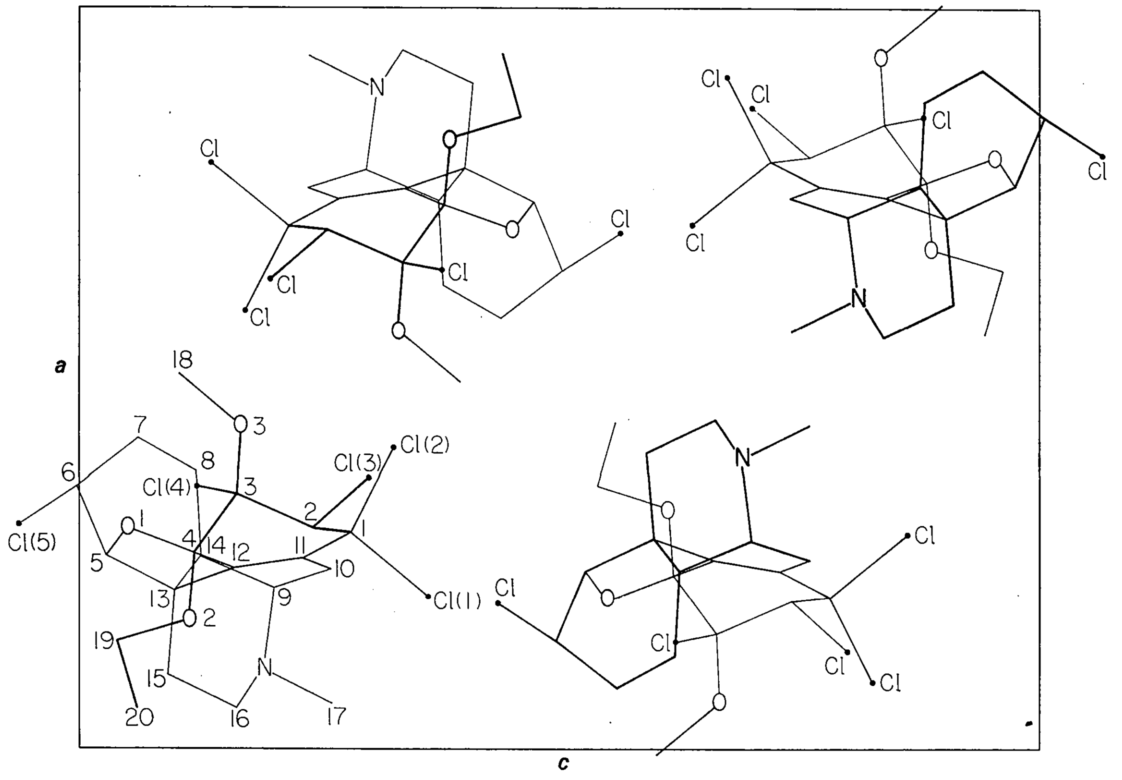


Fig. 1. The orientation of the molecules and the packing in a unit cell viewed along the b axis.

Table 2. *Observed and calculated structure factors*

The column headings are the index l, $|F_o|$, $|F_c|$ and φ (radians).

0 0 L			
2	106.0	110.3	-3.14
4	138.4	153.0	-3.14
6	13.8	17.4	0.00
8	0.0	1.9	-3.14
10	30.6	29.9	-3.14
12	37.7	35.5	-3.14
14	17.2	17.0	-3.14
16	34.7	33.3	0.00
18	15.7	18.1	0.00
0 1 L			
1	72.1	76.7	-1.57
2	4.4	1.6	-1.57
3	42.6	49.9	-1.57
4	171.5	190.7	-1.57
5	47.5	53.3	-1.57
6	31.5	31.6	-1.57
7	64.2	72.1	1.57
8	0.0	1.5	1.57
9	0.0	10.1	-1.57
10	0.0	0.9	1.57
11	26.4	30.8	-1.57
12	18.1	17.1	1.57
13	12.1	13.2	-1.57
14	0.0	11.6	-1.57
15	0.0	2.8	-1.57
16	45.5	52.9	1.57
17	20.5	24.1	1.57
0 2 L			
0	72.1	76.5	0.00
1	32.8	23.9	0.00
2	46.2	40.4	-3.14
3	0.0	11.4	3.14
4	63.3	54.9	-3.14
5	23.0	14.8	-0.00
6	23.0	14.5	0.00
7	55.6	58.7	3.14
8	12.1	14.1	-3.14
9	18.4	13.6	3.14
10	69.9	68.1	-3.14
11	56.1	54.0	0.00
12	15.7	15.6	-3.14
13	0.0	5.6	0.00
14	17.1	9.9	0.00
15	0.0	14.6	-3.14
16	27.7	21.3	0.00
0 3 L			
1	30.7	27.0	-1.57
2	95.8	102.6	-1.57
3	61.0	49.4	-1.57
4	32.3	28.6	1.57
6	21.6	17.6	-1.57
7	34.1	34.6	1.57
8	9.5	12.1	1.57
9	36.1	31.5	1.57
10	60.6	57.5	1.57
11	23.0	18.9	1.57
12	46.6	42.1	-1.57
13	30.8	29.6	1.57
14	15.9	15.4	1.57
15	34.7	36.4	-1.57
16	31.9	27.5	1.57
17	35.6	32.8	-1.57
18	0.0	1.0	1.57
19	0.0	9.9	-1.57
20	30.7	19.8	-1.57
21	26.6	18.9	1.57
0 4 L			
0	44.1	44.6	0.00
1	73.9	68.4	-3.14
2	25.6	18.5	0.00
3	83.9	77.3	-3.14
4	52.9	49.5	3.14
5	53.6	45.2	-3.14
6	29.5	25.5	-3.14
7	15.9	4.8	-0.00
8	64.5	61.4	0.00
9	20.5	17.6	0.00
10	43.1	37.2	-0.00
11	7.6	11.1	-0.00
12	31.8	28.7	-3.14
13	56.3	59.5	0.00
14	0.0	2.0	-0.00
15	0.0	1.6	0.00
16	0.0	5.3	-3.14
17	17.3	10.2	-3.14
18	10.1	2.1	-3.14
19	20.8	13.8	0.00
20	19.9	14.8	0.00
0 5 L			
1	0.9	2.7	-1.57
2	50.6	56.2	-1.57
3	52.4	55.9	-1.57
4	29.2	24.8	1.57
5	40.3	36.8	-1.57
6	67.4	67.3	1.57
7	65.9	67.4	1.57
8	32.3	29.9	-1.57
9	31.1	30.3	1.57
10	43.2	41.3	-1.57
11	28.5	25.4	-1.57
12	0.0	1.5	1.57
13	13.8	12.3	1.57
14	0.0	4.4	-1.57
15	13.5	14.6	1.57
16	25.9	26.7	1.57
17	21.0	22.1	-1.57
18	26.8	27.9	-1.57
19	0.0	5.0	-1.57
0 6 L			
0	28.7	27.5	-3.14
1	52.1	56.6	0.00
2	45.9	52.1	-3.14
3	18.9	16.2	-3.14
4	39.3	33.4	0.00
5	49.2	51.1	-3.14
6	47.0	44.0	0.00
7	6.3	6.5	-3.14
8	46.4	43.7	-3.14
9	63.4	62.9	-3.14
10	16.2	15.1	0.00
11	31.6	31.8	0.00
12	37.0	36.9	0.00
13	26.1	31.1	0.00
14	19.5	20.0	-3.14
15	10.0	8.8	-3.14
16	13.3	11.1	-3.14
0 7 L			
1	27.8	31.5	-1.57
0 8 L			
0	41.3	47.0	-3.14
1	21.5	20.1	-3.14
0 9 L			
1	25.2	26.3	1.57
0 10 L			
0	10.0	11.7	-3.14
1	0.0	5.1	0.00
0 11 L			
1	0.0	1.7	-1.57
1 0 L			
1	90.0	94.2	-1.57
2	130.4	140.2	-3.14
3	15.2	21.0	1.57
4	75.7	75.9	-3.14
5	81.6	84.1	1.57
6	69.9	79.7	0.00
7	31.5	34.9	-1.57
8	4.8	2.8	-0.00
9	20.8	20.9	1.57
10	54.1	57.8	-3.14
11	22.5	21.0	-1.57
12	54.8	60.2	-3.14
13	16.5	14.0	-1.57
14	10.0	8.8	-3.14
15	15.2	22.2	1.57
16	58.3	52.1	0.00
17	0.0	4.7	1.57
18	0.0	8.6	0.00
19	16.1	19.5	-1.57
20	17.6	13.3	-3.14
1 1 L			
0	115.1	134.0	-1.57
1	66.4	58.9	1.78
2	66.9	79.1	0.88
3	57.5	51.9	-2.99
4	70.0	74.3	2.11
5	22.8	13.1	-2.49
6	79.2	92.1	-2.27
7	38.6	41.7	0.14
8	52.9	52.7	-1.38
9	26.8	30.0	1.58
10	39.4	35.8	2.20
11	17.2	20.1	-1.46
12	24.4	26.2	0.70
13	29.7	32.1	1.29
14	25.3	26.2	0.52
15	19.0	16.5	1.94
16	18.6	23.7	2.41
17	20.5	24.7	-2.29
1 2 L			
0	15.5	16.0	-1.57
1	148.5	136.9	0.30
2	49.3	46.4	0.31
3	82.2	80.9	-2.67
4	85.9	89.2	0.12
5	67.8	58.4	3.05
6	66.1	63.2	-2.37
7	31.9	27.4	-0.31
8	47.3	38.6	1.23
9	0.0	7.7	2.70
10	28.0	19.8	0.10
11	36.5	31.2	1.80
12	54.5	47.6	-2.66
13	36.9	29.7	-1.39
14	41.9	35.3	1.16
15	24.7	27.0	-0.39
16	17.5	17.8	0.87
1 3 L			
0	49.2	37.8	1.57
1	117.4	110.5	0.95
2	58.1	50.8	-2.11
3	73.8	64.1	3.11
4	92.4	79.8	2.49
5	153.1	130.5	-0.97
6	94.3	84.4	0.44
7	25.2	17.1	3.01
8	77.5	71.9	-1.53
9	58.3	50.7	2.47
10	53.2	50.0	2.96
11	56.3	52.0	1.07
12	17.1	18.6	-1.85
13	51.8	51.9	-1.74
14	18.3	13.9	-0.69
15	13.1	10.0	-0.48
16	0.0	2.0	2.88
17	12.6	15.6	1.03
18	0.0	6.5	0.46
19	0.0	2.6	-1.98
20	18.2	10.9	-0.72
21	14.1	15.2	-1.58
1 4 L			
0	8.9	12.0	-1.57
1	71.2	65.9	0.20
2	95.7	76.8	2.99
3	122.2	105.1	-2.94
4	44.8	35.4	-0.60
5	62.3	56.3	0.33
6	37.0	31.4	-0.44
7	39.8	31.5	2.21
8	37.4	30.2	0.26
9	32.4	24.9	-1.48
10	43.3	41.4	-1.47
11	42.2	49.3	-2.98
12	40.3	40.5	2.43
13	28.4	23.3	0.64
14	0.0	5.0	3.12
15	28.8	24.7	-0.35
16	0.0	8.9	-0.27
17	10.9	8.5	2.79
18	22.6	19.7	-2.98
19	23.4	19.7	3.12
1 5 L			
0	41.3	39.0	-1.57
1	43.7	39.7	-0.53
2	15.7	14.1	1.60
3	47.6	38.4	-3.00
4	44.9	44.6	0.96
5	37.1	37.2	-2.63
6	28.2	16.9	0.36
7	24.9	20.0	0.39
8	26.5	23.2	-2.95
9	17.1	12.3	-2.93
10	19.4	18.0	-0.89
11	39.5	40.1	1.17
12	17.6	18.2	1.73
13	17.8	23.4	-1.85
14	13.8	17.3	-2.54
15	27.0	28.0	2.26
16	10.6	11.4	-1.16
17	9.8	13.0	0.85
18	0.0	1.9	2.69
19	28.1	33.2	-1.70
1 6 L			
0	42.8	40.6	1.57
1	32.5	34.9	-0.34
2	33.9	35.0	-1.12
3	20.5	20.0	-3.09
4	0.0	1.7	2.27
5	45.8	45.6	-3.06
6	36.1	36.8	1.66
7	36.1	34.4	-0.78
8	0.0	5.4	-3.06
9	28.1	27.8	0.98
10	27.2	25.7	-0.27
11	7.5	13.2	2.64
12	30.2	30.1	0.07
13	0.0	8.1	-0.35
14	10.4	12.5	-2.90
15	14.1	16.7	-0.07
16	16.2	20.0	2.72
1 7 L			
0	35.6	35.2	1.57
1	12.2	15.3	2.33
1 8 L			
0	23.1	24.3	-1.57
1	23.2	24.6	-2.53
1 9 L			
0	4.4	4.9	-1.57
1	13.3	14.8	0.74
1 10 L			
0	12.2	14.5	-1.57
1	16.5	17.8	-0.42
1 11 L			
0	10.1	9.0	1.57
1	0.0	10.2	-2.42
2 0 L			
0	280.0	287.9	-3.14
1	43.7	61.2	-1.57
2	0.0	0.8	3.14
3	72.7	81.3	-1.57
4	13.0	19.8	0.00
5	120.0	125.3	1.57
6	39.3	45.5	0.00
7	81.8	92.3	-1.57
8	72.9	75.5	-3.14
9	0.0	7.2	-1.57
10	36.0	38.6	0.00
11	76.3	77.9	1.57
12	55.6	57.3	0.00
13	34.3	33.1	-1.57
14	26.6	24.6	-3.14
15	29.2	31.5	-1.57
16	0.0	10.7	-3.14
17	17.8	19.7	-1.57
18	9.9	6.3	0.00
19	6.5	5.4	1.57
2 1 L			
0	32.5	34.2	0.00
1	153.2	152.9	2.72
2	91.0	95.5	3.06
3	83.7	95.3	0.32
4	91.7	108.7	2.31
5	29.6	32.1	2.12
6	63.4	69.8	1.82
7	77.2	91.1	-2.83
8	34.9	42.8	0.19
9	54.7	63.5	-0.35
10	45.5	52.6	-0.65
11	35.5	38.5	0.56
12	28.6	32.8	3.09
13	22.9	29.0	-2.89
14	0.0	5.6	-0.19
15	16.0	18.5	-0.73
16	37.1	40.9	-1.83
2 2 L			
0	46.0	43.6	-3.14
1	35.5	27.7	-1.18
2	46.6	40.9	2.52
3	99.7	86.7	0.47
4	64.5	61.6	0.85
5	41.6	36.8	-0.86
6	52.0	43.2	1.27
7	63.7	54.6	0.86
8	24.9	24.1	-0.62
9	61.5	61.6	1.30
10	37.6	38.6	0.46
11	32.0	24.9	2.86
12	39.0	37.3	-0.38
13	47.0	47.3	-2.64
14	38.4	37.9	-2.51
15	24.7	23.9	0.08
16	30.3	36.4	2.29
2 3 L			
0	148.0	145.1	-3.14
1	68.1	50.7	0.14
2	77.5	67.1	-1.93
3	30.8	26.7	1.67
4	104.5	91.0	0.95
5	75.3	63.4	-2.76
6	55.6	49.6	-0.13
7	39.0	35.0	-2.05
8	28.7	25.5	-0.99
9	46.1	40.9	-2.11
10	20.7	16.0	-2.87
11	35.0	34.1	0.34
12	36.7	34.8	0.49
13	28.4	24.1	-0.96
14	41.2	44.7	-1.01
15	15.0	16.5	1.40
16	0.0	9.0	-2.83
17	30.6	23.6	1.30
18	28.6	20.8	-2.96
19	0.0	9.5	1.98
20	19.5	15.4	1.03
21	15.5	13.6	-1.94
2 4 L			
0	17.6	14.3	-3.14
1	35.6	31.6	-1.52
2	47.1	38.2	2.04
3	76.1	72.9	0.95
4	74.5	58.3	1.17
5	42.3	36.5	-1.44
6	44.3	36.8	-2.20
7	56.6	50.6	-1.52
8	32.3	30.9	1.53
9	31.3	25.2	1.67
10	16.5	13.2	2.45
11	10.9	7.5	-2.47
12	30.0	23.4	-1.00
13	45.5	40.9	2.96
14	20.4	23.9	-1.13
15	14.4	16.0	2.06
16	0.0	8.7	-2.21
17	22.9	21.5	-1.05
2 5 L			
0	43.6	47.9	0.00
1	61.3	58.4	2.89
2	36.4	28.6	-2.98
3	62.1	59.8	1.72
4	44.1	42.8	-2.89
5	29.1	25.3	-0.18
6	37.9	36.6	-0.72
7	51.8	53.7	-1.30
8	9.5	9.3	-0.27
9	10.0	8.5	-1.48
10	46.8	46.3	1.59
11	45.5	48.2	-3.05
12	0.0	8.6	-0.44
19	17.1	16.4	0.78
2 6 L			
0	75.1	74.9	0.00
1	46.1	44.0	1.28
2	47.6	52.2	1.31
3	46.7	47.4	-1.24
4	41.8	39.3	-2.36
5	20.2	17.9	-0.47
6	42.8	42.6	1.75
7	26.0	25.7	0.31
8	9.6	9.6	-1.95
9	21.3	21.0	-0.01
10	20.7	17.9	-1.94
11	7.5	10.6	-2.76
12	20.0	17.3	2.66
13	19.9	23.3	-2.32
14	7.3	11.4	-0.64
15	14.0	19.7	1.54
2 7 L			
0	27.7	29.7	0.00
1	12.4	11.2	0.29
2 8 L			
0	55.9	65.6	0.00
1	6.2	6.3	0.99
2 9 L			
0	6.2	9.8	3.14
1	16.6	21.9	-2.33
2 10 L			
0	16.1	13.9	0.00
1	14.2	15.7	2.57
2 11 L			
0	0.0	0.2	0.00
1	12.3	12.0	0.22
3 0 L			
1	58.2	55.5	1.57
2	35.2	28.3	-3.14
3	97.5	97.2	-1.57
4	75.7	84.6	-3.14
5	14.3	9.4	-1.57
6	29.0	38.8	0.00
7	8.3	11.1	1.57
8	15.4	13.3	-3.14
9	9.5	3.9	1.57
10	15.5	14.4	0.00
11	23.4	21.5	1.57
12	49.6	55.0	0.00
13	0.0	8.6	1.57
14	0.0	12.5	0.00
15	16.4	17.7	-1.57
16	25.5	26.6	-3.14
17	0.0	9.9	-1.57
18	0.0	5.6	0.00
19	9.0	14.3	1.57
3 1 L			
0	35.2	28.0	1.57
1	84.3	77.7	-0.93
2	39.5	34.2	-3.12
3	30.1	27.7	0.68
4	49.8	46.9	-3.01
5	43.8	46.4	-2.10
6	51.8	56.4	-0.56
7	45.0	54.4	2.39
8	58.7	75.3	1.33
9	40.0	44.7	-1.37
10	10.6	18.0	-1.30
11	33.8	45.2	-1.01
12	22.2	25.3	-1.45
13	27.8	27.1	1.96
14	22.3	20.7	2.21
15	9.3	12.5	-2.02
3 2 L			
0	90.6	79.4	-1.57
1	131.4	119.3	-1.01
2	42.7	42.3	2.71
3	81.0	75.0	-1.85
4	80.5	79.1	0.58
5	68.0	61.7	0.97
6	41.4	42.2	-2.79
7	0.0	8.3	0.43
8	40.9	34.8	-2.97
9	51.5	50.4	3.11
10	14.6	13.0	0.48
11	43.6	39.9	-0.93
12	0.0	10.7	-0.55
13	41.2	37.6	1.55
14	30.0	30.3	-2.03
15	42.9	45.8	2.94
16	27.5	27.1	-2.07
3 3 L			
0	33.0	34.5	1.57
1	34.1	29.5	1.49
2	97.1	91.8	-0.71
3	51.0	37.6	0.10
4	55.6	43.9	-0.14
5	101.1	86.0	2.96
6	113.8	102.7	-3.11
7	35.1	26.9	1.62
8	37.7	26.3	0.27
9	44.1	38.1	-1.80
10	67.7	64.0	0.37
11	16.8	13.2	-2.23
12	27.8	23.5	-0.86
13	31.4	31.6	1.91
14	27.7	26.2	-2.62
15	22.7	20.0	-2.45
16	24.0	22.1	1.71
17	0.0	11.4	-0.29
18	0.0	8.3	-1.60
19	26.8	19.1	1.35
20	18.8	16.4	-3.01
21	13.2	8.6	2.25
3 4 L			
0	33.1	28.3	1.57
1	68.2	64.2	-2.99
2	52.2	47.1	-2.84
3	32.5	27.6	0.37
4	73.6	64.0	0.50
5	19.9	14.3	0.68
6	18.2	15.7	1.42
7	24.1	22.7	-2.18
8	43.7	39.4	-2.87
9	22.7	17.0	1.16
10	67.6	70.7	0.86
11	31.4	25.7	0.17
12	34.4	33.4	-2.06
13	40.6	40.3	-2.62
14	11.8	15.5	-1.51
3 5 L			
0	0.0	0.2	1.57
1	39.3	43.6	-1.95
2	28.5	27.5	2.65
3	39.1	34.1	-1.68
4	8.0	8.3	-0.41
5	59.0	58.7	0.69
6	33.2	30.2	2.75
7	9.3	8.7	-1.10
8	15.5	16.3	0.19
9	14.5	14.7	-1.69
10	15.1	13.9	0.05
11	15.6	14.0	-0.99
12	21.0	22.5	1.88
3 6 L			
0	48.4	53.6	-1.57
1	19.0	13.7	-2.43
2	14.1	14.7	0.21
3	38.5	43.2	-0.07
4	18.4	18.4	2.75
5	25.9	25.1	2.81
6	27.2	24.5	-1.82
7	25.0	24.3	1.40
8	12.1	10.8	-3.08
9	38.2	37.1	-0.53
10	16.6	19.8	1.29
11	13.0	10.8	-1.61
12	0.0	11.2	1.86
13	0.0	7.0	-2.08
14	10.2	17.7	-2.08
15	9.7	12.7	2.41
16	14.8	15.6	-0.65
17	17.1	15.8	1.67
3 7 L			
0	22.0	21.7	-1.57
1	40.3	40.7	-0.98
3 8 L			
0	24.1	27.1	1.57
1	6.3	6.9	-2.02
3 9 L			
0	17.4	19.8	-1.57
1	23.4	28.7	1.97
3 10 L			
0	0.0	4.1	1.57
1	13.9	19.3	0.34
3 11 L			
0	3.9	6.2	1.57
1	19.5	20.3	0.40
4 0 L			
0	23.2	33.2	-3.14
1	125.4	128.9	1.57
2	13.3	11.1	0.00
3	36.9	34.5	-1.57
4	33.9	28.9	-0.00
5	27.5	25.9	-1.57
6	71.4	64.4	-3.14
7	34.6	37.2	1.57
8	54.6	54.4	0.00
9	51.8	54.4	-1.57
10	50.0	57.2	-3.14
11	34.2	33.7	-1.57
12	0.0	1.2	-3.14
13	10.0	12.4	1.57
14	12.6	14.2	0.00
15	25.5	24.5	1.57
16	16.4	15.2	-3.14
17	17.4	19.2	1.57
18	9.5	7.7	-3.14
19	15.1	18.5	-1.57
4 1 L			
0	58.8	63.2	-3.14
1	57.2	65.7	-2.30
2	61.4	66.2	-0.72
3	36.4	32.7	1.17
4	47.6	47.3	0.15
5	115.7	144.2	0.30
6	38.3	41.7	-2.00
7	47.1	47.9	-1.43
8	9.8	14.5	1.94
9	31.5	33.9	2.52
10	23.3	23.7	1.47
11	8.2	11.3	2.31
12	17.2	15.3	-1.45
13	20.0	26.3	2.70
14	0.0	13.8	-0.08
15	27.8	35.0	1.86
4 2 L			
0	96.1	89.0	0.00
1	46.4	47.8	2.99
2	86.3	78.5	-1.50
3	61.3	49.8	2.76
4	64.3	58.7	-2.59
5	21.3	18.2	-2.35
6	45.2	29.8	-2.18
7	0.0	7.7	-2.12
8	38.2	33.1	-0.89
9	40.4	38.3	-1.70
10	30.2	29.1	0.62
11	38.8	34.3	-2.43
12	30.9	34.7	3.02
13	32.0	29.9	0.07
14	37.0	34.4	0.97
4 3 L			
0	38.3	37.0	0.00
1	21.3	21.8	-2.82
2	81.5	79.3	0.53
3	25.9	20.2	-2.56
4	76.6	73.4	-1.72
5	39.5	33.8	-1.45
6	84.8	75.8	2.41
7	36.0	36.9	0.64
8	29.9	29.6	2.85
9	38.4	38.3	1.95
10	21.8	16.3	-0.64
11	32.3	26.0	-1.86
12	37.9	34.0	-2.92
13	0.0	8.6	-0.12
14	24.5	23.4	1.69
15	0.0	9.2	-2.96
16	0.0	7.3	0.58
17	0.0	10.1	-2.94
18	27.2	25.1	-0.01
19	17.1	15.5	-1.11
20	0.0	8.0	-1.50
4 4 L			
0	5.4	6.5	0.00
1	23.5	20.5	-0.06
2	64.6	67.8	-1.30
3	58.7	56.7	2.20
4	57.0	56.2	-1.55
5	31.8	31.7	-1.33
6	28.7	26.1	1.14
7	6.7	8.5	1.21
8	36.8	34.9	-2.48
9	33.1	27.7	2.34
10	20.4	17.4	-2.20
11	42.7	42.3	-0.95
12	36.7	34.3	1.33
13	0.0	6.9	-1.23
14	33.3	32.8	2.09
4 5 L			
0	0.0	6.6	0.00
1	31.1	32.3	-1.48
2	40.0	39.2	-0.44
3	20.1	14.8	-0.84
4	33.6	28.1	0.62
5	43.0	42.9	2.22
6	48.1	48.5	-1.89
7	16.8	15.6	1.66
8	58.2	55.9	2.88
9	27.8	28.6	-1.20
10	23.1	19.0	-1.09
11	31.5	28.6	0.33
12	0.0	3.8	2.33
13	27.6	24.0	1.56
14	19.2	16.7	3.03
15	10.6	17.4	-2.73
16	18.7	18.2	-0.61
17	11.2	12.3	-0.74
18	26.1	23.4	0.20
4 6 L			
0	5.5	3.6	-0.00
1	82.1	85.7	-2.63
2	11.6	8.8	-0.25
3	15.8	15.3	2.33
4	24.8	20.7	-2.43
5	31.5	29.0	0.78
6	11.6	12.1	2.58
7	9.8	3.6	-2.79
8	37.9	35.6	0.08
9	20.8	21.7	1.62
10	26.0	29.8	-2.36
11	20.0	19.8	2.29
12	0.0	10.8	1.36
13	13.4	14.1	0.83
4 7 L			
0	5.9	5.0	0.00
1	48.5	47.3	2.86
4 8 L			
0	22.7	24.1	-3.14
1	18.9	21.0	-1.13
4 9 L			
0	19.2	21.5	-3.14
1	12.4	15.3	-1.49
4 10 L			
0	9.4	9.9	-3.14
1	3.9	5.7	-1.82
4 11 L			
0	0.0	0.2	0.00
5 0 L			
1	78.6	82.4	1.57
2	18.3	14.1	3.14
3	46.2	50.4	1.57
4	29.3	31.3	0.00
5	83.3	74.8	-1.57
6	71.3	69.1	-3.14
7	32.0	36.3	1.57
8	8.1	10.9	-3.14
9	8.5	5.8	-1.57
10	28.4	31.7	0.00
11	23.1	20.4	-1.57
12	0.0	2.6	0.00
13	19.0	19.0	-1.57
14	14.7	15.3	-3.14
15	16.5	1.1	-1.57
16	17.7	12.5	-3.14
17	12.0	17.1	1.57
18	6.5	9.6	0.00
19	7.2	4.7	1.57
5 1 L			
0	26.0	22.2	1.57
1	128.8	145.1	1.30
2	28.3	22.7	-2.65
3	53.4	54.7	2.87
4	24.0	25.3	0.30
5	25.1	26.0	-1.27
6	26.4	34.1	-0.70
7	38.1	40.9	0.09
8	32.7	36.6	2.94
9	7.7	11.5	1.69
10	11.5	8.7	0.27
11	29.4	36.9	2.21
12	12.5	17.5	-2.59
13	15.7	6.6	2.53
5 2 L			
0	46.4	40.0	1.57
1	30.1	22.5	-2.81
2	27.1	21.8	-1.19
3	54.9	49.4	2.14
4	49.3	49.3	-1.72
5	46.2	36.5	-0.86
6	70.8	72.1	0.64
7	33.2	24.2	2.87
8	14.2	16.0	-1.75
9	29.9	28.1	2.26
10	31.3	28.0	-1.74
11	30.5	29.5	-0.80
12	35.8	39.1	1.60
13	30.0	27.0	-2.15
5 3 L			
0	23.6	25.0	-1.57
1	20.2	22.5	-2.89
2	50.8	51.1	2.54
3	31.0	25.1	0.31
4	45.4	45.7	0.70
5	47.2	48.3	-3.07
6	43.1	38.9	-0.20
7	43.9	41.6	0.89
8	40.8	38.0	2.84
9	30.6	28.1	-0.24
10	19.1	16.0	-2.62
11	33.1	31.6	-2.24
12	20.3	19.5	2.09
13	13.1	14.7	-0.30
14	0.0	7.0	0.27
15	0.0	7.2	-0.59
16	0.0	7.6	-1.44
17	20.2	20.7	-2.93
18	0.0	7.7	0.93
19	0.0	5.8	2.70
20	18.5	14.7	-0.33
5 4 L			
0	38.7	43.1	1.57
1	34.8	29.8	-1.80
2	22.2	24.7	-0.31
3	27.3	23.2	-0.57
4	8.9	8.1	-0.94
5	19.6	19.5	1.78
6	43.1	41.2	-3.14
7	34.4	31.3	-0.73
8	0.0	1.9	1.96
9	30.7	30.5	0.69
10	27.5	25.0	-1.29
11	16.3	18.6	2.73
12	0.0	11.4	-2.98
13	33.4	26.1	-0.57
14	28.6	26.1	2.02
15	13.9	12.5	2.12
16	13.1	15.3	1.49
17	12.1	14.9	-1.21
18	17.1	13.6	-1.37
19	14.5	17.2	-2.33
5 5 L			
0	5.2	4.7	1.57
1	15.4	13.2	2.51
2	29.6	28.9	-1.96
3	44.2	45.6	1.24
4	25.9	22.7	-2.18
5	35.5	27.3	-1.75
6	39.8	41.1	-0.60
7	41.2	39.2	-2.71
8	0.0	5.5	-2.16
9	30.6	35.2	0.59
10	38.4	41.0	2.42
11	39.6	35.1	1.68
12	13.8	16.9	-1.18
16	18.0	23.9	2.66
5 6 L			
0	11.5	12.5	-1.57
1	29.0	29.2	2.63
2	45.4	48.0	2.67
3	31.4	33.2	-1.17
4	24.6	25.6	-0.16
5	25.3	25.8	1.01
6	17.1	14.2	-0.62
7	37.9	45.6	2.48
8	19.4	19.7	2.82
9	18.3	13.3	-3.04
10	32.0	29.2	-1.51
11	0.0	6.5	-2.48
12	0.0	8.0	-2.23
13	0.0	11.3	1.14
14	18.2	18.9	1.26
15	15.7	15.9	-0.50
16	7.1	8.2	1.26
17	24.7	23.3	-2.58
5 7 L			
0	26.8	23.0	-1.57
1	23.0	24.9	1.39
5 8 L			
0	6.2	6.4	1.57
1	12.6	16.1	0.11
5 9 L			
0	0.0	1.9	-1.57
1	0.0	4.0	0.55
5 10 L			
0	6.4	7.2	1.57
1	15.1	19.6	-2.63
5 11 L			
0	18.3	21.9	-1.57
6 0 L			
0	63.0	58.8	-3.14
1	48.1	50.6	-1.57
2	67.2	65.3	0.00
3	29.2	22.5	1.57
4	31.1	27.1	3.14
5	39.1	36.8	-1.57
6	27.9	27.5	-3.14
7	36.9	22.8	1.57
8	34.9	39.8	0.00
9	55.5	55.7	1.57
10	16.3	17.5	0.00
11	29.3	32.1	1.57
12	34.5	36.8	-3.14
13	0.0	7.8	-1.57
14	14.7	17.1	0.00
15	14.6	19.4	-1.57
16	0.0	11.5	0.00
17	0.0	5.8	1.57
18	0.0	5.0	-3.14
19	21.3	17.8	1.57
6 1 L			
0	29.8	30.1	-3.14
1	42.9	44.0	1.89
2	63.0	61.8	-1.59
3	20.1	13.1	-1.53
4	22.6	19.9	-2.49
5	82.3	103.3	-2.61
6	28.4	31.1	-0.03
7	23.4	22.5	1.82
8	20.5	27.7	-0.09

Table 2 (*cont.*)

9	28.0	32.2	1.34
10	25.3	26.6	2.46
6 2 L			
0	12.0	11.6	0.00
1	84.9	84.7	-1.07
2	70.0	70.2	1.21
3	26.5	24.4	2.74
4	34.0	32.1	1.14
5	55.6	63.3	2.32
6	51.7	49.3	-2.34
7	53.9	46.4	-0.83
8	36.8	39.8	1.72
9	27.1	22.3	1.67
10	19.9	14.5	-2.86
11	20.6	21.3	1.36
6 3 L			
0	31.1	32.7	0.00
1	39.0	34.6	-2.90
2	39.8	42.9	2.73
3	0.0	6.9	-0.40
4	36.2	35.4	3.12
5	25.5	22.3	2.66
6	30.5	26.0	-0.24
7	23.8	20.8	2.67
8	42.8	41.6	0.35
9	22.6	23.9	0.17
10	23.3	22.8	-1.79
11	0.0	8.4	-2.17
18	25.9	21.6	2.87
6 4 L			
0	41.8	43.7	0.00
1	18.4	22.5	2.53
2	45.8	53.2	2.04
3	6.6	8.8	1.01
4	28.7	30.9	-3.05
5	22.1	22.5	-1.12
6	21.6	17.5	0.43
7	29.8	28.1	3.14
8	13.3	15.0	0.93
9	11.2	6.6	1.13
10	0.0	4.7	-0.60
11	0.0	12.3	2.17
12	25.0	23.6	-1.44
13	14.4	14.9	-0.50
14	30.3	30.8	-1.97
15	0.0	3.5	-1.31
16	27.2	29.4	1.13
6 5 L			
0	24.9	27.2	-3.14
1	39.6	40.8	0.74
2	26.5	28.1	2.24
3	49.4	59.1	-1.50
4	23.9	25.4	-1.46
5	24.5	26.1	0.05
6	41.8	42.5	1.33
7	25.9	21.2	1.26
8	30.7	31.7	0.90
9	31.3	28.7	2.34
10	22.5	18.8	-0.68
11	19.6	18.9	0.86
12	11.2	8.7	-2.41
13	26.9	24.3	-2.42
14	0.0	12.8	0.23
15	0.0	9.5	-1.67
16	13.7	10.6	-1.95
17	18.5	15.2	1.49
18	28.5	31.0	2.74
6 6 L			
0	53.2	50.3	-3.14
1	19.1	16.3	0.23
2	30.1	32.6	1.20
3	33.4	35.8	1.29
4	34.0	34.0	1.28
5	12.3	13.8	-1.51
6	14.5	22.0	-2.01
7	33.0	33.0	2.94
8	15.0	13.0	1.42
9	33.8	35.7	-0.93
10	26.2	26.9	0.55
11	22.4	21.2	-0.85
12	10.3	15.7	-1.66
13	17.2	16.5	2.30
6 7 L			
0	16.3	19.9	-3.14
1	10.8	9.3	2.36
6 8 L			
0	10.7	15.9	-3.14
1	14.1	17.1	1.39
6 9 L			
0	13.0	13.0	0.00
1	9.3	11.4	1.55
6 10 L			
0	4.3	3.0	-0.00
1	15.1	16.5	-0.03
6 11 L			
0	6.9	7.2	-3.14
7 0 L			
1	64.2	61.1	-1.57
2	18.5	10.8	-0.00
3	44.6	47.2	-1.57
4	34.4	34.4	-0.00
5	40.5	48.8	1.57
6	8.4	10.6	-3.14
11	14.3	16.6	-1.57
12	12.6	12.4	-3.14
13	29.4	28.1	1.57
14	0.0	7.5	-3.14
15	17.6	14.3	-1.57
16	23.8	22.6	0.00
17	14.3	12.4	-1.57
18	0.0	2.4	-0.00
19	17.4	19.7	1.57
7 1 L			
0	31.6	26.5	-1.57
1	62.8	62.7	-1.96
2	9.7	4.9	3.01
3	35.2	38.1	-0.72
4	45.0	50.2	0.37
5	0.0	8.0	3.07
6	38.9	43.4	3.02
7	29.6	34.9	-3.06
8	28.4	31.1	-0.86
9	0.0	11.2	-2.20
10	27.8	33.4	-0.03
11	20.2	25.4	0.47
12	20.6	30.3	2.46
13	20.7	24.9	-1.24
7 2 L			
0	52.8	46.5	1.57
1	35.1	32.9	1.26
2	37.8	39.0	-1.16
3	13.6	9.5	1.25
4	22.0	19.8	2.84
5	0.0	5.5	-1.82
6	31.4	32.5	1.71
7	15.3	15.1	-1.99
8	25.0	26.3	-1.58
9	25.9	23.5	-0.66
10	31.5	38.7	1.40
11	24.4	35.2	2.37
7 3 L			
0	50.2	50.9	-1.57
1	28.2	27.3	-1.87
2	38.5	39.7	1.93
3	30.1	27.3	-0.04
4	13.3	9.9	1.61
5	20.9	18.1	0.71
6	52.0	50.1	-1.93
7	29.0	25.0	-3.07
8	25.9	25.2	0.98
9	23.4	22.9	0.67
10	0.0	2.8	-2.09
11	13.0	8.6	0.65
12	18.5	18.6	-2.11
13	0.0	6.2	-1.26
14	0.0	3.5	0.85
15	21.1	19.1	1.81
16	19.8	17.9	0.71
17	9.0	7.1	3.02
18	29.6	21.2	-2.86
19	22.3	20.4	-0.95
7 4 L			
0	65.1	67.1	-1.57
1	36.4	37.7	-1.56
2	7.0	7.9	0.63
3	26.6	24.1	-1.50
4	29.0	30.5	2.63
5	36.4	36.0	-2.81
6	28.5	26.4	0.24
7	7.8	8.7	0.68
8	27.7	25.1	-1.12
9	11.5	8.9	2.36
10	16.6	12.5	-2.86
11	16.7	18.8	-0.66
12	11.7	17.2	0.24
13	0.0	7.7	1.89
14	11.1	14.3	-0.27
15	14.8	13.7	1.07
16	19.4	20.5	-2.25
17	0.0	9.2	1.17
18	19.0	16.3	1.40
7 5 L			
0	8.1	12.9	1.57
1	4.1	4.5	-1.35
2	39.0	42.5	-0.22
3	28.8	26.1	-0.51
4	31.1	32.6	2.71
5	33.3	36.1	3.11
6	32.3	32.1	3.12
7	29.0	23.7	0.99
8	46.6	50.8	0.67
9	0.0	5.1	1.98
10	0.0	5.8	-0.95
11	38.9	38.5	-2.51
12	27.0	24.7	-1.39
7 6 L			
0	26.3	28.3	1.57
1	31.2	27.5	0.45
2	12.3	15.9	2.65
3	35.2	36.3	2.11
4	0.0	4.4	1.60
5	25.5	27.4	-1.52
6	0.0	10.4	-1.96
7	26.1	24.0	-1.08
8	0.0	5.5	0.30
9	0.0	1.5	0.80
10	27.9	26.6	1.50
11	0.0	10.4	-2.96
12	17.2	17.4	-1.37
7 7 L			
0	23.4	27.1	1.57
1	10.0	10.6	-0.56
7 8 L			
0	26.3	28.9	-1.57
1	23.1	27.0	1.43
7 9 L			
0	0.0	2.3	1.57
1	8.9	12.7	-1.39
7 10 L			
0	16.8	20.6	1.57
8 0 L			
0	0.0	1.4	-3.14
1	0.0	5.0	1.57
2	13.1	17.7	-3.14
3	47.8	46.4	1.57
4	8.6	5.0	0.00
5	24.9	21.8	-1.57
6	6.4	1.0	0.00
7	0.0	2.8	-1.57
8	27.2	27.6	0.00
9	9.9	9.8	-1.57
10	36.7	40.8	0.00
11	47.7	55.0	-1.57
12	12.8	12.5	-3.14
13	0.0	3.1	-1.57
19	13.1	10.6	-1.57
8 1 L			
0	37.5	38.7	0.00
1	40.0	38.3	-0.38
2	30.0	25.9	2.57
3	22.8	25.2	1.84
4	13.4	16.5	2.69
5	31.8	42.8	-0.77
6	28.3	33.9	0.68
7	11.9	16.5	0.07
8	19.3	22.1	-3.10
9	28.1	32.4	-2.50
10	0.0	14.2	-1.95
8 2 L			
0	64.3	66.6	-3.14
1	55.2	58.3	1.10
2	25.2	23.6	0.31
3	18.1	14.4	-0.82
4	28.1	31.3	-2.10
5	57.5	63.7	-1.45
6	19.3	23.6	1.73
7	34.3	32.1	1.55
8	16.6	14.3	1.84
9	20.8	23.3	1.79
10	32.4	28.9	-1.12
8 3 L			
0	0.0	4.5	-3.14
1	3.8	2.4	1.32
2	21.1	21.1	0.91
3	51.8	48.3	1.35
4	16.5	18.0	-0.63
5	33.6	28.6	1.37
6	12.1	9.2	1.98
7	41.0	38.0	-1.70
8	40.6	39.5	2.74
9	38.7	34.3	-1.83
10	9.2	6.6	-1.39
11	22.7	19.4	0.02
12	36.8	33.9	-0.24
13	27.0	25.1	2.46
14	17.4	18.7	2.20
15	11.6	13.3	-2.57
16	23.8	23.7	-2.06
17	8.2	6.8	-0.31
18	29.4	24.8	0.41
8 4 L			
0	8.9	7.8	-0.00
1	19.6	21.0	-0.63
2	26.0	28.8	-1.24
3	32.2	35.5	-0.50
4	20.4	24.2	1.45
5	29.3	26.6	1.51
6	22.6	24.3	-1.83
7	25.7	21.8	0.19
8	28.5	29.0	-1.63
9	40.7	35.9	-0.58
10	31.2	27.2	1.04
11	33.2	29.0	2.79
12	19.9	15.5	1.93
13	15.7	16.0	2.90
14	12.9	15.8	1.50
8 5 L			
0	17.6	19.3	-3.14
1	16.9	17.9	-2.84
2	22.6	24.8	-0.31
3	20.1	20.5	0.83
4	28.7	30.7	-1.30
5	13.5	11.9	1.12
6	29.4	32.0	2.28
7	27.5	26.4	-2.44
8	11.3	11.7	-0.01
9	16.0	15.2	-1.65
10	15.8	17.1	-2.33
11	13.4	10.3	1.05
12	13.0	14.8	3.04
8 6 L			
0	24.8	24.6	0.00
1	14.3	13.3	0.81
2	55.0	59.8	-1.79
8 7 L			
0	21.4	20.2	-3.14
1	17.8	20.0	-0.67
8 8 L			
0	0.0	1.9	-3.14
1	16.9	19.2	-2.20
8 9 L			
0	5.2	9.8	0.00
8 10 L			
0	17.3	14.3	0.00
9 0 L			
1	0.0	0.9	1.57
2	56.5	57.7	-3.14
3	0.0	1.0	1.57
4	16.0	16.0	0.00
5	28.3	28.3	-1.57
6	37.5	38.6	0.00
7	7.0	6.3	1.57
8	28.5	31.0	-3.14
9	10.2	11.0	-1.57
10	14.7	14.2	-3.14
11	12.8	6.4	-1.57
17	14.8	13.5	1.57
18	16.8	18.6	-3.14
19	12.9	20.6	-1.57
9 1 L			
0	31.2	29.1	1.57
1	36.8	36.0	-1.12
2	21.5	21.9	-1.57
3	14.2	19.1	-1.31
4	16.7	19.4	-1.36
5	22.5	28.0	2.20
6	21.2	23.0	1.16
7	19.8	19.0	-2.03
8	18.0	24.0	1.85
9	27.5	36.2	0.68
10	20.7	27.6	-2.79
11	32.1	20.7	-1.99
12	27.6	10.9	-0.13
9 2 L			
0	8.7	7.3	-1.57
1	22.5	23.8	2.94
2	0.0	11.3	2.27
3	44.8	56.3	-0.51
4	0.0	13.5	-1.55
5	25.8	30.4	-2.98
6	0.0	3.2	-2.52
7	41.5	54.5	1.24
9 3 L			
0	32.3	31.5	1.57
1	15.0	12.2	0.06
2	0.0	4.2	-2.85
3	43.8	42.1	2.78
4	23.1	22.1	-2.64
5	0.0	3.6	1.20
6	23.8	18.8	-0.54
7	51.3	48.9	-1.35
8	13.0	7.6	2.24
9	18.5	13.5	-0.80
10	13.1	10.2	-0.43
9 4 L			
0	10.7	7.3	1.57
1	30.7	36.0	1.52
2	21.0	19.7	0.77
3	8.0	6.5	1.86
4	34.3	33.8	-2.30
5	32.6	32.8	-0.81
6	14.3	12.0	-0.55
7	28.8	25.6	2.17
8	31.2	31.1	1.45
9	8.3	10.3	-2.86
10	24.7	23.5	3.14
11	11.4	11.4	-0.71
12	11.0	12.2	0.12
13	12.9	10.3	2.69
14	0.0	3.8	-0.74
15	24.5	17.7	-3.02
9 5 L			
0	53.7	54.1	-1.57
1	19.2	14.9	-0.27
2	27.1	23.7	1.91
3	0.0	7.5	-2.92
4	19.4	16.4	1.64
5	22.5	17.8	2.04
6	25.2	19.9	-0.14
7	19.5	16.6	1.78
8	31.8	30.7	-2.91
9	27.2	23.2	-1.10
10	10.9	12.8	-1.94
11	10.5	12.1	-0.43
12	22.4	20.2	1.09
13	9.4	7.7	1.84
14	10.5	8.4	1.58
15	26.3	22.3	-1.92
9 6 L			
0	11.2	13.1	-1.57
1	8.8	7.2	-1.95
2	30.2	25.5	0.13
9 7 L			
0	14.8	16.5	1.57
1	11.5	11.9	2.73
9 8 L			
0	11.8	10.6	1.57
1	15.0	17.4	-2.97
9 9 L			
0	7.1	6.6	-1.57
9 10 L			
0	13.2	13.3	-1.57
10 0 L			
0	12.1	9.5	0.00
1	10.9	8.4	-1.57
2	0.0	2.0	-0.00
3	0.0	4.1	-1.57
4	0.0	3.8	-3.14
5	24.4	26.3	1.57
6	7.2	9.9	3.14
7	25.1	27.4	-1.57
8	27.4	30.9	-3.14
9	10.4	11.3	-1.57
17	17.0	13.5	-1.57
10 1 L			
0	28.7	28.1	0.00
1	11.9	6.1	-1.07
2	32.4	36.4	1.94
3	21.4	27.7	-1.40
4	35.3	45.5	-1.61
5	35.8	49.8	2.04
10 2 L			
0	61.5	57.5	0.00
1	38.3	37.5	-2.93
2	16.6	7.7	2.13
3	23.7	21.4	2.90
4	16.9	15.8	-1.54
5	29.6	34.3	0.85
10 3 L			
0	0.0	3.7	0.00
1	12.8	11.3	1.13
2	15.6	14.2	-2.01
3	50.9	49.8	-1.71
4	28.8	23.3	-1.26
5	34.3	30.9	-1.26
6	13.1	13.1	-0.50
7	34.7	32.6	1.62
8	9.3	5.9	2.52
9	24.4	19.3	1.26
16	24.8	20.9	1.21
10 4 L			
0	28.4	26.1	-3.14
1	6.2	7.2	-2.82
2	8.2	11.5	-0.82
3	37.0	36.2	-2.49
4	8.3	7.4	0.07
5	16.7	16.1	1.80
6	16.7	12.5	-2.88
7	0.0	0.8	2.44
8	11.7	15.6	1.70
9	21.5	19.3	3.08
10	8.0	11.0	-1.28
11	18.8	15.1	0.98
12	7.3	2.6	-2.14
13	15.3	14.6	-0.47
14	7.6	4.3	0.47
15	23.3	19.1	-2.70
10 5 L			
0	0.0	2.7	-3.14
1	31.0	29.2	-2.36
2	19.6	17.5	1.63
3	21.1	23.0	1.88
4	19.5	18.1	1.97
5	13.8	10.3	-2.09
6	13.7	10.9	-2.54
7	0.0	5.8	0.93
8	15.4	15.9	-0.58
9	21.3	23.7	1.23
10	0.0	10.5	1.28
11	24.9	26.2	-2.05
10 6 L			
0	17.1	19.5	-3.14
1	9.8	9.8	0.76
3	23.7	20.6	-2.66
10 7 L			
0	15.3	16.7	0.00
1	11.0	11.5	0.61
10 8 L			
0	0.0	2.8	-3.14
1	8.3	7.9	0.06
10 9 L			
0	10.2	11.8	0.00
11 0 L			
1	4.3	2.9	-1.57
2	49.1	49.8	0.00
3	10.2	11.6	1.57
4	17.8	13.4	-3.14
5	0.0	0.7	-1.57
6	25.4	31.2	-3.14
7	25.5	32.8	-1.57
8	22.1	27.3	0.00
9	10.3	7.7	1.57
10	14.3	16.5	0.00
11	26.1	29.4	1.57
12	23.2	25.9	-3.14
13	15.5	20.3	-1.57
11 1 L			
1	8.7	9.7	2.49
3	31.6	29.9	0.96
11 2 L			
0	24.5	20.9	-1.57
1	9.8	7.6	-1.02
11 3 L			
1	9.9	9.7	1.18
9	23.5	17.1	2.25
15	20.9	16.9	2.46
11 4 L			
0	7.6	6.7	1.57
1	23.7	21.3	1.33
7	28.1	20.6	1.49
10	21.0	16.3	0.87
15	27.9	26.5	-0.32
11 5 L			
0	36.8	39.2	1.57
1	34.8	32.3	1.60
2	13.7	15.9	-2.58
3	0.0	5.3	2.22
4	19.1	16.7	-0.76
5	20.5	22.2	-0.67
11 6 L			
0	5.9	5.2	-1.57
1	14.6	13.6	-0.93
11 7 L			
0	0.0	2.1	-1.57
1	6.7	7.8	-2.77
11 8 L			
0	5.6	2.6	1.57
1	16.0	15.5	-1.19
11 9 L			
0	15.1	17.5	1.57
12 0 L			
0	9.8	2.0	-3.14
1	16.1	14.7	1.57
2	0.0	0.2	3.14
3	19.0	22.8	-1.57
4	10.4	5.6	-3.14
12	14.9	20.1	0.00
14	21.4	23.7	-3.14
12 1 L			
0	23.2	20.2	-3.14
1	8.9	8.4	0.48
2	32.1	24.8	-1.03
12 2 L			
0	17.6	20.6	-3.14
1	17.9	15.8	-3.02
12 3 L			
0	6.2	3.7	0.00
7	23.3	12.0	-0.98
8	17.2	18.3	-0.03
9	11.7	14.2	-1.58
10	21.0	12.3	1.07
11	27.4	19.2	2.18
12 4 L			
0	14.9	10.2	-3.14
1	32.3	27.7	0.60
12 5 L			
0	10.0	7.5	0.00
1	19.0	18.4	0.22
2	21.3	18.6	-2.16
3	12.9	15.3	1.22
12 6 L			
0	18.8	16.5	0.00
1	8.7	6.2	0.74
12 7 L			
0	10.9	7.1	0.00
1	9.9	8.5	-2.42
12 8 L			
0	17.2	17.9	0.00
13 0 L			
1	23.3	22.3	-1.57
2	0.0	5.2	-0.00
3	17.7	14.7	-1.57
4	0.0	3.8	-3.14
5	18.8	17.9	1.57
10	17.3	18.7	-3.14
13 1 L			
1	22.9	18.6	1.68
13 2 L			
0	4.3	4.6	-1.57
1	4.4	3.5	-1.59
13 3 L			
0	12.6	15.3	1.57
1	14.8	12.1	-0.99
6	35.3	26.8	1.25
7	8.1	5.9	1.46
8	15.5	8.6	0.09
9	23.9	11.8	-2.74
10	26.8	15.4	-1.90
11	23.3	16.3	-0.76
12	21.8	16.1	1.68
13 4 L			
0	9.1	9.9	-1.57
1	9.2	9.1	-1.37
13 5 L			
0	0.0	2.7	1.57
1	22.9	22.1	-1.20
13 6 L			
0	5.9	6.9	1.57
1	11.1	12.1	-2.96
13 7 L			
0	11.8	12.4	-1.57
14 0 L			
0	21.9	20.5	0.00
1	5.9	10.2	1.57
14 1 L			
0	16.3	10.0	-3.14
14 2 L			
1	15.2	12.7	1.12
14 3 L			
0	11.6	10.3	-3.14
1	5.5	8.3	-0.36
14 4 L			
0	16.2	16.7	0.00
1	18.0	17.8	-2.83
14 5 L			
0	19.0	16.9	0.00
1	7.1	8.1	0.34
14 6 L			
0	13.5	11.7	-3.14
15 1 L			
0	10.9	7.3	-1.57
1	11.1	11.1	-0.32
15 2 L			
0	22.9	15.6	1.57
1	13.9	7.6	-0.31
15 3 L			
0	4.1	1.3	1.57
1	11.0	10.4	1.38
15 4 L			
0	3.7	0.7	-1.57
1	11.3	10.3	-2.08
15 5 L			
0	11.7	12.0	1.57
1	5.5	4.3	2.35
16 0 L			
1	15.1	11.4	-1.57
16 1 L			
0	3.7	2.2	0.00
1	6.5	5.6	-1.56
16 2 L			
0	4.9	3.8	0.00
1	9.4	5.5	-0.49
16 3 L			
1	11.1	7.4	-1.22

A phase was accepted to be used as input in the tangent formula if the structure factor computed from the known partial structure had $|E| > 1{\cdot}5$ and $|F_c| > k|F_o|$, where k is roughly proportional to the scattering power of the known portion, with a maximum value for $k \sim 0{\cdot}6$. In the first cycle, in addition to the four Cl atoms, Cl(5), O(1), O(2) and five C atoms were located and the following cycle based on twelve known atoms

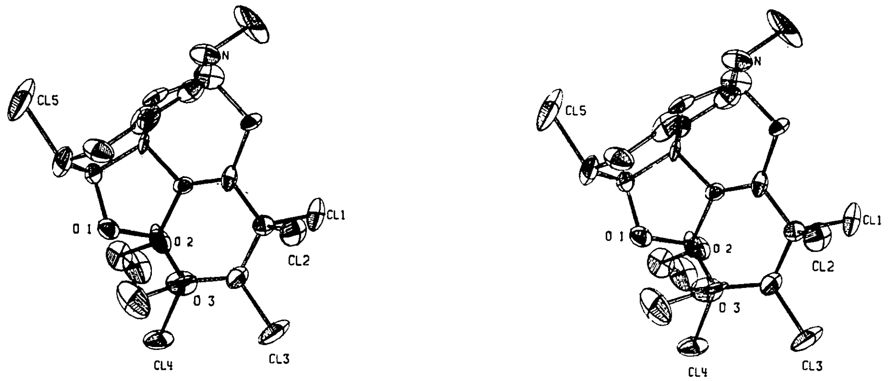


Fig. 2. Stereodiagrams of a molecule of pentachloroethoxycodide drawn by a computer program prepared by Johnson (1965).

Table 3. *Fractional coordinates for pentachloroethoxycodide*

The thermal parameters are of the form

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right].$$

Each thermal parameter is $\times 10^4$.

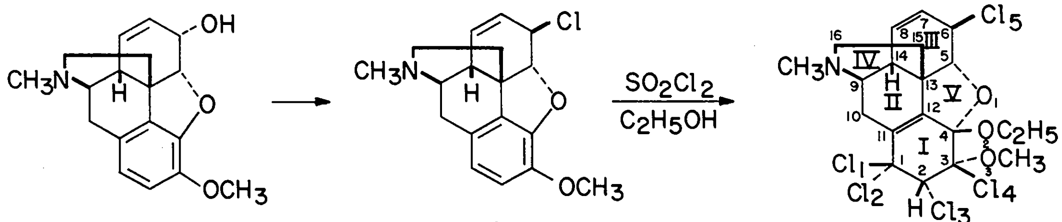
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0·2050	0·4417	0·3610	64	150	15	19	1	−14
Cl(2)	0·4079	0·3678	0·3246	46	96	27	5	−16	3
Cl(3)	0·3653	0·6897	0·2994	99	81	45	−15	−25	−28
Cl(4)	0·3510	0·7292	0·1209	75	41	44	−7	−12	8
Cl(5)	0·3019	0·0651	−0·0628	139	174	33	58	−4	−49
O(1)	0·2976	0·4274	0·0480	42	66	20	−4	−4	12
O(2)	0·1729	0·5428	0·1136	52	75	25	19	1	18
O(3)	0·4353	0·4937	0·1679	39	71	40	5	−11	9
N	0·1081	0·0301	0·1900	45	85	44	−27	2	7
C(1)	0·2923	0·4207	0·2820	57	47	20	1	3	−1
C(2)	0·2979	0·5724	0·2426	57	97	24	−22	3	−17
C(3)	0·3434	0·5529	0·1638	68	39	25	−34	−20	−1
C(4)	0·2649	0·4724	0·1189	69	56	10	34	5	13
C(5)	0·2594	0·2876	0·0262	65	60	12	−7	−2	3
C(6)	0·3537	0·2059	−0·0027	86	99	21	13	13	−19
C(7)	0·4168	0·1472	0·0602	49	56	37	6	7	13
C(8)	0·3724	0·0903	0·1220	38	86	38	26	8	−25
C(9)	0·2167	0·0476	0·2018	17	77	38	13	−6	8
C(10)	0·2427	0·1590	0·2625	85	41	21	−19	14	−15
C(11)	0·2568	0·3064	0·2305	30	85	11	15	−6	−3
C(12)	0·2431	0·3326	0·1600	29	40	19	3	3	−4
C(13)	0·2154	0·2250	0·1000	34	52	5	16	−2	−5
C(14)	0·2588	0·0825	0·1257	44	46	27	−8	−10	−17
C(15)	0·0980	0·2104	0·0924	56	73	14	−11	−7	−3
C(16)	0·0541	0·1500	0·1625	37	104	37	−22	−7	−14
C(17)	0·0596	−0·0316	0·2594	104	255	58	−84	24	67
C(18)	0·5049	0·4914	0·1055	49	184	50	12	30	19
C(19)	0·1455	0·6072	0·0408	84	96	31	51	−21	34
C(20)	0·0565	0·7042	0·0586	90	157	51	70	3	38
Standard deviations									
Cl	0·0005	0·0007	0·0003	4	8	2	5	3	4
O	0·0011	0·0015	0·0008	9	19	5	10	6	9
N	0·0013	0·0019	0·0011	11	24	7	13	8	13
C(1–16)	0·0016	0·0022	0·0011	13	29	7	16	9	13
C(17–20)	0·0019	0·0031	0·0014	19	45	11	25	12	18

revealed all the atoms except C(7) and C(18) which were found in a difference map. Fig. 1 shows the molecule and its symmetry equivalents in the unit cell.

The coordinates and isotropic thermal parameters for the 29 atoms were refined by least-squares (*ORFLS* program, Busing, Martin & Levy, 1962) for several cycles and then refinement was continued with anisotropic thermal parameters. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with $w=1$ for $|F_o|<25$ and $w=25/|F_o|$ for $|F_o|>25$. The values for the atomic scattering factors were taken from *International Tables for X-ray Crystallography*. A difference map did not reveal the hydrogen atoms and none were included in the refinement. The maximum electron density in the difference map was $\sim \pm 0{\cdot}7$ e.Å^{-3} and occurred at, or near, the positions of the five Cl atoms. The final R value was 11·2%. Table 2 lists the observed and calculated structure factors. The coordinates and thermal parameters are listed in Table 3.

Discussion

The primary objective of this structure determination was to establish the structural formula and the stereoconfiguration of pentachloroethoxycodide. The chlorination of codeine [1] is stepwise, first replacing the $-OH$ group with $-Cl$, then reacting with the phenyl group to add four more Cl atoms and an O atom:



[1] CODEINE

[2] α-CHLOROCODIDE

[3] PENTACHLORO-ETHOXYCODIDE

These four Cl atoms were added on C(1), C(2) and C(3) and the O atom was substituted on C(4) in the configuration shown in [3]. Thus the structural formula of this molecule was established. Atoms Cl(3) and Cl(4) are in the equatorial positions, whereas Cl(5) is in the axial position. The methoxy group is in an axial position and *trans* to the ethoxy group at C(4) which is also in an axial orientation.

The relative configuration of codeine (Lindsey & Barnes, 1955) and the closely related morphine (Mackay & Hodgkin, 1955) had been established by the X-ray analysis of their hydrobromide and hydroiodide salts. The configuration of the nucleus of the pentachloroethoxycodide derivative is similar to codeine and morphine, except for the changes caused by saturating two of the double bonds in ring I. Stereo drawings of the molecule shown in Fig. 2 illustrate the configuration. The thermal parameters are not particularly well determined since the crystals were disintegrating during the X-ray exposures. They were included in the drawing, however, to illustrate qualitatively the large tangential oscillations of the atoms around the periphery of the molecule. This motion may increase under X-ray bombardment and play a role in the disintegration of the crystal.

The absolute configuration of morphine and codeine has been established chemically (Kalvoda, Buchschacher & Jeger, 1955) and by X-ray analysis (Kartha, Ahmed & Barnes, 1962). It is assumed that the chlorinated product [3] has the same absolute configuration as the parent compound [1]. The molecule as illustrated in Figs. 1 and 2 and the coordinates in Table 3 are consistent with the absolute configurations of morphine and codeine.

Rings I and II sharing a double bond would be expected to have the half-chair conformations. The conformation of both rings is distorted from the ideal half-chair not only by the five membered ring V which is fused to both rings I and II, but also by the spacing between the atoms Cl(2) and O(3), both axial to ring I, which is approximately 3·0 Å. Atoms (1), (4), (10), (11), (12) and (13) are nearly in a plane, with (12) having the largest deviation of 0·05 Å from the plane. Atoms (2) and (3) are respectively 0·14 and 0·72 Å above and below the plane while atoms (9) and (14) are both below the plane by 0·13 and 0·82 Å respectively.

The piperidine ring IV has the chair conformation with atoms (14) and (16) 0·75 Å below and 0·49 Å above the plane formed by atoms (9), (13), (15) and N. Ring III which has a double bond at C(7)–C(8) is boat shaped with atoms (6), (7), (8) and (14) in a plane with a maximum deviation of ±0·009 Å. Atoms (5) and (13) are both below the plane by 0·95 and 1·00 Å, respectively. In the five-membered ring V, the four atoms O(1), (5), (13) and (12) are coplanar within ±0·03 Å while atom (4) is 0·40 Å above that plane.

Bond distances and angles are shown in Figs. 3(*a*) and (*b*). The standard deviations based only on the least-squares fit are 0·022 Å for C–Cl bonds and 0·030 Å for C–C bonds with the exception that they are 0·033 Å for those bonds involving C(17) through

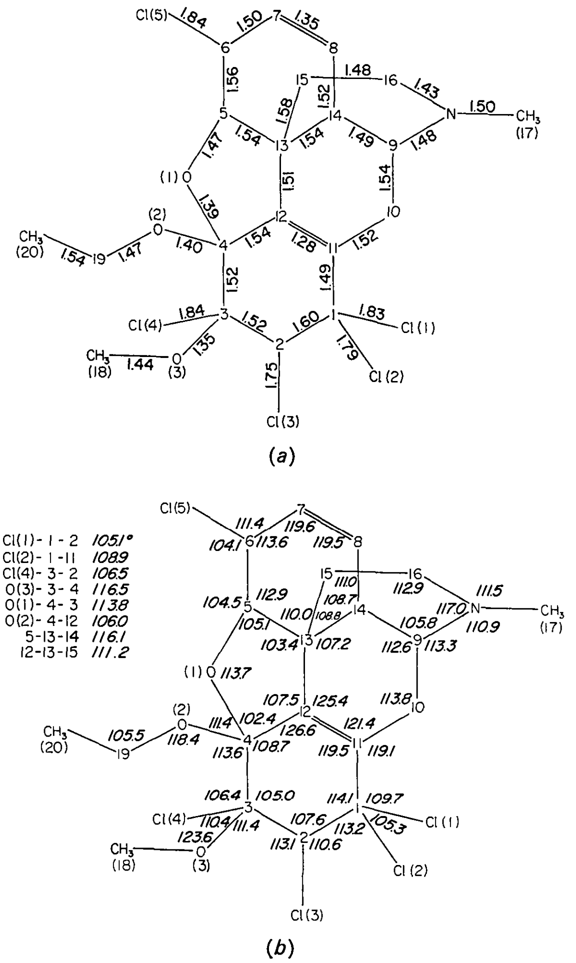


Fig. 3. (*a*) Bond distances. (*b*) Bond angles.

C(20). For the angles the standard deviations are ~1·7°. Within the accuracy of the experiment there are no unusual bond lengths, but it is of interest to note the range of the C–Cl bonds which is 1·75 to 1·84 Å. In various aromatic compounds, the C–Cl bond appears to lie in the range of 1·72–1·77 Å [see *e.g.* Palenik (1965); Folting, Lipscomb & Jerslev (1964); Gafner & Herbstein (1962); Karle & Karle (1967)]. Aliphatic C–Cl bonds appear to be somewhat longer. In 2α, 3β-dichloro-5α-cholestone the two C–Cl bond distances are 1·76 and 1·82 Å (Geise & Romers, 1966).

Fig. 1 illustrates the packing of the molecules. There is no hydrogen bonding and the intermolecular separations are governed by van der Waals forces. The nearest approaches between molecules are listed in Table 4.

Table 4. *Nearest intermolecular approaches*

Cl(4)···C(8′)	$x, 1+y, z$	3·44 Å
Cl(4)···C(14′)	$x, 1+y, z$	3·58
Cl(1)···O(1′)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$	3·51
Cl(2)···Cl(4′)	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	3·61
C(16)···C(17)	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	3·65

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