Acta Cryst. (1971). B**27**, 523

The Crystal Structure of 1,8-Diazacyclotetradecane-2,9-dione, a Cyclic Dimeric Model of Nylon 6*

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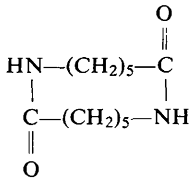
(*Received* 1 *October* 1969 *and in revised form* 6 *May* 1970)

The crystal structure of 1,8-diazacyclotetradecane-2,9-dione has been solved by direct methods using X-ray intensity data collected with an automatic diffractometer. The triclinic unit cell contains 4 molecules located on symmetry centers and has the dimensions $a=15·469$, $b=8·985$, $c=8·918$ Å, $\alpha=89°23'$, $\beta=88°32'$, $\gamma=91°55'$. The molecules are linked together by N–H···O=C hydrogen bonds into sheets parallel to the (100) plane. Continuous streaks and 'extra' reflections are observed along reciprocal lattice rows parallel to **a***. A qualitative interpretation of these phenomena is given in terms of a partially ordered structure.

Introduction

This investigation is the third in a series of X-ray crystallographic studies of oligomeric models of polyamides. The previous studies were concerned with the cyclic monomer and dimer of nylon 66, poly(hexamethylene adipamide) (Northolt & Alexander, 1968; Northolt, 1970). In the present paper we report the crystallographic investigation of the cyclic dimer, c[Cap]$_2$, of nylon 6 (polycaproamide) with the formal configuration



$$\begin{array}{ccc} & & \mathrm{O} \\ & & \| \\ \mathrm{HN} & -(\mathrm{CH_2})_5- & \mathrm{C} \\ | & & | \\ \mathrm{C} & -(\mathrm{CH_2})_5- & \mathrm{NH} \\ \| & & \\ \mathrm{O} & & \end{array}$$

The preparation of this oligomer has been described by Zahn & Determann (1957).

Experimental

Crystals were grown from a solution of acetonitrile and dimethylformamide. Weissenberg and precession photographs showed the crystals to be triclinic and gave preliminary unit-cell constants that were subsequently refined by the method of least squares using 2θ angles measured on a diffractometer. The cell constants and other crystallographic data are listed in Table 1. The quality of the crystals was rather poor as judged from the appearance of the X-ray photographs. They were composed of several slightly displaced blocks that gave the reflection spots on the film an uneven appearance. All the crystals examined gave diffraction patterns showing various degrees of continuous streaking along reciprocal-lattice rows and 'extra' reflections at half orders, $h=\frac{1}{2}, \frac{2}{3}, \frac{5}{2}$, *etc.*, between reciprocal-lattice points of the regular lattice. Both phenomena occur along lattice rows parallel to **a*** for which $k+l$ is odd. Fig. 1 is a photograph exhibiting these effects to a pronounced degree. Visual examination of X-ray photographs taken from many crystals showed that as the intensity of the extra spots increased, the streaking was also enhanced. These effects occurred at the expense of the intensity of the regular reflections on lattice rows with $k+l$ odd, indicating a tendency toward body centering in a doubled cell with dimensions $a'=2a$, $b'=b$, and $c'=c$. However, for all the crystals examined, the relative intensities of the reflections on lattice rows parallel to **a*** with $k+l$ even remained constant. The following systematic absences were observed: $h00$ for h odd with the exception of reflection 900, $0k0$ for k odd, and $00l$ for l odd.

Table 1. *Crystal data*

M.W. 226·32, m.p. 348°
Space group $P\bar{1}$
a = 15·469 (3) Å $\alpha=89°23'$ (1′)
b = 8·985 (2) $\beta=88°32'$ (1′)
c 8·918 (2) $\gamma=91°55'$ (1′)
V = 1238·31 Å^3
D_m = 1·22 g.cm^{-3}
D_x = 1·21 g.cm^{-3}
Z = 4
$F(000)=496$
Absorption coefficient for Cu $K\alpha$ X-rays ($\lambda=1·5418$ Å):
μ = 6·3 cm^{-1}
Habit: colorless, rectangular-shaped plates

Since crystals without any degree of streaking could not be found, a crystal with dimensions 0·27 × 0·18 × 0·14 mm showing only minimal (very weak) streaking

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* This investigation was supported in part by Public Health Service Grant GM-12396 from the National Institutes of Health.

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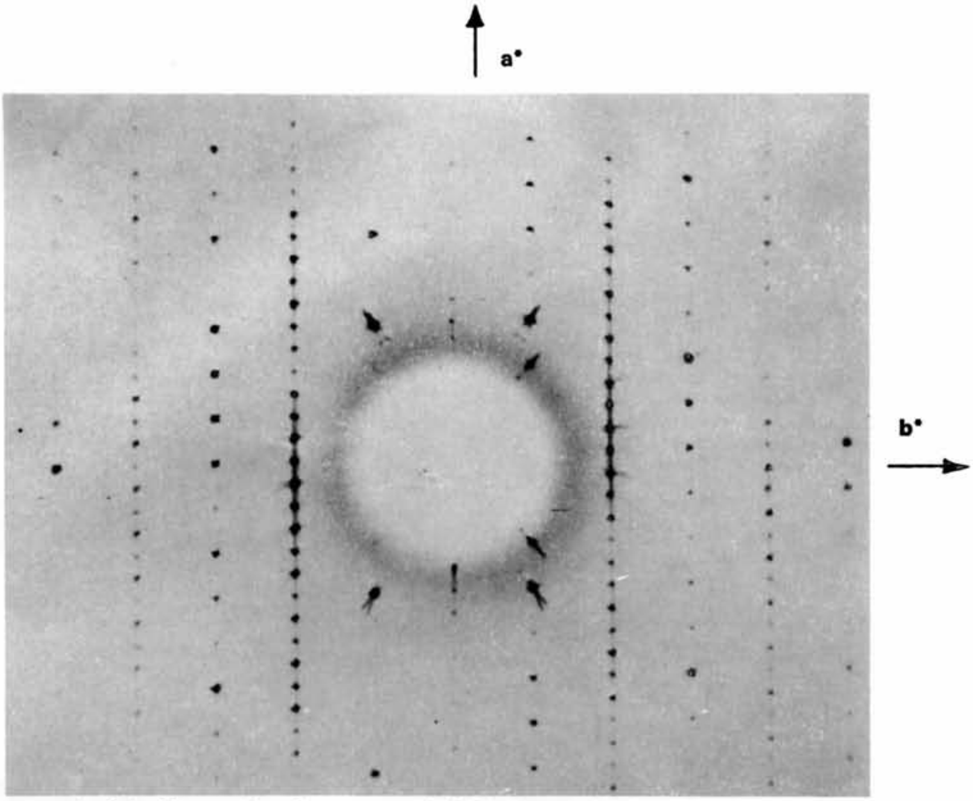

Fig. 1. Precession photograph of the *hk*1 net plane from a crystal of c[Cap]$_2$ showing heavy streaking and extra reflections (Cu $K\alpha$, Ni-filtered, 40kV–20mA, 17 hr).

and extra reflections was selected for the data collection. The crystal was mounted on a General Electric automatic diffractometer with the *b* axis parallel to the goniometer axis. Nickel-filtered Cu $K\alpha$ radiation together with pulse-height discrimination was used in conjunction with the θ–2θ scan technique. The maximum value of $(\sin\theta)/\lambda$ was 0·5313 Å^{-1}. However, when it became evident that a precise structure determination could not be expected, the maximum value of $(\sin\theta)/\lambda$ in the refinement was limited to 0·47 Å^{-1} yielding 2153 independent reflections, of which 194 were classed as unobserved. Details of the procedures followed for data gathering and processing to observed and unobserved structure factors and a description of the weighting scheme have been presented earlier (Northolt & Alexander, 1968). The Fourier computations and least-squares refinement were performed using the *X-ray 67 Programs System* (Stewart & High, 1967).

Table 2. *Observed and calculated structure factors*(× 10)

OBSERVED REFLECTIONS

H	L	FOBS	FCAL
**K =		0****	
0	-8	86	68
1	-8	57	0
2	-8	17	-15
3	-8	50	35
4	-8	55	-9
4	-7	26	0
5	-7	48	-21
6	-7	69	-68
0	-6	118	-117
1	-6	159	148
2	-6	54	-34
3	-6	78	78
4	-6	102	117
5	-6	279	-318
6	-6	256	230
7	-6	92	86
8	-6	48	36
9	-6	169	157
0	-5	29	-22
1	-5	103	-100
2	-5	82	-73
3	-5	34	-9
4	-5	91	77
5	-5	128	127
6	-5	44	37
8	-5	28	-7
9	-5	67	-63
10	-5	37	-32
11	-5	43	-48
0	-4	163	-140
1	-4	238	-226
2	-4	57	-124
3	-4	339	522
4	-4	65	-51
5	-4	60	-35
6	-4	53	-63
7	-4	96	-73
8	-4	212	-224
9	-4	92	-137
10	-4	71	-81
11	-4	24	-27
12	-4	17	-15
1	-3	32	18
2	-3	109	-18
3	-3	113	-55
4	-3	73	-58
5	-3	45	-68
6	-3	43	-77
7	-3	29	-42
8	-3	15	-7
9	-3	33	29
10	-3	77	72
11	-3	54	52
12	-3	20	34
13	-3	37	-33
0	-2	159	179
1	-2	807	-795
2	-2	315	-395
3	-2	164	83
4	-2	169	93
5	-2	223	211
6	-2	156	150
7	-2	295	267
8	-2	270	-239
9	-2	22	1
10	-2	83	127
11	-2	141	-140
12	-2	20	-20
14	-2	87	-75
1	-1	204	225
2	-1	219	251
3	-1	128	178
5	-1	49	-42
6	-1	73	-63
7	-1	78	-52
8	-1	36	58
9	-1	28	30
10	-1	58	62
11	-1	48	34
12	-1	45	-49
13	-1	83	-75
14	-1	56	-50
2	0	492	489
4	0	932	-1031
6	0	322	-294
7	0	16	22
8	0	75	73
9	0	37	0
10	0	541	557
11	0	22	-13
12	0	50	25
14	0	43	-28
1	1	156	-191
2	1	246	-291
3	1	141	-194
4	1	18	-19
5	1	48	33
6	1	92	87
7	1	64	64
8	1	41	-36
9	1	22	-35
10	1	90	-106
11	1	19	-18
12	1	29	24
13	1	52	56
14	1	71	68
1	2	720	-656
2	2	603	-584
3	2	33	20
4	2	270	207
5	2	204	147
6	2	150	169
7	2	405	398
8	2	459	-431
9	2	105	109
10	2	34	40
11	2	143	-152
12	2	31	40
13	2	128	-135
14	2	19	10
1	3	31	-3
2	3	94	5
3	3	121	62
4	3	64	62
5	3	40	77
6	3	31	58
8	3	40	46
9	3	46	-45
10	3	59	-54
11	3	37	-27
12	3	33	-43
13	3	40	31
1	4	281	-280
2	4	117	-163
3	4	377	369
4	4	67	81
5	4	27	6
6	4	193	-197
7	4	102	113
8	4	345	-340
9	4	74	-92
10	4	30	-43
12	4	65	66
1	5	60	75
2	5	96	99
3	5	26	25
4	5	50	-31
5	5	125	-125
6	5	55	-57
7	5	26	-68
8	5	45	24
9	5	53	40
10	5	37	50
11	5	43	66
1	6	184	144
3	6	50	54
4	6	184	202
5	6	238	-265
6	6	82	67
7	6	174	174
8	6	45	34
9	6	127	122
10	6	41	38
4	7	22	-18
5	7	38	18
6	7	54	40
7	7	30	16
8	7	15	5
2	8	55	-39
3	8	35	39
4	8	41	-17
11	4	92	-101
**K =		1****	
-4	-8	15	22
-3	-8	81	-77
-2	-8	84	78
-1	-8	40	-28
0	-8	18	8
1	-8	35	34
2	-8	105	-72
3	-8	23	-51
-8	-7	74	-76
-7	-7	104	78
-6	-7	30	62
-5	-7	57	49
-4	-7	82	109
-3	-7	28	2
-2	-7	21	-56
-1	-7	57	-25
1	-7	35	-45
2	-7	178	-175
3	-7	109	79
4	-7	44	76
5	-7	71	83
6	-7	183	177
7	-7	23	31
-10	-6	43	-49
-9	-6	27	22
-8	-6	191	-166
-7	-6	36	46
-6	-6	73	-61
-5	-6	134	155
-4	-6	86	88
-3	-6	138	129
-2	-6	51	-33
-1	-6	91	-113
0	-6	75	-61
1	-6	142	-138
2	-6	26	32
3	-6	33	13
5	-6	175	235
6	-6	47	-58
7	-6	178	162
8	-6	61	-59
9	-6	46	-62
-11	-5	60	55
-10	-5	73	86
-9	-5	15	-3
-8	-5	176	-182
-7	-5	81	-72
-6	-5	83	80
-5	-5	109	-149
-4	-5	98	57
-3	-5	44	3
-2	-5	79	-122
-1	-5	218	230
0	-5	365	352
1	-5	55	95
2	-5	33	-51
3	-5	46	-43
5	-5	92	-127
6	-5	35	11
7	-5	83	-97
8	-5	151	-133
10	-5	121	146
11	-5	32	40
-12	-4	64	63
-10	-4	31	27
-9	-4	27	28
-8	-4	112	-99
-7	-4	187	208
-6	-4	91	-97
-5	-4	328	309
-4	-4	17	-20
-3	-4	57	10
-2	-4	96	142
-1	-4	346	-327
0	-4	313	327
1	-4	70	-54
2	-4	213	192
3	-4	296	254
4	-4	66	-150
5	-4	154	188
6	-4	181	-212
7	-4	43	20
9	-4	30	-34
10	-4	41	76
11	-4	40	32
12	-4	68	69
-13	-3	17	-32
-12	-3	22	-33
-11	-3	201	-213
-10	-3	54	58
-9	-3	51	26
-8	-3	48	-60
-7	-3	314	327
-6	-3	125	130
-5	-3	264	-210
-4	-3	31	-51
-3	-3	447	-375
-2	-3	348	-325
-1	-3	388	-373
0	-3	276	221
1	-3	78	59
2	-3	242	-213
3	-3	160	197
4	-3	82	-115
5	-3	377	-366
6	-3	126	121
7	-3	92	-108
8	-3	33	19
9	-3	81	51
10	-3	86	72
11	-3	37	-46
12	-3	90	-110
13	-3	37	-26
-14	-2	66	-59
-13	-2	101	-102
-12	-2	83	-100
-11	-2	27	-34
-10	-2	122	110
-9	-2	18	14
-8	-2	249	237
-7	-2	136	-94
-6	-2	203	-112
-5	-2	278	-275
-4	-2	607	-692
-3	-2	236	-221
-2	-2	108	94
-1	-2	289	-266
0	-2	862	897
1	-2	552	-541
2	-2	341	323
3	-2	405	-397
4	-2	386	-449
5	-2	49	36
6	-2	400	-367
7	-2	135	165
8	-2	153	120
9	-2	73	-62
10	-2	105	112
11	-2	157	-185
12	-2	24	33
13	-2	88	-112
-14	-1	18	24
-13	-1	141	132
-11	-1	44	-26
-9	-1	53	18
-7	-1	26	-34
-6	-1	29	33
-5	-1	351	-339
-4	-1	12	7
-3	-1	1151	1152
-2	-1	18	2
-1	-1	115	-58
0	-1	13	11
1	-1	554	-584
2	-1	16	-16
3	-1	633	587
5	-1	46	-14
6	-1	18	18
7	-1	288	263
8	-1	20	5
9	-1	42	-79
11	-1	118	-166
13	-1	227	223
14	-1	16	-2
-14	0	49	-59
-13	0	44	46
-12	0	32	-48
-11	0	45	-22
-10	0	54	71
-9	0	47	-69
-8	0	29	46
-7	0	47	26
-6	0	64	-75
-5	0	42	32
-4	0	13	42
-3	0	130	-184
-2	0	205	255
-1	0	193	-223
0	0	15	-17
1	0	186	226
2	0	211	-277
3	0	118	179
4	0	11	-9
5	0	63	-73
6	0	99	101
7	0	58	-57
8	0	15	-16
9	0	52	83
10	0	94	-89
11	0	47	53
12	0	42	50
13	0	73	-79
14	0	86	75
-14	1	46	-47
-13	1	176	172
-12	1	39	70
-11	1	100	-88
-10	1	141	165
-9	1	17	-27
-8	1	56	-73
-7	1	174	145
-6	1	268	-289
-5	1	187	-162
-4	1	49	-24
-3	1	871	840
-2	1	423	471
-1	1	344	-316
0	1	10	3
1	1	281	-271
2	1	372	-424
3	1	825	841
4	1	72	51
5	1	216	-181
6	1	209	217
7	1	169	137
8	1	39	49
9	1	20	-35
10	1	94	-105
11	1	100	-83
12	1	53	-40
13	1	183	176
14	1	28	24
-13	2	189	197
-12	2	16	-5
-11	2	132	181
-10	2	174	-181
-9	2	27	-18
-8	2	159	-138
-7	2	126	-188
-6	2	379	339
-5	2	132	60
-4	2	491	558
-3	2	576	545
-2	2	381	-352
-1	2	475	502
0	2	821	-872
1	2	300	278
2	2	27	6
3	2	77	85
4	2	436	482
5	2	208	215
6	2	102	33
7	2	146	120
8	2	231	-224
10	2	26	-28
11	2	37	30
12	2	75	98
14	2	18	12
-12	3	105	-120
-11	3	119	-147
-10	3	13	-16
-8	3	45	32
-7	3	89	89
-6	3	365	346
-5	3	142	-146
-4	3	168	-170
-3	3	103	-55
-2	3	629	-577
-1	3	340	-317
0	3	259	209
1	3	86	-92
2	3	78	74
3	3	95	-57
4	3	86	44
5	3	425	-397
6	3	104	-117
7	3	48	31
8	3	64	-95
9	3	82	45
10	3	153	163
11	3	90	-78
13	3	50	-44
-12	4	45	-64
-11	4	18	31
-10	4	57	-78
-9	4	39	46
-8	4	38	16
-7	4	71	[illegible]
-6	4	85	124
-5	4	298	-313
-4	4	55	112
-3	4	125	-167
-2	4	64	[illegible]
-1	4	224	241
0	4	274	-341
1	4	155	192
2	4	411	-355
3	4	175	-144
4	4	53	17
5	4	207	-194
6	4	232	252
7	4	138	-117
8	4	113	153
9	4	15	[illegible]
10	4	42	-65
11	4	41	24
12	4	138	-116
-10	5	127	141
-9	5	29	48
-8	5	232	[illegible]
-7	5	81	[illegible]
-6	5	15	2
-5	5	65	[illegible]
-4	5	44	12
-3	5	27	-62
-2	5	25	-47
-1	5	43	43
0	5	388	354
1	5	215	235
2	5	91	-85
3	5	27	-27
4	5	63	59
5	5	120	-137
6	5	61	49
7	5	26	-22
8	5	153	-167
10	5	95	104
11	5	43	47
-9	6	56	29
-8	6	127	96
-7	6	45	-53
-6	6	161	133
-5	6	145	-203
-4	6	85	-64
-3	6	134	-135
-2	6	72	-71
-1	6	118	149
0	6	80	64
1	6	90	120
2	6	129	78
4	6	43	-2
5	6	82	-131
6	6	29	-50
7	6	188	-189
8	6	78	73
9	6	61	-44
10	6	62	53
-6	7	154	134
-4	7	31	66
-3	7	139	145
-2	7	100	-102
0	7	16	9
1	7	71	-74
2	7	103	-122
3	7	58	-67
4	7	66	67
5	7	105	112
6	7	83	85
7	7	158	164
8	7	87	-84
-2	8	77	44
-1	8	57	-42
0	8	24	-33
1	8	50	23
2	8	77	-66
3	8	118	113
**K =		2****	
-1	-8	50	-41
1	-8	60	-66
2	-8	17	18
-7	-7	37	30
-6	-7	25	34
-5	-7	105	-84
-4	-7	82	48
-3	-7	124	-91
-2	-7	24	-25
0	-7	98	-89
1	-7	56	60
2	-7	31	-0
3	-7	46	-28
4	-7	78	69
5	-7	169	-128
6	-7	44	-36
-8	-6	22	2
-7	-6	109	109
-6	-6	15	8
-5	-6	38	-33
-4	-6	26	18
-3	-6	62	98
-1	-6	140	-139
1	-6	107	-102
2	-6	52	48
3	-6	114	132
4	-6	94	-114
5	-6	40	-38
6	-6	106	-89
7	-6	74	67
8	-6	35	51
9	-6	35	18
-11	-5	55	-44
-10	-5	74	86
-9	-5	38	21
-8	-5	216	194
-7	-5	140	109
-6	-5	139	116
-4	-5	149	-141
-3	-5	75	-76
-2	-5	27	-8
-1	-5	131	-59
0	-5	255	262
1	-5	32	26
2	-5	158	173
3	-5	122	110
4	-5	34	4
5	-5	52	53
6	-5	19	14
7	-5	49	-65
8	-5	158	173
9	-5	46	-26
10	-5	97	96
-12	-4	44	-35
-11	-4	28	-22
-10	-4	50	69
-9	-4	23	14
-8	-4	59	99
-7	-4	18	-36
-6	-4	57	-44
-5	-4	272	-314
-4	-4	136	-73
-2	-4	99	116
-1	-4	16	3
0	-4	159	197
1	-4	98	75
2	-4	97	69
3	-4	156	179
4	-4	71	-64
5	-4	158	-184
6	-4	40	7
7	-4	15	-18
9	-4	16	-17
10	-4	15	-28
11	-4	74	-59
-13	-3	70	47
-12	-3	32	21
-11	-3	24	28
-10	-3	33	-34
-9	-3	19	-23
-8	-3	139	-118
-7	-3	128	-150
-6	-3	135	-69
-5	-3	58	-54
-4	-3	52	56
-3	-3	324	337
-2	-3	97	65
-1	-3	279	280
0	-3	73	-63
1	-3	23	-37
2	-3	192	-178
3	-3	243	-173
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Table 2 (*cont.*)

OBSERVED REFLECTIONS

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7	5	129	-122
8	5	19	7
9	5	41	-25
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-4	6	43	-52
-2	6	73	94
-1	6	104	-96
0	6	59	-80
1	6	97	-108
2	6	53	-37
3	6	92	109
4	6	142	-150
6	6	80	-90
7	6	97	-87
-4	7	45	51
-3	7	48	-41
-2	7	75	-60
-1	7	40	-39
0	7	68	-58
1	7	19	43
2	7	74	45
3	7	18	8
4	7	39	35
K = 5**			
-5	-6	90	74
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-3	-6	62	-66
-2	-6	41	-44
-1	-6	198	-178
0	-6	39	-42
1	-6	91	-77
2	-6	41	36
3	-6	69	59
4	-6	67	73
-8	-5	18	-7
-7	-5	29	-44
-6	-5	19	-17
-5	-5	98	127
-3	-5	125	-118
-2	-5	18	13
1	-5	55	29
3	-5	111	-141
4	-5	18	1
5	-5	74	108
7	-5	18	4
-9	-4	27	-22
-8	-4	130	-124
-7	-4	45	-42
-6	-4	100	-103
-5	-4	58	-74
-4	-4	27	27
-3	-4	15	3
-2	-4	47	73
-1	-4	28	27
0	-4	72	56
1	-4	83	-95
2	-4	22	9
3	-4	64	-84
4	-4	78	-71
5	-4	38	-43
6	-4	61	-69
7	-4	18	13
8	-4	44	-57
-10	-3	57	-54
-9	-3	86	-66
-8	-3	188	175
-7	-3	148	-138
-6	-3	165	154
-5	-3	72	74
-3	-3	67	33
-2	-3	91	-112
-1	-3	135	117
0	-3	85	-123
1	-3	33	-26
2	-3	268	276
3	-3	128	-119
4	-3	114	119
5	-3	82	135
6	-3	62	-66
9	-3	37	-4
-11	-2	22	25
-10	-2	48	39
-9	-2	168	177
-8	-2	113	-79
-7	-2	218	216
-6	-2	80	-72
-5	-2	61	-63
-4	-2	60	47
-3	-2	140	-140
-2	-2	81	86
-1	-2	150	151
0	-2	65	43
1	-2	214	234
2	-2	85	-63
3	-2	91	113
4	-2	132	-115
5	-2	28	-26
7	-2	68	103
8	-2	53	59
9	-2	168	169
10	-2	18	-11
-11	-1	43	34
-10	-1	79	-94
-9	-1	30	-24
-8	-1	158	172
-7	-1	68	-54
-6	-1	93	-88
-5	-1	84	-129
-4	-1	48	-33
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-1	-1	221	227
0	-1	421	-373
1	-1	63	77
2	-1	30	41
3	-1	51	-55
5	-1	57	-104
7	-1	51	-86
8	-1	142	141
9	-1	31	41
10	-1	123	-163
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-12	0	33	-39
-11	0	35	29
-10	0	52	-65
-9	0	71	62
-8	0	37	-19
-6	0	62	86
-5	0	55	-68
-4	0	66	73
-3	0	47	62
-2	0	75	-91
-1	0	45	37
0	0	39	28
1	0	95	-96
2	0	58	70
3	0	14	19
4	0	130	-122
5	0	108	106
6	0	62	-77
7	0	16	26
8	0	45	24
9	0	62	-57
10	0	59	79
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-9	1	23	30
-8	1	152	172
-7	1	67	-62
-6	1	67	-55
-5	1	138	-151
-4	1	48	-53
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-1	1	259	254
0	1	427	-381
1	1	34	39
2	1	24	65
3	1	26	-39
4	1	29	-12
5	1	54	-84
7	1	56	-86
8	1	153	166
9	1	47	57
10	1	125	-153
11	1	38	33
-11	2	36	-38
-10	2	18	-3
-9	2	110	-118
-8	2	19	-45
-7	2	52	-103
-6	2	18	-29
-5	2	33	-46
-4	2	138	130
-3	2	52	-88
-2	2	70	84
-1	2	251	-254
0	2	113	-50
1	2	100	-114
2	2	114	-132
3	2	158	139
4	2	38	-16
5	2	32	30
6	2	157	151
7	2	228	-213
8	2	42	-14
9	2	158	-185
10	2	51	-50
-9	3	49	-23
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-5	3	74	102
-4	3	233	200
-3	3	190	-182
-2	3	150	138
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0	3	146	-172
1	3	150	161
2	3	36	33
3	3	97	75
4	3	45	55
5	3	20	-1
6	3	106	86
7	3	191	-190
8	3	89	59
10	3	69	-60
-9	4	47	-41
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-7	4	50	37
-6	4	130	130
-5	4	50	66
-4	4	23	11
-3	4	32	27
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0	4	32	-10
1	4	16	-5
2	4	17	2
3	4	57	78
4	4	17	-4
5	4	59	63
6	4	52	41
7	4	29	5
8	4	47	40
9	4	20	19
-8	5	19	-12
-7	5	21	-17
-5	5	69	104
-4	5	52	66
-3	5	102	-127
-2	5	57	-45
1	5	16	-20
2	5	59	45
3	5	94	-112
4	5	60	-66
5	5	80	125
6	5	20	34
7	5	18	-17
-5	6	94	-69
-4	6	75	-69
-3	6	31	-17
-2	6	33	33
-1	6	192	183
0	6	54	59
1	6	147	149
2	6	56	-57
3	6	22	8
4	6	61	-47
5	6	93	-91
K = 6**			
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-4	-5	33	27
-3	-5	26	-17
-2	-5	160	-164
-1	-5	62	76
0	-5	152	-136
1	-5	21	3
2	-5	21	12
3	-5	54	-75
4	-5	69	49
-7	-4	39	36
-6	-4	61	-73
-5	-4	62	-71
-4	-4	84	-81
-3	-4	100	-98
-2	-4	17	17
-1	-4	108	101
0	-4	92	-97
1	-4	125	99
2	-4	48	63
3	-4	22	-15
4	-4	75	-99
5	-4	27	31
6	-4	109	-106
-9	-3	57	-48
-7	-3	56	-67
-6	-3	35	-18
-5	-3	62	-52
-4	-3	28	32
-3	-3	67	33
-2	-3	42	-4
-1	-3	91	91
1	-3	26	97
2	-3	32	-24
3	-3	41	31
5	-3	35	-52
6	-3	115	114
7	-3	93	-106
-10	-2	56	-61
-9	-2	19	-12
-8	-2	62	46
-7	-2	103	-113
-6	-2	18	1
-5	-2	47	45
-4	-2	19	0
-3	-2	49	-69
-2	-2	17	-25
-1	-2	148	160
1	-2	95	83
2	-2	52	56
3	-2	107	-129
4	-2	94	-111
5	-2	61	64
6	-2	101	-82
7	-2	77	-67
8	-2	34	41
9	-2	37	-29
-9	-1	147	140
-8	-1	32	-4
-7	-1	144	170
-6	-1	88	98
-5	-1	67	-67
-4	-1	174	190
-3	-1	29	-36
-2	-1	14	-7
-1	-1	129	111
0	-1	183	-167
1	-1	48	28
2	-1	94	-91
3	-1	18	-8
4	-1	89	145
6	-1	201	232
7	-1	38	34
8	-1	29	9
9	-1	48	38
-9	0	140	-138
-8	0	34	40
-7	0	187	-184
-6	0	106	96
-5	0	197	240
-4	0	197	216
-3	0	79	-77
-2	0	20	-26
-1	0	131	-107
0	0	141	-145
1	0	129	-128
2	0	27	-6
3	0	75	-61
4	0	104	129
5	0	239	291
6	0	247	229
7	0	116	-124
8	0	60	42
9	0	140	-138
-9	1	103	-84
-8	1	120	-120
-7	1	21	13
-6	1	128	-156
-5	1	17	26
-4	1	45	-90
-3	1	110	-73
-2	1	56	71
-1	1	123	-90
0	1	165	177
1	1	24	-9
2	1	20	-18
3	1	135	135
4	1	147	-200
5	1	41	-62
6	1	94	-130
7	1	187	-154
8	1	27	10
9	1	28	-6
-9	2	87	-82
-8	2	63	76
-7	2	39	-49
-6	2	59	-55
-5	2	89	81
-3	2	134	-131
-2	2	19	18
-1	2	136	139
0	2	21	-33
1	2	159	141
2	2	35	39
3	2	93	-119
4	2	53	-62
5	2	47	-45
6	2	16	11
7	2	120	-117
9	2	44	52
-9	3	23	27
-8	3	28	-34
-7	3	119	128
-5	3	37	46
-4	3	21	1
-3	3	101	-69
-2	3	43	-23
-1	3	73	-105
0	3	22	14
1	3	60	-93
3	3	20	33
4	3	23	-30
5	3	31	42
6	3	32	-43
7	3	46	68
-7	4	101	86
-6	4	108	-101
-5	4	31	-38
-4	4	107	-110
-3	4	86	-103
-2	4	45	-35
-1	4	156	149
0	4	90	-112
1	4	90	90
2	4	72	85
3	4	28	-21
4	4	42	-47
6	4	48	-52
7	4	20	-7
-5	5	76	72
-4	5	45	-35
-3	5	86	93
-2	5	88	101
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0	5	179	182
1	5	68	-86
2	5	64	59
3	5	35	35
4	5	90	-76
5	5	84	89
K = 7**			
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-3	-4	44	73
-2	-4	92	-46
-1	-4	105	113
0	-4	35	12
2	-4	44	6
3	-4	44	-47
-6	-3	137	-116
-5	-3	28	3
-4	-3	53	60
-3	-3	69	-82
-2	-3	159	135
-1	-3	26	-25
0	-3	42	-64
1	-3	42	-65
2	-3	79	-65
3	-3	78	-73
4	-3	46	-27
5	-3	24	35
-7	-2	30	-13
-6	-2	30	29
-5	-2	61	45
-4	-2	158	105
-2	-2	46	18
-1	-2	71	-66
0	-2	59	-73
1	-2	60	-43
2	-2	19	-5
3	-2	61	80
4	-2	133	111
5	-2	29	-18
6	-2	145	116
-8	-1	87	91
-7	-1	104	96
-6	-1	36	-77
-5	-1	65	54
-4	-1	79	-103
-3	-1	32	-18
-2	-1	26	66
-1	-1	63	-32
0	-1	31	44
1	-1	32	-47
2	-1	186	196
3	-1	111	89
4	-1	72	-97
5	-1	74	92
6	-1	181	-186
-8	0	17	14
-7	0	21	3
-6	0	39	-13
-2	0	24	-16
-1	0	17	10
0	0	17	0
1	0	21	-4
2	0	18	8
3	0	31	-17
5	0	81	-72
6	0	52	46
-8	1	93	93
-7	1	147	163
-6	1	106	-108
-5	1	98	110
-4	1	63	-64
-3	1	66	-71
-2	1	116	124
-1	1	78	-65
1	1	16	0
2	1	92	104
3	1	118	121
4	1	48	-86
5	1	28	42
6	1	110	-114
-7	2	137	107
-6	2	144	-118
-5	2	28	-33
-4	2	112	-82
-3	2	76	-75
-2	2	50	-31
-1	2	51	47
0	2	23	41
1	2	100	98
2	2	24	-16
3	2	21	-15
4	2	93	-68
5	2	79	-70
6	2	20	2
7	2	31	22
-6	3	140	-112
-4	3	28	1
-3	3	17	11
-2	3	68	57
-1	3	58	31
0	3	25	-9
1	3	131	-145
2	3	38	36
3	3	139	-131
4	3	39	-36
5	3	68	81
6	3	47	-40
-4	4	18	2
-3	4	89	56
-2	4	30	-48
0	4	24	22
1	4	128	-90
2	4	51	52
3	4	17	3
4	4	38	26
K = 8**			
-3	-2	38	-49
-2	-2	21	7
-1	-2	42	37
1	-2	41	46
-4	-1	72	-72
-3	-1	81	-73
-2	-1	68	-47
-1	-1	54	-47
0	-1	16	27
1	-1	54	47
2	-1	78	-15
3	-1	70	55
-5	0	131	132
-4	0	65	-19
-3	0	31	-38
-2	0	38	-15
-1	0	17	-27
0	0	98	79
1	0	37	-4
2	0	32	-16
3	0	27	-19
4	0	68	-20
-4	1	74	70
-3	1	48	35
-2	1	116	87
-1	1	75	63
0	1	23	-33

UNOBSERVED REFLECTIONS

H	L	FOBS	FCAL
K = 0**			
0	-7	22	1
1	-7	16	-13
2	-7	15	2
3	-7	16	-9
7	-7	16	9
7	-5	15	37
0	-3	11	-3
13	-2	19	-14
0	-1	8	8
4	-1	11	5
1	0	7	1
3	0	12	0
5	0	20	13
13	0	17	-13
7	3	13	16
2	6	15	11
1	7	15	17
2	7	17	16
3	7	15	-4
1	8	15	37
K = 1**			
0	-7	16	-17
4	-6	15	6
4	-5	14	-5
9	-5	17	49
-11	-4	15	-22
8	-4	14	9
-12	-1	15	-1
-10	-1	14	-22
-8	-1	12	0
4	-1	11	3
10	-1	15	-16
12	-1	16	-15
9	2	14	-9
13	2	16	21
-13	3	15	-2
-9	3	14	-10
12	3	15	-9
-11	5	16	-6
9	5	16	16
3	6	15	-20
-7	7	18	-16
-5	7	15	25
-1	7	15	16
-3	8	15	-14
4	8	15	18
K = 2**			
-2	-8	15	1
0	-8	15	12
-1	-7	15	40
-9	-6	10	12
-2	-6	15	-9
0	-6	15	-18
-5	-5	14	6
-3	-4	12	35
8	-4	15	28
12	-3	15	-22
-11	-2	15	1
-8	-2	13	31
1	-2	11	24
5	-2	12	-10
-12	0	16	-7
-3	0	10	13
9	0	14	3
13	0	16	4
-14	1	15	28
9	3	14	11
12	3	16	24
-12	4	16	22
8	4	15	33
10	4	16	-13
11	4	15	-9
2	6	15	28
2	8	15	-4
3	8	18	5
K = 3**			
-1	-7	15	-37
-4	-6	15	35
4	-6	15	5
8	-5	18	-2
10	-5	15	-24
-11	-4	15	6
-6	-4	14	-17
-12	-3	18	4
-10	-3	15	16
-8	-3	15	-1
0	-3	11	-2
4	-3	12	6
8	-3	15	0
10	-3	15	1
11	-3	15	-13
12	-3	15	4
10	-2	15	-18
-12	-1	16	29
-12	0	16	8
0	0	11	-16
1	0	11	19
12	0	16	-6
13	0	15	0
-12	1	16	17
-11	2	16	22
-10	3	16	22
0	3	12	-2
7	4	14	36
1	5	14	3
6	5	15	48
10	5	16	11
-3	6	15	-10
3	6	16	-1
K = 4**			
3	-7	16	57
-2	-6	15	10
3	-6	15	0
-3	-5	15	-29
0	-5	15	13
6	-5	16	-2
8	-5	15	9
-11	-4	15	3
-9	-4	16	2
5	-4	14	5
7	-4	15	6
8	-4	15	-11
9	-4	15	3
-9	-3	16	-32
9	-3	15	-18
7	-2	14	15
8	-2	15	28
-9	-1	15	-8
11	0	16	9
12	0	15	-17
-10	1	15	12
-9	1	15	-25
10	1	15	23
-11	2	16	20
-10	2	15	-9
-7	3	14	-17
-6	3	14	18
-9	5	15	-27
-7	6	15	6
-5	6	16	28
-3	6	16	-6
5	6	15	22
K = 5**			
-4	-5	15	-0
-1	-5	15	29
0	-5	16	1
2	-5	15	5
8	-5	15	-10
-4	-3	14	21
7	-3	15	-32
8	-3	15	7
10	-3	15	19
6	-2	14	12
-3	-1	13	-9
4	-1	13	-2
6	-1	14	13
-7	0	15	-12
6	1	15	16
11	2	14	-11
-10	3	16	-12
-8	3	15	-14
-6	3	15	-53
9	3	15	22
-1	4	15	-10
-6	5	16	-16
-1	5	15	0
0	5	15	1
K = 6**			
-8	-3	16	0
0	-3	15	1
4	-3	15	12
8	-3	15	-2
0	-2	15	-27
-10	-1	16	-2
5	-1	16	11
-10	0	16	17
-10	1	16	3
-4	2	15	16
8	2	16	9
-6	3	16	-21
2	3	15	16
8	3	15	-7
5	4	15	-34
K = 7**			
1	-4	15	-23
-3	-2	16	1
7	-1	16	24
-5	0	16	15
-4	0	16	24
-3	0	16	20
4	0	16	5
7	0	16	-12
0	1	15	2
7	1	15	8
-5	3	16	2
-1	4	15	-16
K = 8**			
0	-2	15	6
2	-2	15	15

Solution and refinement

Preliminary statistics based on the $N(z)$ test (Howells, Phillips & Rogers, 1950) for the $hk0$, $h0l$, $0kl$ and hkl data sets pointed strongly to the space group $P\bar{1}$. The structure was solved with the symbolic-addition method for centrosymmetric crystals (Hauptman & Karle, 1953) using a program written by S. R. Hall and adapted for the CDC 1604 computer by E. N. Maslen. The $|E|$ statistics together with the corresponding theoretical values (in parentheses) are: $\langle|E|\rangle=0{\cdot}806$ (0·798), $\langle|E|^2\rangle=1{\cdot}056$ (1·000), $\langle|E^2-1|\rangle=1{\cdot}019$ (0·968); reflections with $|E|>3{\cdot}0$ comprised 0·45% (0·3%), reflections with $|E|>2{\cdot}0$ comprised 5·4% (5·0%), and reflections with $|E|>1$ comprised 31·9% (32·0%) of the total. The atomic scattering factors used in calculations were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

From precession photographs it was observed and subsequently confirmed by the diffractometrically collected data that the intensities $I(0kl)$ were approximately equal to $I(0k\bar{l})$. The quasi-equality and the observed non-space-group absences along **b*** and **c*** led to the assumption that the [100] projection of the unit cell had pseudo *pgg* symmetry. The symmetry of the plane group results in phase relations among the $0kl$ reflections. This additional information was employed in a manual symbolic-addition procedure applied to the 210 reflections with $|E|>1{\cdot}9$, using the results of a search carried out by the program for sets of reflections that satisfy the $\sum_2$ relationship. Three origin-defining reflections were selected and four additional reflections were assigned symbols indicative of unknown phases. They are:

hkl	$\|E\|$	Phase or symbol
13 4 0	4·008	π
$\bar{3}$ 1 $\bar{1}$	3·262	0
$\overline{13}$ 1 2	3·157	0
10 0 0	4·655	*a*
$\bar{8}$ 2 5	3·167	*b*
0 5 1	2·757	*c*
0 1 $\bar{2}$	2·457	*d*

The results of the manual symbolic addition procedure strongly suggested the relations $c=\pi$, $c-b+d=0$ and $a+b=\pi$. When the symbol d is disregarded there are four possible sets of phases expressed in terms of the symbols a and b.

A starting set of phases with the values 0 and π assigned respectively to a and b was extended and refined in ten cycles as described by Oh & Maslen (1968) using the tangent formula. At the end of this process the phases of 339 reflections with $|E|\geq 1{\cdot}65$ had been determined and an E Fourier synthesis was calculated. It revealed all the heavy atoms as peaks that were well above the noise level. A structure-factor calculation incorporating a uniform isotropic temperature factor yielded an R value of 28% and confirmed the correctness of the structure as found from the E map.

The asymmetric unit consists of four half molecules. Molecules 1 and 2 are located in the layer at $x=\frac{1}{2}$ on the symmetry centers $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ and $(\frac{1}{2}\,0\,0)$ respectively. Molecules 3 and 4 in the layer at $x=0$ are located on the symmetry centers $(0\,\frac{1}{2}\,0)$ and $(0\,0\,\frac{1}{2})$ respectively. Fig. 2 shows projections of the two layers along the a axis. Figs. 3 and 4 show the projections along the b and c axes respectively.

Three cycles of isotropic full-matrix least-squares refinement yielded R and wR values of 17·2 and 16·5% respectively. At this stage further refinement could not be obtained, and it was obvious that a closer look at the disorder phenomena was required.

Interpretation of the disorder phenomena

In this section only a qualitative interpretation of the observed order–disorder phenomena will be presented

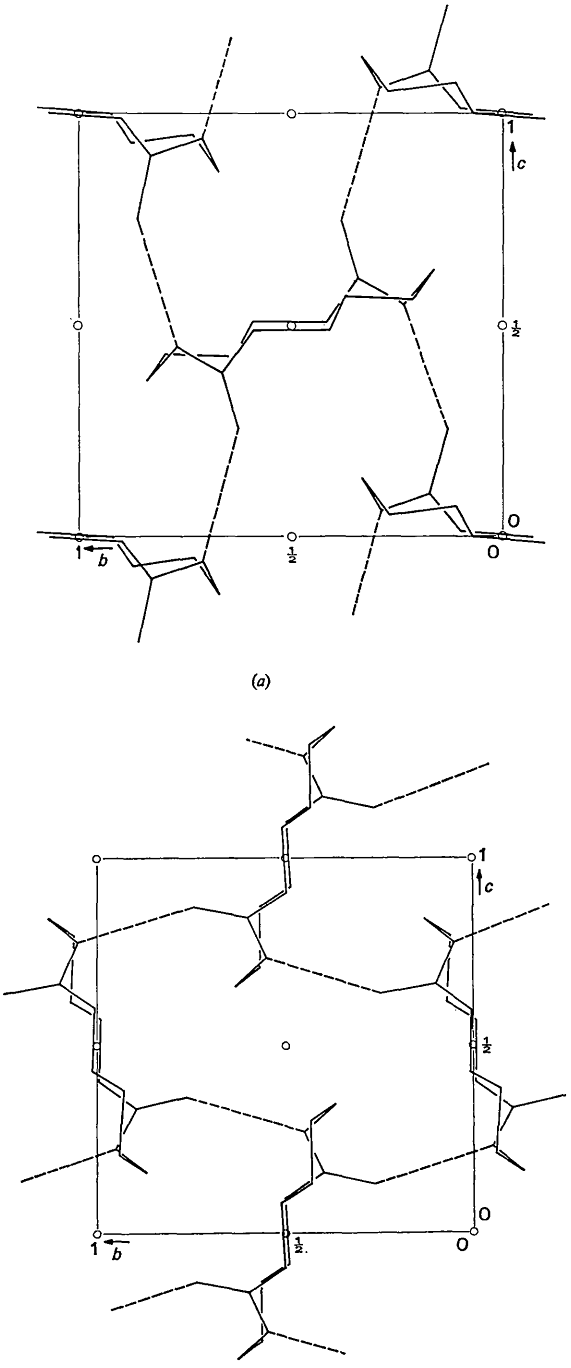

Fig. 2. Hydrogen bonding in (*a*) layer *B* located at $x=\frac{1}{2}$. Projection is parallel to the *a* axis. (*b*) Layer *A* located at $x=0$. Projection is parallel to the *a* axis.

since a quantitative approach is beyond the scope of this investigation. The appearance of (1) maxima at half-integral values of h and (2) continuous streaking along row lines parallel to $\mathbf{a}^*$ indicate a partially ordered structure. The structure deduced by the direct phasing method is the fully ordered arrangement, which consists of two kinds of layers, A and B, parallel to the (100) planes, as shown in Fig. 2. The stacking of layers along the a axis, therefore, is $ABABAB\ldots$

In the partially ordered structure the same sequence of layers A and B exists except for a planar disordering parallel to the (100) planes described by the translation vector $\frac{1}{2}\mathbf{b}+\frac{1}{2}\mathbf{c}$. For a^* lattice rows with $k+l$ even, this kind of stacking fault does not affect the intensities nor produce streaking. In addition there is a tendency toward body centering, as was noted earlier for crystals showing heavy streaking and strong extra spots. This can be explained by interpreting the discrete intensity pattern on the basis of the doubled unit-cell with dimensions $a'=2a$, $b'=b$ and $c'=c$. In this doubled cell a stacking of layers with body centering, which we shall designate mode I, is the following:

(1) A layer A at $x'=0$
(2) A layer B at $x'=\frac{1}{4}$
(3) A layer A at $x'=\frac{1}{2}$ translated by the vector $\frac{1}{2}\mathbf{b}+\frac{1}{2}\mathbf{c}$
(4) A layer B at $x'=\frac{3}{4}$ translated by the vector $\frac{1}{2}\mathbf{b}+\frac{1}{2}\mathbf{c}$.

Comparison of structure factors for the mode I sequence of layers with the estimated intensities of the extra reflections showed reasonable qualitative agreement. The pure form of this kind of layer stacking, $ABA_TB_TABA_TB_T\ldots$, where the subscript T denotes a translated layer, has not been observed in any of the crystals examined. The occurrence of extra reflections at half orders along a^* rows has invariably been accompanied by streaking, and in addition the reflections at integral values of h (or h' even) with $k+l$ odd have never faded out completely.

In principle, the doubling of the a cell dimension coupled with disorder streaking could also be caused

Table 3. *Fractional positional coordinates and isotropic temperature factors with e.s.d.'s in parentheses*

The first digit of the labeling number indicates the molecule.

	x	y	z	B
Molecule 1				
O(1)	0·3879 (5)	0·6202 (9)	0·2532 (9)	5·3 (2) Å^2
N(1)	0·4273 (6)	0·7669 (11)	0·4505 (10)	3·9 (2)
C(11)	0·3764 (8)	0·6588 (14)	0·3914 (12)	4·4 (3)
C(12)	0·3077 (8)	0·5861 (14)	0·4891 (13)	4·6 (3)
C(13)	0·3115 (8)	0·4114 (14)	0·4919 (13)	4·3 (3)
C(14)	0·3980 (8)	0·3714 (13)	0·5673 (13)	4·4 (3)
C(15)	0·4115 (7)	0·2050 (13)	0·5620 (12)	4·1 (3)
C(16)	0·5002 (7)	0·1595 (14)	0·6312 (12)	4·9 (3)
Molecule 2				
O(2)	0·3806 (5)	−0·1363 (9)	−0·2477 (9)	5·7 (2)
N(2)	0·4225 (7)	−0·2711 (12)	−0·0504 (11)	5·9 (3)
C(21)	0·3712 (9)	−0·1721 (16)	−0·1014 (14)	5·7 (4)
C(22)	0·3023 (8)	−0·1019 (14)	−0·0089 (13)	5·5 (3)
C(23)	0·3132 (8)	−0·0709 (14)	−0·0057 (13)	4·9 (3)
C(24)	0·3973 (8)	0·1169 (14)	0·0729 (13)	4·9 (3)
C(25)	0·4165 (8)	0·2848 (15)	0·0624 (14)	5·1 (3)
C(26)	0·5060 (8)	0·3331 (15)	0·1359 (13)	5·7 (3)
Molecule 3				
O(3)	0·1172 (5)	0·2578 (10)	0·1280 (9)	5·6 (2)
N(3)	0·0716 (6)	0·4527 (11)	0·2697 (10)	4·6 (3)
C(31)	0·1255 (8)	0·3978 (14)	0·1589 (14)	5·6 (3)
C(32)	0·1927 (8)	0·4982 (15)	0·0889 (13)	4·5 (3)
C(33)	0·1882 (8)	0·4934 (15)	−0·0829 (13)	5·7 (3)
C(34)	0·1046 (9)	0·5674 (16)	−0·1287 (14)	5·7 (4)
C(35)	0·0885 (8)	0·5677 (15)	−0·2953 (14)	5·7 (3)
C(36)	0·0003 (7)	0·6320 (14)	−0·3418 (13)	5·0 (3)
Molecule 4				
O(4)	0·1139 (5)	−0·2448 (10)	0·3621 (9)	5·4 (2)
N(4)	0·0752 (8)	−0·0512 (14)	0·2230 (12)	7·8 (3)
C(41)	0·1249 (9)	−0·1011 (16)	0·3288 (14)	6·4 (4)
C(42)	0·1955 (8)	−0·0076 (14)	0·3997 (13)	5·1 (3)
C(43)	0·1864 (8)	−0·0128 (15)	0·5732 (14)	5·2 (3)
C(44)	0·1038 (8)	0·0722 (14)	0·6195 (13)	4·8 (3)
C(45)	0·0854 (8)	0·0635 (15)	0·7904 (14)	5·3 (3)
C(46)	−0·0023 (8)	0·1342 (14)	0·8405 (13)	5·5 (3)

by admixture of the basic layer sequence *ABABABAB* ... with three other possible stacking modes:

II $AB_TA_TBAB_TA_TB$ ...
III ABA_TBABA_TB ...
IV $ABAB_TABAB_T$ ...

Mode II is enantiomorphic to mode I, $ABA_TB_TABA_TB_T$ ..., described in the preceding paragraph and as such would give identical diffraction effects. Modes III IV, on the other hand, would generate distinctive diffraction effects; however, calculated structure factors for both III and IV showed conspicuous disagreement with the visually estimated intensities of the reflections of half orders. Therefore, it was felt that any contribution of stacking sequences III and IV to the disordering must be very minor relative to the role played by the body centering modes I and II.

On the basis of the foregoing discussion it is proposed that a crystal of 1,8-diazacyclotetradecane-2,9-dione contains domains with the fully ordered arrangement *ABABABAB* ... as defined by the small unit cell, and domains with partial disorder arising principally from admixture of stacking modes I and II, as described above. Since no quantitative measurements were made of the intensities of the a^* streaks and the reflections of half-integral h indices, it is not possible to reach a conclusion concerning the relative frequencies of the layer pairs *AB* and A_TB_T in the disordered state. However, it was observed that, together with the tendency for body centering, the maxima of half-integral indices were as well defined as the reflections of the regular lattice. This indicates that the partial disorder has a tendency to degenerate into a superlattice with the sequence $ABA_TB_TABA_TB_T$ ... or its enantiomorph $AB_TA_TBAB_TA_TB$ ....

Table 4. *Bond distances and angles with e.s.d.'s in parentheses*

Molecule	1	2	3	4
C(1)–C(2)	1·487 (16) Å	1·492 (18) Å	1·475 (17) Å	1·511 (18) Å
C(2)–C(3)	1·572 (17)	1·557 (18)	1·537 (16)	1·550 (17)
C(3)–C(4)	1·565 (17)	1·540 (18)	1·536 (19)	1·559 (18)
C(4)–C(5)	1·517 (17)	1·529 (19)	1·513 (17)	1·544 (17)
C(5)–C(6)	1·583 (16)	1·596 (19)	1·563 (18)	1·574 (18)
C(6)–N	1·457 (14)	1·457 (16)	1·457 (15)	1·461 (17)
N——C(1)	1·349 (15)	1·299 (18)	1·383 (16)	1·317 (18)
O——C(1)	1·293 (14)	1·343 (16)	1·294 (16)	1·327 (16)
C(1)–C(2)–C(3)	113 (1)°	113 (1)°	110 (1)°	111 (1)°
C(2)–C(3)–C(4)	107 (1)	110 (1)	108 (1)	108 (1)
C(3)–C(4)–C(5)	111 (1)	112 (1)	115 (1)	112 (1)
C(4)–C(5)–C(6)	113 (1)	113 (1)	115 (1)	114 (1)
C(5)–C(6)–N	110 (1)	110 (1)	110 (1)	110 (1)
N——C(1)——C(2)	118 (1)	124 (1)	118 (1)	124 (1)
N——C(1)——O	120 (1)	117 (1)	118 (1)	115 (1)
O——C(1)——C(2)	121 (1)	120 (1)	123 (1)	121 (1)

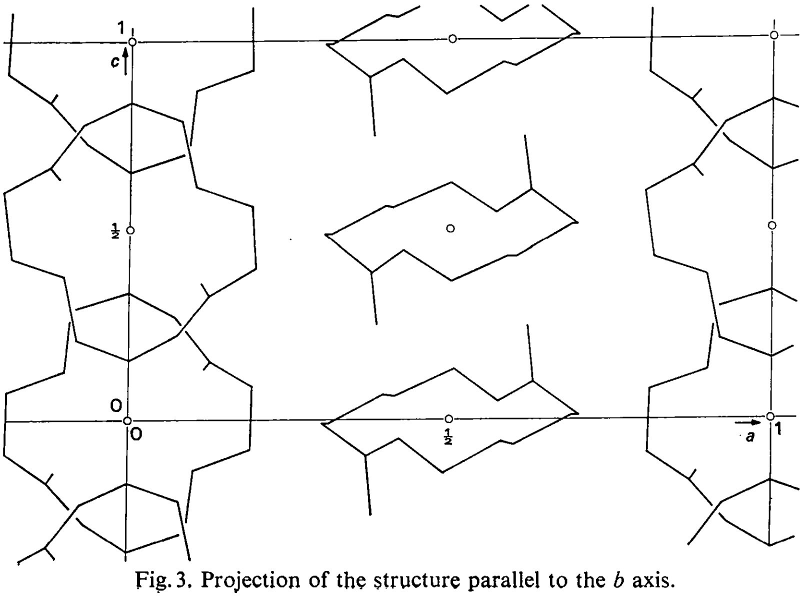

Fig. 3. Projection of the structure parallel to the b axis.

Final refinement and discussion

As discussed in the preceding paragraph, the intensities of reflection with $k+l$ even are not affected by the degree of ordering in the structure. It seemed proper, therefore, to use only these reflections in an attempt at further refinement. Three cycles of isotropic full-matrix least-squares refinement gave, for 952 observed reflections with $k+l$ even, final values for R and wR of 14·2 and 13% respectively. A structure-factor calculation including all the observed reflections but employing the atomic parameters from this last refinement gave an R value of 16·5%, whereas the corresponding value for reflections with $k+l$ odd was 19%. A difference map at this stage did not reveal the hydrogen atoms, and it was not deemed feasible to attempt further refinement including anisotropic temperature factors and the contributions of the hydrogen atoms. Table 2 lists the observed and calculated structure factors, Table 3 gives the atomic parameters, and Table 4 gives the bond angles and bond distances.

Contrary to the assumption made by Hermans (1953, 1956) on the basis of a kinetic analysis of the hydrolysis of this oligomer, the molecule does not have an intramolecular hydrogen bond. In the linear polymer of c[Cap]$_2$ the conformation adopted is one that consists of planar chains of CH_2 groups and amide groups (Holmes, Bunn & Smith, 1955). The 14-membered ring of the cyclic dimer resolves itself into two pairs of planar elements related by a symmetry center (Fig. 5). Here again, as in the cyclic monomer and dimer of nylon 66, it appears that the conformation of minimal potential energy is one that consists of a relatively small number of planar elements, formed by the inherently planar amide groups or planar sequences of methylene groups. More specifically, this shows up in the resemblance of the box-like configuration of the cyclic monomer of nylon 66, a 14-membered ring also, to the configuration of the c[Cap]$_2$ molecule.

The plane containing the amide group (A) is perpendicular to the average plane through the ring atoms (M), as was found in the cyclic monomer and dimer of nylon 66. However, in c[Cap]$_2$ a perpendicular orientation of the plane through the atoms of the pentamethylene group (P) with respect to plane M would cause a large amount of strain in the ring. This strain is relieved and at the same time the planarity of the P group is preserved by a 60° rotation of the plane P out of the perpendicular orientation. A complete analysis of the planar elements is given in Table 5.

Table 5. *Analysis of the planar elements in the molecules*

Labeling of the planes is as follows: M-plane through the ring atoms, A-plane through atoms of amide group, P-plane through atoms of $(CH_2)_5$ group.

(*a*) Distances from least-squares plane in Å

Molecule No.	1	2	3	4
Atoms of plane *M*				
O	1·71	1·70	1·69	1·68
N	−0·34	−0·33	−0·34	−0·33
C(1)	0·42	0·36	0·40	0·36
C(2)	−0·27	−0·25	−0·29	−0·27
C(3)	0·18	0·20	0·21	0·24
C(4)	−0·29	−0·32	−0·27	−0·33
C(5)	0·21	0·23	0·18	0·21
C(6)	−0·20	−0·23	−0·21	−0·23
Atoms of plane *A*				
O	0·00	0·01	0·01	0·02
N	0·03	0·04	0·04	0·06
C(1)	0·01	0·00	−0·01	−0·02
C(2)	−0·02	−0·02	−0·01	−0·02
C(6)	−0·02	−0·03	−0·02	−0·04

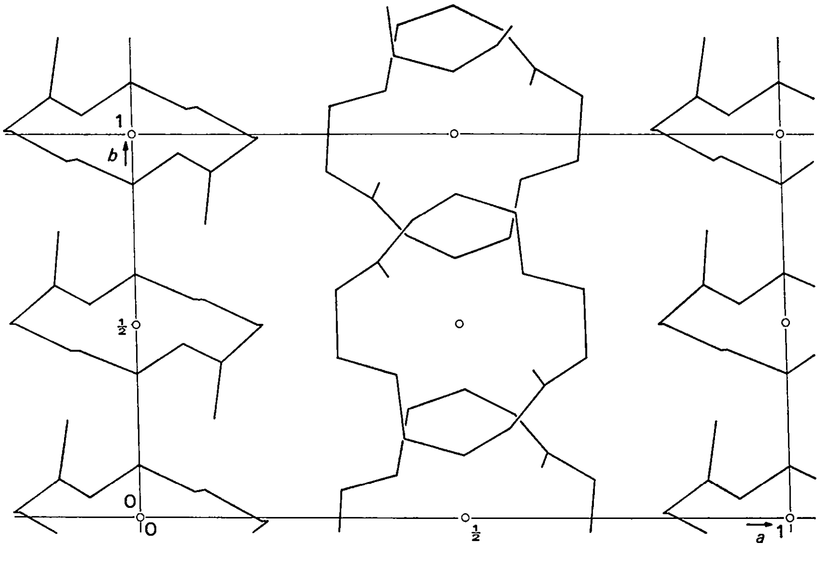

Fig. 4. Projection of the structure parallel to the *c* axis.

Table 5 (*cont.*)

Atoms of plane P

C(2)	0·04	0·05	0·02	0·04
C(3)	−0·01	−0·02	0·02	0·01
C(4)	−0·06	−0·08	−0·05	−0·08
C(5)	0·02	0·02	−0·01	−0·01
C(6)	0·02	0·03	0·03	0·04

(*b*) Interplanar angles in degrees

Molecule No.	1	2	3	4
$M\wedge A$	88	89	90	90
$M\wedge P$	30	33	31	34
$A\wedge P$	89	88	89	88

The conformations of a few 14-membered rings have been studied previously. In the molecules 1,8-diazacyclotetradecanehydrobromide (Dunitz & Meyer, 1965) and 1,8-dihydroxy-1,8-diazacyclotetradecane (Brown, 1966) the stable ring conformation is based on the diamond lattice (Dunitz, 1968).* Both molecules described in these studies contain rings consisting exclusively of sp^3-hybridized atoms. For the cyclic monomer of nylon 66 (Northolt & Alexander, 1968) and the cyclic dimer of nylon 6, $c[\mathrm{Cap}]_2$, it is sterically possible to construct a conformation that closely approximates the ring conformation based on the diamond lattice. However, neither of these molecules actually does adopt this ring conformation, and it may be noted that both have zigzag chain elements containing sp^2-hybridized atoms.

The configuration and the dimensions of the four molecules in the unit cell are the same within the precision of the experimental observations. This conclusion is derived from a consideration of the molecular dimensions, including the internal rotation angles listed in Table 6, and from the analysis of the planar elements in Table 5.

Table 6. *Internal rotation angles in degrees*

Molecule No.	1	2	3	4
N(1)C(1)C(2)–C(1)C(2)C(3)	127	122	129	128
C(1)C(2)C(3)–C(2)C(3)C(4)	114	115	110	111
C(2)C(3)C(4)–C(3)C(4)C(5)	174	173	178	175
C(3)C(4)C(5)–C(4)C(5)C(6)	177	177	175	174
C(4)C(5)C(6)–C(5)C(6)N(1)	120	114	120	116
C(5)C(6)N(1)–C(6)N(1)C(1)	111	115	111	110

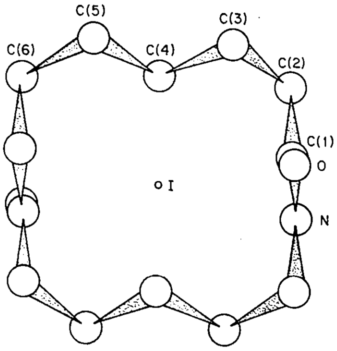

Fig. 5. Projection of the molecule on the least-squares plane through the atoms of the ring.

Although the structure has triclinic symmetry, interesting pseudosymmetry operations exist between the molecules. An operation which brings molecule 2 into coincidence with molecule 1 is a glide plane parallel to (010) at $y=\frac{1}{4}$ with a translation component **c**/2. Molecules 3 and 4 are related by a glide plane parallel to (001) at $z=\frac{1}{4}$ with a translation component **b**/2. In addition there is a pseudo 4_2 axis parallel to **a** located, for example, at $y=\frac{1}{4}$, which brings molecule 1 into coincidence with 4 and molecule 2 into coincidence with 3. This pseudo-symmetry is preserved in the disordered state. For each pair of molecules related by the pseudo screw axis the dihedral angle between the average molecular planes is 89°. Because of the pseudosymmetry elements described above the following approximate relations between the coordinates of equivalent atoms in the four molecules exist:

$x,$	$y,$	z
$x,$	$\frac{1}{2}-y,$	$-\frac{1}{2}+z$
$\frac{1}{2}-x,$	$z,$	$-\frac{1}{2}+y$
$\frac{1}{2}-x,$	$-\frac{1}{2}+z,$	$1-y$

Each molecule is linked by four hydrogen bonds to four other molecules, thereby forming sheets parallel to the (100) planes. In layer A the lengths of the two independent hydrogen bonds are O(4)–N(3) = 2·91 and O(3)–N(4) = 2·94 Å; in layer B they are O(1)–N(2) = 2·90 and O(2)–N(1) = 2·92 Å.

The authors wish to thank Professor Helmut Zahn of the Technische Hochschule, Aachen, for supplying the compound and Professor P. M. de Wolff of the Technological University of Delft for valuable discussions. They are grateful for the assistance of Dr Robert F. Stewart and Dr E. N. Maslen, who respectively adapted the *X-ray* 67 *Programs System* and S. Hall's symbolic addition program for use on the CDC 1604 computer at Mellon Institute.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Brown, C. J. (1966). *J. Chem. Soc.* (C) p. 1108.

Dunitz, J. D. (1968). *Perspectives in Structural Chemistry*, Vol. II, p. 18. New York: John Wiley.

Dunitz, J. D. & Meyer, E. F. (1965). *Helv. Chim. Acta*, **48**, 1441.

Hauptman, H. & Karle, J. (1953). *Solution of the Phase Problem.* I. *The Centrosymmetric Crystal.* A.C.A. Monograph No. 3.

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* The authors are indebted to a referee for calling their attention to the review by Dunitz (1968) of the structures of other 14-membered ring systems.

HERMANS, P. H. (1953). *Rec. Trav. Chim. Pays-Bas*, **72**, 798.
HERMANS, P. H. (1956). *Nature, Lond.* **177**, 127.
HOLMES, D. R., BUNN, C. W. & SMITH, D. J. (1955). *J. Polymer Sci.* **17**, 159.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
NORTHOLT, M. G. (1970). *Acta Cryst.* **B26**, 240.
NORTHOLT, M. G. & ALEXANDER, L. E. (1968). *J. Phys. Chem.* **72**, 2838.
OH, Y. L. & MASLEN, E. N. (1968). *Acta Cryst.* **B24**, 883.
STEWART, J. M. & HIGH, D. (1967). *X-ray 67 Programs System.* Univ. of Maryland, College Park, and Univ. of Washington, Seattle.
ZAHN, H. & DETERMANN, H. (1957). *Chem. Ber.* **90** 21,76.

Acta Cryst. (1971). B**27**, 531

The Crystal and Molecular Structure of 3β-Chloro-5-androsten-17β-ol

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(*Received* 25 *April* 1969 *and in revised form* 11 *March* 1970)

The crystal structure of the methanol complex of 3β-chloro-5-androsten-17β-ol ($C_{19}H_{29}OCl.\frac{1}{2}CH_3OH$) has been determined from three-dimensional X-ray data collected by the stationary-counter stationary-crystal technique and refined to a final reliability index of $R=9\cdot0\%$ for 2456 observed reflections. Crystals formed in methanol are monoclinic, space group $P2_1$, with cell constants $a=22\cdot565$, $b=12\cdot319$, $c=6\cdot656$ Å, and $\beta=95\cdot5°$. The asymmetric unit consists of one methanol and two steroid molecules which are all joined by hydrogen bonds to form helices in the direction of the c axis. The two steroid molecules in the asymmetric unit are related by a non-crystallographic, approximate twofold rotation axis.

Introduction

Two features of the crystal and molecular structure of 3β-chloro-5-androsten-17β-ol (Fig. 1) are of particular interest. First, it was desired to determine what, if any, distortion of the normal geometry of the steroid nucleus is caused by the presence of unsaturation at the C(5)–C(6) bond. Previous crystal structure determinations of molecules possessing isolated double bonds at this position (Carlisle & Crowfoot, 1945; Burki & Nowacki, 1956; O'Donnell & Ladd, 1967; Solo, Singh, Shefter & Cooper, 1968) have been relatively inaccurate because of the presence of very heavy atoms.

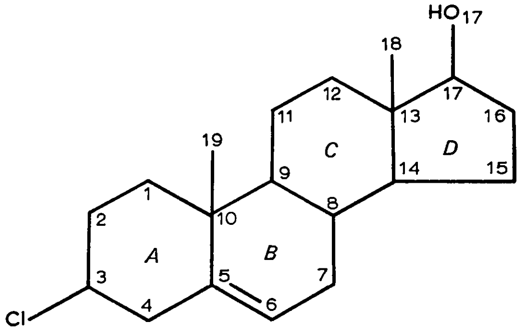

Fig. 1. Atomic numbering for 3β-chloro-5-androsten-17β-ol.

The second interesting feature of this molecule is that two steroid molecules are present in the asymmetric unit. The early crystallographic investigations of steroids by Bernal and his collaborators revealed that the presence of more than one molecule in the asymmetric unit is frequent among the sterols (Bernal, Crowfoot & Fankuchen, 1940), and later X-ray studies have shown that this phenomenon occurs in other classes of steroids as well including the estrogens (Ohrt, Haner & Norton, 1964), pregnanes (Haner & Norton, 1963), and androstanes (Norton, Lu & Campbell, 1962). Consequently, the presence of more than one molecule in the asymmetric unit of steroid crystal structures does not appear to be correlated in a simple way with any particular hydrocarbon skeleton or the nature and location of functional groups.

Experimental

Slow evaporation of a solution of 3β-chloro-5-androsten-17β-ol in methanol results in the formation of a crystalline 2:1 complex of the steroid with methanol. The systematic absences (0k0 for k odd) in the diffraction pattern of these crystals are consistent with the monoclinic space group $P2_1$. The unit-cell dimensions were determined by a least-squares analysis of 35 independent measurements of 2θ for high angle data. The crystal data are:

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