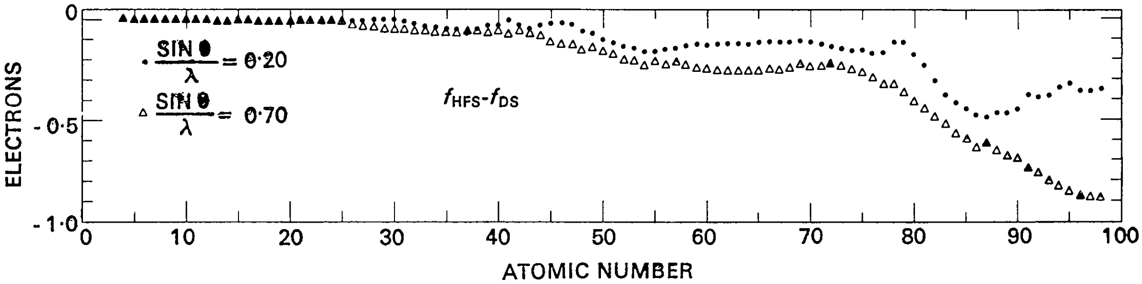

Fig. 7. ($f_{HFS}-f_{DS}$) plotted *vs* atomic number at $\sin\theta/\lambda = 0·20$ and $0·70$ Å^{-1}.

effects are negligible and these two models differ only in this respect. The differences are essentially zero. (The small deviation from zero of the plotted differences at low atomic number arises for the most part from small inaccuracies in the analytic fits used to compute the differences). At the higher atomic numbers the difference is always negative because the relativistic DS atomic model is more compact than the nonrelativistic HFS model.

As a general rule, the inclusion of exchange has a greater effect on the scattering factors than does relativity. At the heaviest elements the two effects appear to be comparable.

Conclusions

Crystallographers now are overwhelmed with scattering factors and one might well ask which of these he should use. For the lighter elements, up to Rb^+, the values given in *International Tables for X-ray Crystallography* (1962) are the best ones, for they have been computed from Hartree–Fock wave functions and in some cases from even more accurate wave functions. For these lighter elements, relativistic effects are trivial. For heavier elements it is suggested that the Dirac–Slater scattering factors are to be preferred because relativistic effects are accounted for and at least an approximation for exchange has been made.

References

Abrahamson, A. A. (1961). *Phys. Rev.* **123**, 538.

Boyd, R. G., Larson, A. C. & Waber, J. T. (1963). To be published.

Cromer, D. T., Larson, A. C. & Waber, J. T. (1963). Los Alamos Scientific Laboratory Report, LASL-2987.

Cromer, D. T., Larson, A. C. & Waber, J. T. (1964). *Acta Cryst.* **17**, 1044.

Cromer, D. T. & Waber, J. T. (1964). Los Alamos Scientific Laboratory Report, LASL-3056.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Liberman, D., Waber, J. T. & Cromer, D. T. (1965). *Phys. Rev.* **137**, A 27.

Waber, J. T. & Cromer, D. T. (1965). *J. Chem. Phys.* In the press.

Acta Cryst. (1965). **19**, 227

The Crystal Structure of [18]annulene. I. X-ray Study

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(*Received* 29 *October* 1964 *and in revised form* 8 *January* 1965)

The crystal structure of [18] annulene has been determined by least-squares analysis of photographic X-ray data recorded at the temperature of boiling nitrogen. The molecules occupy crystallographic centers of symmetry in a structure closely resembling that of coronene. This molecular symmetry rules out the possibility of a structure with alternate long and short C–C bonds. Final carbon coordinates have estimated standard deviations averaging less than 0·004 Å; the hydrogen atoms have not been reliably located.

Introduction

The synthesis by Sondheimer and his collaborators (Sondheimer & Wolovsky, 1959; Sondheimer & Gaoni, 1960, 1961, 1962; Sondheimer, Wolovsky & Gaoni, 1960; Sondheimer, Wolovsky & Amiel, 1962; Sondheimer, 1963) of the monocyclic alternant hydrocarbons C_nH_n ($n = 14,16,18,20,24,30$) has made available a class of compounds ('annulenes') of considerable

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theoretical interest. In cooperation with Prof. Sondheimer, Dr R. Wolovsky, and Dr Y. Gaoni, we have undertaken structure analyses of two compounds in this series that are sufficiently stable to permit X-ray work. An account of the partial analysis of [14]annulene has been given by one of us (Bregman, 1962); preliminary results of the structure determination of [18]annulene were presented at the Cambridge meeting of the I.U.Cr. (Bregman & Rabinovich, 1960). The present paper reports the three-dimensional analysis of [18]annulene near 80 °K; the following paper (part II) gives the results of this study together with a discussion of the in-plane and out-of-plane molecular deformations.

Experimental

Crystals of [18]annulene, grown from slowly cooled solutions in chloroform, are thin monoclinic laths, dark brown, with occasional greenish sheen. They are elongated along [010], showing {001} and $\{20\bar{1}\}$, with pronounced cleavage along planes parallel to [010]. Room-temperature Cu $K\alpha$ photographs, which record few reflexions beyond $\sin\theta = 0{\cdot}32$, yield the cell constants listed in Table 1. Systematically absent are reflexions $h0l$ with h odd, $0k0$ with k odd; the space group is $P2_1/a$. At the temperature of boiling nitrogen these crystals reflect throughout the reciprocal-lattice region accessible to Cu $K\alpha$ radiation; cell dimensions (Table 1) were determined from high-angle reflexions. The systematic absences of $P2_1/a$ were obeyed throughout the range of recorded reflexions. With two molecules of $C_{18}H_{18}$ per unit cell, the calculated density is 1·144 at 80 °K. The space group then demands that the molecule be centrosymmetric, unless the structure is disordered. This last contingency has been ruled out by refinement of an ordered model to a structure yielding acceptable agreement between F_o and F_c and showing no anomalies in the thermal parameters (see part II). [18] Annulene cannot, therefore, be formulated as a molecule with alternate single and double bonds.

Examination of a large number of crystals revealed the frequent occurrence of twinning across (001), made possible by the near equality (within 1·2%) of c^* and $4a^*\cos\beta^*$. The twinned crystals give, at room temperature, X-ray photographs that appear to have been produced by crystals having a doubled c axis and showing non-space-group extinctions for h even, L $(=2l)$ odd. At low temperature high-angle spots are found to be split, suggesting that the phenomenon observed is one of twinning rather than of polymorphism or super-lattice formation. This conclusion is confirmed by the fact that the positions and intensities of all spots appearing on photographs of a twinned crystal can be exactly simulated by the superposition in mirror orientation of pairs of reciprocal-lattice nets derived from photographs of untwinned crystals. This superposition brings into near coincidence spots due to reflexions h, k, l and $h, k, -\frac{1}{2}(h+2l)$.

Reflexions from an untwinned crystal were recorded with Cu $K\alpha$ radiation by the equi-inclination Weissenberg technique in levels perpendicular to [010] up to $k=3$. The crystal was held near the temperature of boiling nitrogen by the device described by Hirshfeld & Schmidt (1956). From a crystal trimmed with a razor blade $0kl$ intensity data were collected that enabled us to place $I(hkl)$ ($k=0$, 1, 2, 3) on a common scale. However, the quality of cut crystals was inadequate to permit intensity photographs about another axis. The numbers of reflexions, observed plus unobserved, were 183, 356, 335, and 284, respectively, for $k=0$, 1, 2, and 3. Ten $04l$ reflexions were also included in the refinement process.

The intensities were estimated visually and corrected in the usual way; corrections for spot-shape extension, due to Phillips (1956), were applied to the data from upper-level photographs.

Solution and refinement

Comparison of the cell dimensions of [18]annulene and of coronene (Table 1) suggests a similarity in molecular shape and packing arrangement; since the strong high-order $h0l$ reflexions (207; $40\bar{5}$; 602; $10,0,\bar{3}$; $14,0,1$; $14,0,\bar{8}$; $16,0,\bar{1}$), used by Robertson & White (1945) for the solution of the latter structure, were, with the exception of 14,0,1, outstandingly strong in [18]annulene too, the x, z parameters of the peripheral carbon atoms of coronene were inserted into $F(h0l)$ structure-factor and least-squares calculations. The correctness of this model quickly became evident.

Refinement was accomplished on WEIZAC by a least-squares program modelled after the procedure described by Rossmann, Jacobson, Hirshfeld & Lipscomb (1959). This program seeks to minimize the discrepancy function

$$r=\Sigma w(K^2F_o^2-F_c^2)^2/\Sigma wK^4F_o^4 \tag{1}$$

with respect to the scale factor K^2 and the positional and thermal parameters of the atoms in the asymmetric unit. It uses the linear diagonal approximation for

Table 1. *Crystal data for* [18]*annulene and coronene*

	a (Å)	b (Å)	c (Å)	β	Z	Space group
$C_{18}H_{18}$ at 80°K	14·889 ±0·004	4·800 ±0·002	10·235 ±0·003	111·60° ±0·14°	2	$P2_1/a$
$C_{18}H_{18}$, room temperature	15·33	4·88	10·27	111·8°	2	$P2_1/a$
Coronene, room temperature	16·10	4·695	10·15	110·8°	2	$P2_1/a$

the computation of the shifts in all parameters, except that the scale factor K^2 and an average, isotropic, thermal parameter are adjusted separately by solution of an appropriate 2×2 matrix (Cruickshank, 1961).

For each reflexion, the weighting factor w_{hkl} was obtained by the summation of weights assigned to the individual spots on the several films on which the reflexion was recorded. These individual weights were a function of the film blackening and of the factors required for translation of the spot readings into scaled values of F_o^2. This procedure yielded weights that varied roughly as F_o^{-4} for most reflexions, with decreased weights for the weak and the very strong reflexions. The summations in equation (1) comprise all except those unobserved reflexions for which $|F_c| < KF_t$, where F_t is a threshold value estimated for each unobserved reflexion. Scattering-factor curves were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and from McWeeny (1951) for hydrogen.

Refinement of the (010) projection proceeded satisfactorily, initially with isotropic carbon atoms only. Next, hydrogen coordinates derived from a difference synthesis $\Delta\varrho(x, z)$ were inserted into the least-squares calculations, and the refinement of the carbon parameters was continued for several additional cycles.

In the next stage y parameters of all atoms were derived for a hypothetical planar molecule; this model was tested by structure-factor calculations for $F(h1l)$ and found to give reasonable agreement.

Because of the diagonal approximation used in the least-squares program, it was desirable to refer the structure to nearly orthogonal axes. The coincidence in cell dimensions responsible for the twinning (see above) provided such a coordinate system, based on a unit cell four times the size of the primitive cell. The axes of this cell, having a monoclinic angle of 90·26°, are obtained from the conventional axes by the transformation whose matrix is

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 4 \end{pmatrix}$$

In the first four three-dimensional refinement cycles, only the scale factor K^2, the y parameters, and the isotropic thermal parameters (B) of the carbon atoms were varied; next all the carbon parameters were re-

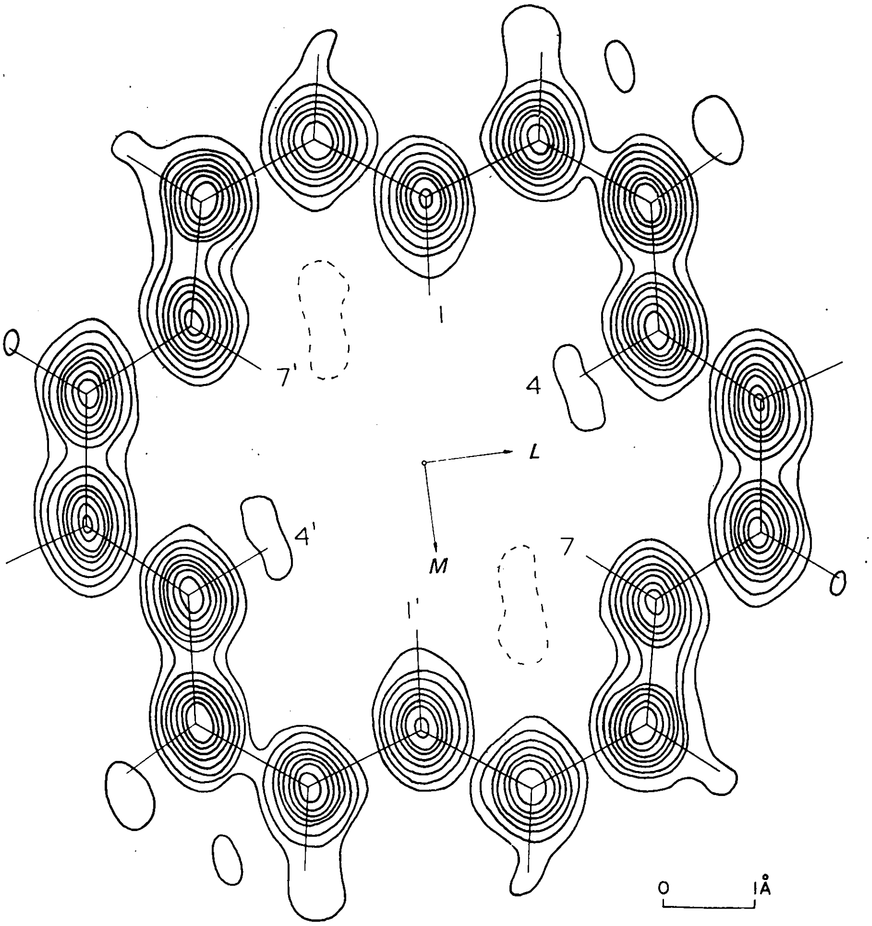

Fig. 1. Electron density in mean molecular plane. Contours at intervals of 1 e.Å^{-3}, zero contour broken. Molecular outline shows projected atomic positions based on least-squares refinement.

Table 2. *Atomic coordinates*

	Referred to crystal axes			Referred to molecular axes		
Atom	x	y	z	L(Å)	M(Å)	N(Å)
C(1)	−0·1147	−0·4574	0·0430	0·424	−2·881	0·061
C(2)	−0·1068	−0·5089	0·1807	1·742	−3·323	−0·015
C(3)	−0·0441	−0·3627	0·2988	2·864	−2·467	−0·058
C(4)	0·0151	−0·1483	0·2903	2·775	−1·091	−0·053
C(5)	0·0836	−0·0082	0·3995	3·807	−0·178	0·010
C(6)	0·1430	0·2077	0·3781	3·594	1·236	0·041
C(7)	0·1416	0·2877	0·2474	2·343	1·828	0·085
C(8)	0·1885	0·5084	0·2154	2·034	3·162	−0·013
C(9)	0·1771	0·5884	0·0770	0·715	3·675	−0·064
H(1)	−0·072	−0·278	0·031	0·31	−1·79	0·00
H(2)	−0·143	−0·668	0·197	1·90	−4·30	0·04
H(3)	−0·043	−0·427	0·390	3·74	−2·91	−0·06
H(4)	0·006	−0·078	0·195	1·86	−0·69	−0·14
H(5)	0·095	−0·054	0·499	4·76	−0·47	0·05
H(6)	0·187	0·320	0·464	4·41	1·87	−0·02
H(7)	0·107	0·168	0·174	1·64	1·24	0·25
H(8)	0·227	0·626	0·297	2·81	3·77	−0·15
H(9)	0·211	0·749	0·060	0·55	4·63	−0·16

fined. After several further cycles anisotropic carbon thermal parameters β_{ij} $(i, j=1, 2, 3)$ were introduced (Cruickshank, 1956), and only when the nine parameters per carbon atom had reached essentially stationary values were the positional and isotropic thermal parameters of the hydrogen atoms allowed to vary. After 28 cycles the discrepancy factor r had reached 0·0372.

At this stage bond lengths and angles were calculated, as well as the equation of the best plane through the carbon skeleton and the deviations of the carbon and hydrogen atoms from this plane. The carbon skeleton conformed closely to symmetry $\bar{3}$; on the other hand, the displacements of hydrogen atoms from the mean plane did not follow a similar pattern. In particular, the position of H(1) appeared, on the criterion of molecular symmetry $\bar{3}$, to be in serious error. A three-dimensional difference synthesis based on $F_o - F_c'$ (with the sign of F_c, including hydrogen contributions, attached to F_o; carbon contributions alone for F_c') was computed in the neighborhood of H(1) and H(4). While for the latter the electron-density maximum coincided within 0·02 Å with the position derived by the least-squares procedure, the electron density near H(1) indicated a position 0·11 Å above, rather than 0·14 Å below, the mean plane of the carbon atoms. This more plausible location for H(1) was inserted into further least-squares calculations, but these returned the atom to its former position.

The entire set of intensity data was re-checked for human errors, and minor corrections were made in the intensities of about 100 reflexions, especially at high angles. About 60 further reflexions were assigned zero weights because of high background scattering or because of suspected interference by the beam catcher. New hydrogen coordinates were postulated, based on the last set of carbon coordinates and the assumption that each C–H bond, of length 1·00 Å, lay in the plane defined by the three adjacent carbon atoms and bisected the C–C–C angle. The positional and thermal parameters of the carbon atoms were refined for another five cycles, after which the hydrogen parameters were again allowed to change.

The final hydrogen positions did not show any significant improvement, though the anomaly in H(1) was smaller than before. A new three-dimensional difference synthesis, calculated in the same way as the previous one, showed maxima at positions differing by up to 0·14 Å from the hydrogen positions given by least-squares. All hydrogen atoms showed marked anisotropy; the electron-density distributions resembled

Table 3. *Direction cosines of the molecular inertial axes with respect to the crystal axes*

	a	b	c
L	−0·0393	0·0266	0·9433
M	0·6593	0·7517	−0·2370
N	0·7509	−0·6587	−0·2325

Table 4. *Estimated standard deviations (average) of atomic coordinates and thermal tensor components, referred to the edges of a nearly orthogonal cell having* $a=14{\cdot}889$, $b=4{\cdot}800$, $c'=38{\cdot}059$ Å, $\beta'=90{\cdot}26°$

(This is the cell used for the diagonal least-squares refinement)

Carbon:

$a\sigma(x') = 0{\cdot}0024$ Å $b\sigma(y) = 0{\cdot}004$ Å $c'\sigma(z') = 0{\cdot}0023$ Å

$\sigma(U'_{11}) = 0{\cdot}0010$ Å^2 $\sigma(U'_{22}) = 0{\cdot}0026$ Å^2 $\sigma(U'_{33}) = 0{\cdot}0010$ Å^2

$\sigma(U'_{12}) = 0{\cdot}0013$ Å^2 $\sigma(U'_{23}) = 0{\cdot}0014$ Å^2 $\sigma(U'_{13}) = 0{\cdot}0008$ Å^2

Hydrogen:

$a\sigma(x') = 0{\cdot}030$ Å $b\sigma(y) = 0{\cdot}038$ Å $c'\sigma(z') = 0{\cdot}027$ Å

$\sigma(u^2) = 0{\cdot}008$ Å^2

Table 5. *Observed and calculated structure factors*

Those marked with an asterisk were eliminated from the final refinement because of high background scattering or because of possible interference by the backstop.

h	k	l	100 F_o	100 F_c
18	0	-1*	1325	1589
		-2	713	713
		-3	540	-480
		-4	458	436
		-5	342	-376
		-6	223	234
		-7	531	492
		-8*	946	-1162
16	0	2*	480	684
		1	967	-971
		0	313	268
		-1	2386	2307
		-2	763	-743
		-3	737	-717
		-4	513	469
		-5	<203	214
		-6	<249	69
		-7	603	-528
		-8	1025	1103
		-9	342	398
		-10	547	-582
14	0	4	844	-871
		3	<214	33
		2	417	343
		1	1785	-1723
		0	611	-650
		-1	618	-682
		-2	975	-982
		-3	962	972
		-4	844	849
		-5	707	695
		-6	1098	-1182
		-7	611	630
		-8	3755	3377
		-9	349	-441
		-10	822	-762
		-11	618	620
		-12	<79	-101
12	0	6	240	273
		5	<214	-70
		4	1034	-925
		3	<219	98
		2	276	249
		1	<234	-140
		0	<226	-246
		-1	502	-440
		-2	815	794
		-3	830	-818
		-4	226	-225
		-5	676	666
		-6	1740	-1882
		-7	<234	-118
		-8	394	-488
		-9	1201	-1396
		-10	815	826
		-11	707	768
		-12	298	295
10	0	7	<186	153
		6	1034	1123
		5	801	911
		4	<226	35
		3	283	235
		2	1170	1251
		1	1550	1548
		0	641	667
		-1	547	563
		-2	641	-621
		-3	3144	-3195
		-4	466	406
		-5	458	334
		-6	962	-947
		-7	931	-898
		-8	1158	-1190
		-9	560	636
		-10	<219	226
		-11	<242	-210
		-12	473	477
		-13	626	-947
8	0	9*	865	-1108
		8	458	502
		7	458	324
		6	<226	-150
		5	<234	-198
		4	<226	80
		3	707	646
		2	1513	-1414
		1	1208	-1042
		0	480	476
		-1	1607	1511
		-2	946	826
		-3	291	139
		-4	931	875
		-5	1201	1119
		-6	1819	1821
		-7	924	896
		-8	226	215
		-9	234	-238
		-10*	1477	-1817
		-11	<249	-52
		-12	249	354
		-13*	641	-785
6	0	10*	102	-324
		9	880	771
		8	390	334
		7	1812	-1838
		6	1521	-1449
		5	[illegible]	-1586
		4	1076	1097
		3	<188	-132
		2	4057	-4381
		1	422	364
		0	1790	1792
		-1	975	854
		-2	2710	1510
		-3	1310	1259
		-4	924	859
		-5	551	-562
		-6	<181	-4
		-7	954	938
		-8	<219	92
		-9	<226	-113
		-10	<226	-8
		-11	626	587
		-12	<175	-59
		-13*	379	313
4	0	10	553	526
		9	472	472
		8	1506	-1550
		7	1696	1756
		6	1310	1266
		5	1440	-1481
		4	1696	1613
		3	226	89
		2	758	735
		1	3078	2815
		0	5328	-5116
		-1	7125	-6315
		-2	4533	-4259
		-3	2038	2047
		-4	540	-534
		-5	5124	-5260
		-6	254	-209
		-7	1069	1102
		-8	269	204
		-9	997	1115
		-10	1063	1197
		-11	<249	144
		-12	370	-400
2	0	10	1208	1137
		9	1091	-1234
		8	234	182
		7	4563	4819
		6	<203	-162
		5	1521	-1643
		4	931	930
		3	1208	1261
		2	1529	1464
		1	5952	-5890
		0	2373	2123
		-1	1382	1229
		-2	5109	-5498
		-3	3369	3395
		-4	916	-935
		-5	291	-304
		-6	1951	1855
		-7	1288	-1230
		-8	1513	-1520
		-9	858	-849
		-10	611	627
		-11	<242	-61
		-12	1506	-1331
0	0	12	750	-782
		11	181	-236
		10	1193	1067
		9	1841	-1895
		8	656	-651
		7	649	-653
		6	1498	-1559
		5	1295	1299
		4	1041	1118
		3	2015	2205
		2	4314	-4635
		1*	916	945
-6	1	13*	262	-353
-13	1	12*	278	-384
-12			139	244
-11			255	259
-10			240	317
-9			<181	9
-8			321	270
-7			474	-454
-6			<188	70
-5			787	-755
-4			181	-156
-3			452	-477
-2			372	-337
-1			299	219
0			<117	-62
-15	1	11*	511	665
-14			<125	38
-13			248	-259
-12			663	-630
-11			599	-592
-10			219	-220
-9			505	481
-8			<231	163
-7			810	714
-6			<231	-90
-5			669	818
-4			360	265
-3			761	684
-2			606	602
-1			271	229
0			591	561
1			481	-401
2			693	582
3*			563	-668
-16	1	10*	620	-762
-15			<139	72
-14			<161	-53
-13			658	607
-12			497	-375
-11			<242	-78
-10			724	-630
-9			682	721
-8			<212	144
-7			334	351
-6			372	362
-5			854	-859
-4			262	-266
-3			299	-380
-2			610	-574
-1			<204	239
0			<197	77
1			795	780
2			<223	162
3			205	236
4			818	-733
5			547	-508
-17	1	9	818	893
-16			<146	208
-15			1241	-1171
-14			<181	120
-13			832	-705
-12			700	662
-11			752	-711
-10			714	667
-9			<219	78
-8			219	-251
-7			518	554
-6			584	-510
-5			1423	-1517
-4			<219	209
-3			810	-836
-2			540	-577
-1			<219	-75
0			1430	-1522
1			334	-340
2			<212	104
3			849	669
4			<231	145
5			<214	156
6			1021	-942
7			<153	31
8			<81	-68
-18	1	8*	<94	211
-17			767	736
-16			898	800
-15			1125	-1050
-14			434	366
-13			<212	-43
-12			795	-763
-11			964	1026
-10			219	262
-9			577	-508
-8			1145	1100
-7			<212	4
-6			839	-811
-5			780	-782
-4			540	-521
-3			423	379
-2			1795	1875
-1			2342	2588
0			635	653
1			511	-527
2			313	-298
3			1496	-1616
4			1167	1178
5			540	-548
6			730	747
7			423	-418
8			328	-395
9			459	469
-18	1	7	540	-576
-17			181	-205
-16			986	-976
-15			1174	-1022
-14			<212	82
-13			<219	-135
-12			408	-414
-11			2430	2677
-10			1525	-1606
-9			700	715
-8			671	617
-7			380	-410
-6			1372	1319
-5			278	219
-4			832	-836
-3			461	-519
-2			197	81
-1			1257	1367
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4			708	-699
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8			635	655
9			<205	-305
10			<170	-189
11			<107	146
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4			334	-297
5			1358	1548
6			1306	-1375
7			1781	2038
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10			905	893
11			<179	-69
12			<109	-245
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-12			380	356
-11			<212	-10
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-9			752	-759
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-7			1642	-1754
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0			737	656
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2			553	-585
3			<188	-32
4			724	746
5			795	-834
6			505	538
7			<219	72
8			380	-350
9			1051	-1139
10			<249	85
11			547	-487
12			<186	46
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-16			387	-215
-15			627	-674
-14			752	-809
-13			584	-556
-12			431	-390
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-10			395	-325
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-6			810	783
-5			1460	1539
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-3			1000	994
-2			1137	1268
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1			964	-910
2			387	403
3			1248	1384
4			286	262
5			271	248
6			533	573
7			423	-389
8			<219	129
9			350	-559
10			<219	108
11			651	-525
12			<223	-62
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-10			<197	117
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-6			620	-604
-5			255	-213
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-3			212	220
-2			271	-230
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2			2481	-2592
3			1795	-1811
4			1532	-1640
5			452	476
6			372	285
7			1125	1078
8			568	-548
9			979	909
10			<219	-165
11			663	678
12			438	493
13			421	384
14			334	322
15			<143	-107
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-17			979	-986
-16			181	171
-15			293	-317
-14			651	650
-13			561	-519
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2			614	-580
3			767	-757
4			1934	-2002
5			365	326
6			467	435
7			780	782
8			737	696
9			1073	-1052
10			431	-364
11			760	-744
12			591	-549
13			<204	19
14			<223	-86
15			481	345
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-17			927	-906
-16			<269	110
-15			627	575
-14			905	-828
-13			599	585
-12			489	466
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-9			293	247
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Table 5 (*cont.*)

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4			2240	2246
5			176	-141
6			<153	-66
7			1547	1534
8			<181	-154
9			1386	-1416
10			651	626
11			1554	-1535
12			<219	-120
13			<212	104
14			927	-926
15			<214	-89
16			<170	84
17			<98	181
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16			242	-212
15			518	506
14			620	615
13			2006	2043
12			1366	1364
11			<212	-78
10			760	-708
9			328	220
8			1110	-991
7			<161	89
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5			547	-492
4			708	-657
3			4649	4807
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-7			559	520
-6			<138	-134
-5			658	662
-4			<130	-183
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-11			1005	915
-10			481	-390
-9			383	329
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-7			<191	37
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-5			197	213
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1			502	-463
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1			319	-183
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3			404	-279
4			219	-216
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-11			249	185
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-8			693	-772
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3			607	-511
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6			629	552
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3			240	-250
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5			<177	61
6			340	-371
7			<181	108
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3			205	245
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8			842	-772
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-12			205	-189
-11			581	-587
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-9			466	-439
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1			361	-302
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3			197	163
4			205	-291
5			<205	-112
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7			<197	-212
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9			756	-729
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-4			389	-340
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1			<177	-52
2			666	653
3			581	-504
4			240	243
5			425	-441
6			997	-1036
7			<205	-14
8			<197	-234
9			855	-739
10			1456	1392
11			678	-684
12			<146	-84
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-16			<198	-191
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3			1563	1523
4			<183	-150
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6			763	724
7			608	556
8			354	-203
9			1047	1137
10			<191	-87
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12			<191	-245
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3			1895	2034
4			701	-720
5			431	404
6			297	-221
7			756	-767
8			<197	122
9			<205	105
10			<197	197
11			<191	195
12			375	307
13			<191	4
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-16			398	205
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-14			304	269
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-11			1267	-1227
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-9			842	695
-8			2758	2979
-7			1804	1766
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3			<142	-36
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7			1182	-1270
8			531	-469
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11			813	-863
12			446	380
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-8			524	419
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-4			1634	-1734
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3			785	892
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12			1097	-1058
13			<183	168
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15			502	499
16			347	384
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16			396	381
15			155	235
14			1455	-1476
13			<197	-135
12			454	350
11			658	630
10			2208	2174
9			976	933
8			955	-1061
7			439	319
6			1571	-1714
5			1860	1952
4			898	-954
3		*	1449	1867
2		*	177	133
0			2054	2211
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-10		*	<110	-181
-9			737	-796
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-3			369	-300
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-12			663	-668
-11			243	-283
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-9			574	561
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-7			773	-695
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-2			<226	86
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-12			434	-429
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-10			324	-341
-9			1325	1270
-8			972	959
-7			1605	1637
-6			<279	-199
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3			<200	43
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-3			<243	-19
-2			243	-53
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3			516	-360
4			234	183
5			206	-155
6			700	-641
7		*	288	382
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-14			721	-655
-13			500	-488
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2			243	-224
3			552	-475
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5			369	349
6			516	-422
7			<206	38
8			339	-376
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-13			341	228
-12			228	-76
-11			382	312
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1			493	-467
2			862	-839
3			582	-644
4			346	-313
5			<236	-39
6			<228	162
7			<205	269
8			<226	-121
9			-559	-440
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Table 5 (*cont.*)

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1			552	-592
2			<243	55
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5			[illegible]	515
6			<[illegible]	75
7			[illegible]	227
8			[illegible]	253
9			<[illegible]	-283
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-8			<243	-1
-7			803	792
-6			355	227
-5			1384	-1309
-4			398	-425
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1			221	-229
2			279	-259
3			493	512
4			295	-249
5			552	590
6			<252	245
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7			[illegible]	[illegible]
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-10			1393	1386
-9			1540	1524
-8			369	-354
-7			590	-538
-6			648	-604
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2			862	-934
3			485	-501
4			<214	55
5			988	973
6			1000	952
7			243	-286
8			<251	-215
9			677	-648
10			<243	-182
11			610	654
12			<244	225
13			<206	93
14			353	-415
-16	3	1*	236	314
-15			426	419
-14			244	110
-13			516	430
-12			442	-308
-11			677	-691
-10			<251	77
-9			898	-809
-8			331	-317
-7			1119	-1025
-6			<205	12
-5			456	409
-4			<177	14
-3			803	846
-2		*	221	486
-1		*	1148	-954
0		*	2003	2086
2			<163	-94
3			382	-341
4			810	-779
5			1347	1293
6			1355	1396
7			2188	2247
8			<243	293
9			<251	-11
10			1208	-1048
11			<236	-148
12			<221	151
13			333	351
14			<189	147
15			<208	80
15	3	0	171	-100
14			382	323
13			684	678
12			<228	-185
11			574	-574
10			390	-375
9			1090	-1169
8			847	795
7			927	-846
6			302	-254
5			398	-286
4			1355	-1251
3			840	759
2		*	1221	1187
0	4	9	<145	-14
		8	348	470
		7	551	-679
		6	268	-183
		5	1379	1735
		4	<283	-178
		3	642	-667
		2	<276	8
		1	<276	20
		0	551	835

prolate spheroids with their long axes nearly normal to the molecular plane. Final values of r and $R = \Sigma|KF_o - |F_c||/\Sigma KF_o$ were 0·0289 and 0·076, respectively; unobserved reflexions for which $KF_t < |F_c|$ were included in the sums.

Observed and calculated structure factors are compared in Table 5.

An electron-density section in the mean molecular plane is shown in Fig. 1.

The final coordinates of all atoms in the asymmetric unit, derived from the last cycle of least-squares refinement, are listed in Table 2 with respect both to the crystal axes and to a set of orthogonal molecular axes. The latter (Table 3) were chosen to coincide with the principal molecular moments of inertia, calculated for the carbon atoms only, by the same computer program that yielded the equation of the mean plane according to the method of Schomaker, Waser, Marsh & Bergman (1959). Because the molecule has very nearly $\bar{3}$ symmetry (see part II) the moment of inertia is almost axially symmetric; thus the directions of the in-plane inertial axes L and M have slight physical significance.

Table 4 gives the average standard deviations computed by the diagonal approximation:

$$\sigma^2(u_i) = \Sigma w(K^2F_o^2 - F_c^2)^2/(n-s)A_{ii} \tag{2}$$

where $n = 911$ is the number of reflexions, 883 observed plus 28 threshold, included in the summations of the last refinement cycle, $s = 118$ is the number of parameters u_i adjusted, and $A_{ii} = \Sigma w(\partial F_c^2/\partial u_i)^2$ is the diagonal element in the normal equation corresponding to the parameter u_i. The approximate validity of the diagonal approximation follows from the near orthogonality of the axes and the large number of reflexions observed.

Fig. 2 shows the final values of bond lengths and angles and the distances of all atoms from the mean plane of the carbon atoms. This plane has the equation

$$11{\cdot}1795x - 3{\cdot}1616y - 2{\cdot}3798z = 0,$$

in which the left side gives the distance from the plane, in Å, of a point having fractional coordinates (x, y, z).

The results of this analysis are discussed in part II.

We are grateful to Professor Franz Sondheimer and Dr Reuven Wolovsky, who brought this problem to our attention and supplied the crystals for this investigation. It is a privilege to acknowledge our indebtedness to the late Professor I. Fankuchen, whose suggestion led to the proper diagnosis of the twinning phenomenon.

References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BREGMAN, J. (1962). *Nature, Lond.* **194**, 679.

BREGMAN, J. & RABINOVICH, D. (1960). Fifth International Congress, I.U.Cr., Cambridge.

CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747.

CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystallography,* p. 32. Pepinsky, Robertson & Speakman, Eds. Oxford: Pergamon Press.

HIRSHFELD, F. L. & SCHMIDT, G. M. J. (1956). *Acta Cryst.* **9**, 233.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.

ROBERTSON, J. M. & WHITE, J. G. (1945). *J. Chem. Soc.* p. 607.

ROSSMANN, M., JACOBSON, R. A., HIRSHFELD, F. L. & LIPSCOMB, W. N. (1959). *Acta Cryst.* **12**, 530.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

SONDHEIMER, F. (1963). *Pure Appl. Chem.* **7**, 363.

SONDHEIMER, F. & GAONI, Y. (1960). *J. Amer. Chem. Soc.* **82**, 5765.

SONDHEIMER, F. & GAONI, Y. (1961). *J. Amer. Chem. Soc.* **83**, 1259, 4863.

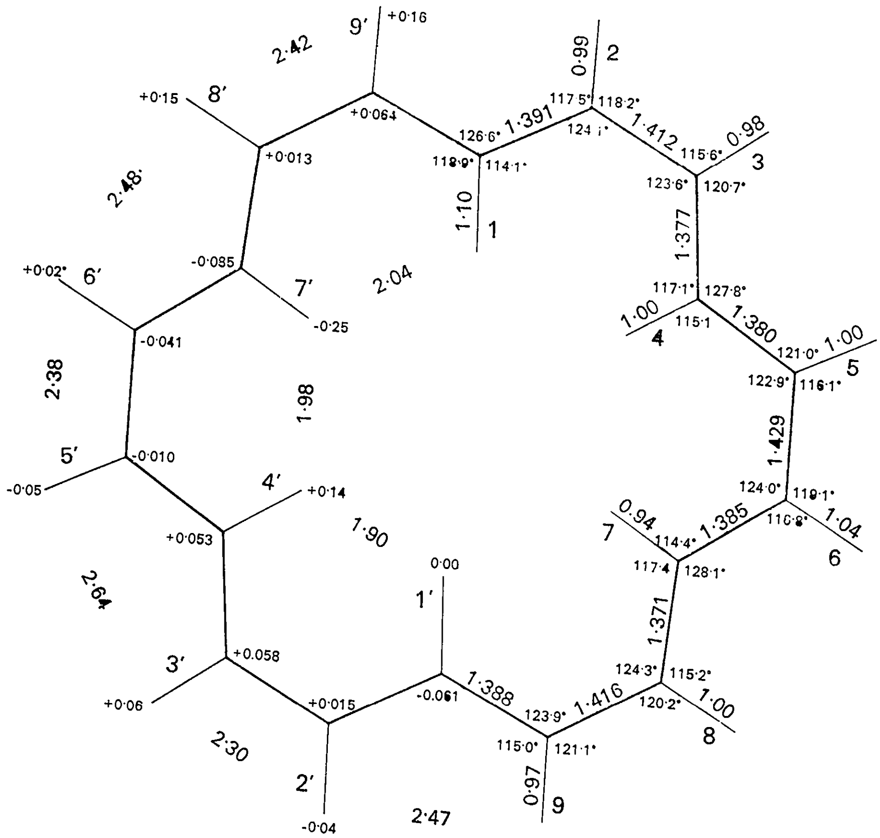

Fig. 2. Interatomic distances (Å) and bond angles. Figures near atomic positions give displacements (Å) from mean molecular plane.

Sondheimer, F. & Gaoni, Y. (1962.) *J. Amer. Chem. Soc.* **84**, 3520.

Sondheimer, F. & Wolovsky, R. (1959). *Tetrahedron Letters*, **3**, 3; *J. Amer. Chem. Soc.* **81**, 4755.

Sondheimer, F., Wolovsky, R. & Amiel, Y. (1962). *J. Amer. Chem. Soc.* **84**, 274.

Sondheimer, F., Wolovsky, R. & Gaoni, Y. (1960). *J. Amer. Chem. Soc.* **82**, 755.