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THE CRYSTAL AND MOLECULAR STRUCTURE OF ALL *CIS*-1,6-DICHLORODECA-1,3,6,8-TETRAENE

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Abstract—The crystal and molecular structure of all *cis*-1,6-dichlorocyclodeca-1,3,6,8-tetraene was determined by X-ray diffraction. The crystals are monoclinic, $P2_1/c$, $a = 7{\cdot}577$, $b = 7{\cdot}878$, $c = 8{\cdot}397$Å, $\beta = 109{\cdot}05°$. There are two centrosymmetric molecules in the unit cell. Diffractometer data were used and the analysis terminated at $R = 9\%$. Details of atomic positions and molecular geometry are listed.

THERE has been considerable interest recently in the annulenes, a family of monocyclic hydrocarbons formally made up of alternating double and single bonds and in the dehydro-annulenes, an analogous group of compounds in which one or more of the double bonds have been replaced by triple bonds.[1, 2]

The two simplest and best known annulenes are benzene and cyclooctatetraene, but series of these compounds containing 12, 14, 16, 18, 20, 24 and 30 C atoms have been prepared. Members of this series, which contain $(4n + 2)$ π-electrons and are reasonably planar, have been shown to be aromatic in that they possess a measurable degree of cyclic delocalization in the ground state. However, some members of the series that have been shown by NMR spectroscopy to be aromatic in that they are able to sustain a diamagnetic ring current in an applied magnetic field, do not possess the kind of stability and the ability to undergo substitution reactions usually associated with the aromatic nature of benzene.

Dichlorocyclodeca-1,3,6,8-tetraene was prepared by Sondheimer and Grohmann,[3] in part for intrinsic interest and in part as a possible precursor in the synthesis of the {10}annulenes—the only series of annulenes for which the unbridged conjugated members are still unknown.

The NMR spectroscopy indicated the presence of six olefinic and four aliphatic protons. Chemical methods were used to establish the locations of the double bonds but could provide no information about the stereochemistry of the two trisubstituted double bonds.

We have determined the detailed geometry and crystal structure of dichlorocyclodeca-1,3,6,8-tetraene by X-ray diffraction methods, using crystals supplied by Sondheimer and Grohmann. Because of the instability of the compound, the X-ray measurements were taken from a crystal sealed in a capillary tube filled with nitrogen. The data were collected on an automatic diffractometer and the structure was solved by the usual heavy-atom method. The analysis has shown that the molecule is centrosymmetric with *cis* stereochemistry at each double bond. A preliminary note about this work has been published[4] and the present paper gives a more detailed account of the experimental methods used and the final results of the analysis.

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Solution and refinement of the structure

A point-sharpened, origin-removed, 3-dimensional Patterson synthesis was computed using ($E^2 - 1$) as coefficients. This map gave two alternative positions for the

TABLE 1. SUMMARY OF REFINEMENT OF ALL *cis*-1,6-DICHLORODECA-1,3,6,8-TETRAENE

		R
1.	Structure-factor calculation Cl only	53·8%
2.	Structure-factor calculation Cl + 5C	24·8%
3.	3 Cycles isotropic least squares calculation	15·6%
4.	2 Cycles anisotropic least-squares calculation	11·2%
5.	Hydrogen atoms located from difference fourier map included	9·8%
6.	2 Cycles mixed-mode least-squares calculation (hydrogens isotropic)	9·6%
7.	New weighting scheme. Coordinates from 1st anisotropic cycle, hydrogens included	14·2%
8.	4 Cycles mixed mode least-squares refinement	9·0%

TABLE 2. FINAL FRACTIONAL ATOMIC COORDINATES AND ESTIMATED STANDARD DEVIATIONS FOR ALL *cis*-1,6-DICHLORODECA-1,3,6,8-TETRAENE

	x	*y*	*z*
Cl(1)	0·2977 (2)	0·1428 (2)	0·5094 (2)
C(1)	0·2160 (6)	0·3528 (7)	0·4902 (6)
C(2)	0·0284 (7)	0·3764 (8)	0·3555 (6)
C(3)	−0·1271 (7)	0·2808 (7)	0·3899 (6)
C(4)	−0·2772 (7)	0·3497 (8)	0·4127 (7)
C(5)	−0·3223 (7)	0·5299 (8)	0·4123 (6)
H(1)	0·006 (7)	0·500 (8)	0·333 (7)
H(2)	0·049 (10)	0·299 (10)	0·247 (10)
H(3)	−0·128 (10)	0·173 (9)	0·383 (9)
H(4)	−0·378 (8)	0·271 (7)	0·422 (7)
H(5)	−0·449 (8)	0·558 (7)	0·331 (7)

TABLE 3. COMPONENTS OF THERMAL VIBRATION COEFFICIENTS (β_{ij}) AT THE CONCLUSION OF THE ANISOTROPIC REFINEMENT

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	0·1329	0·0169	0·0187	0·0024	0·0053	0·0010
C(1)	0·0079	0·0110	0·0102	−0·0006	0·0039	0·0008
C(2)	0·0099	0·0185	0·0081	−0·0020	0·0025	−0·0005
C(3)	0·0112	0·0136	0·0119	−0·0034	0·0010	−0·0020
C(4)	0·0095	0·0201	0·0139	−0·0050	0·0023	−0·0026
C(5)	0·0090	0·0202	0·0126	−0·0019	0·0027	−0·0008

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

TABLE 4. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES FOR ALL *cis*-1,6-DICHLORODECA-1,3,6,8-TETRAENE

COLUMNS ARE l $10|F_o|$ AND $10|F_c|$. REFLEXIONS WITH $F_o < 2\sigma F_c$ ARE MARKED WITH A NEGATIVE SIGN IN THE F_o COLUMN.

0,0,L		
2	385	389
4	101	87
6	130	128
8	133	136
0,1,L		
1	182	165
2	398	378
3	366	-384
4	36	30
5	237	-227
6	119	-113
7	53	-58
8	27	-34
9	13	-14
0,2,L		
0	183	-239
1	297	288
2	181	-143
3	230	211
4	46	-49
5	29	24
6	46	-30
7	33	36
8	44	-47
9	54	59
0,3,L		
1	177	163
2	70	-74
3	240	243
4	94	-79
5	162	153
6	9	-8
7	23	27
8	33	34
9	11	14
0,4,L		
0	383	-370
1	121	-126
2	288	-294
3	166	-146
4	229	-206
5	50	-46
6	180	-174
7	15	12
8	76	-78
0,5,L		
1	91	99
2	77	-73
3	98	90
4	-4	4
5	17	-14
6	38	36
7	9	-13
8	15	19
0,6,L		
0	188	177
1	41	-43
2	140	145
3	55	-50
4	94	89
5	15	-12
6	41	42
7	21	-24
0,7,L		
1	80	-97
2	37	-46
3	98	-88
4	-4	-7
5	57	-54
6	16	13
0,8,L		
0	60	97
1	9	-15
2	68	64
3	-3	-7
4	33	31
5	25	27
0,9,L		
1	13	15
2	-3	-2
1,0,L		
-8	22	-22
-6	-5	11
-4	56	55
-2	283	277
0	188	188
2	595	-616
4	386	-377
6	19	20
8	71	78
1,1,L		
-9	54	-58
-8	103	-106
-7	-3	-3
-6	201	-185
-5	67	63
-4	475	-449
-3	178	145
-2	705	-670
-1	365	360
0	340	-330
1	18	15
2	157	-151
3	138	-117
4	356	-350
5	71	69
6	234	-241
7	134	143
8	50	-46
9	68	58
1,2,L		
-9	15	13
-8	16	-15
-7	73	60
-6	78	60
-5	209	186
-4	86	70
-3	247	226
-2	48	-47
-1	262	247
0	100	-141
1	475	536
2	71	48
3	254	246
4	87	77
5	13	-5
6	29	29
7	24	23
8	5	-4
1,3,L		
-9	18	21
-8	89	-84
-7	12	10
-6	64	-71
-5	49	37
-4	56	-39
-3	12	-12
-2	308	-290
-1	220	-209
0	338	-343
1	196	-217
2	152	-151
3	59	-51
4	108	-86
5	80	-74
6	46	-44
7	102	-111
8	14	-12
1,4,L		
-8	15	-14
-7	9	-11
-6	49	-47
-5	20	14
-4	54	51
-3	68	-59
-2	118	98
-1	195	-207
0	20	21
1	164	-193
2	91	90
3	28	-26
4	96	81
5	46	39
6	30	29
7	19	18
8	16	19
1,5,L		
-8	121	118
-7	34	-34
-6	183	186
-5	10	-11
-4	223	198
-3	72	63
-2	243	280
-1	27	23
0	138	214
1	50	-63
2	182	213
3	59	-55
4	218	206
5	16	-14
6	127	129
7	5	1
1,6,L		
-7	6	6
-6	19	17
-5	80	-79
-4	36	30
-3	142	-138
-2	24	-8
-1	113	-129
0	47	-44
1	89	-114
2	73	-72
3	69	-69
4	47	-44
5	14	-15
6	11	-14
1,7,L		
-6	-4	0
-5	31	34
-4	6	-7
-3	12	9
-2	6	0
-1	24	21
0	9	-19
1	44	48
2	15	-20
3	44	44
4	82	80
5	48	49
1,8,L		
-5	36	41
-4	18	-11
-3	65	68
-2	18	-13
-1	46	30
0	13	7
1	25	25
2	23	-22
3	33	38
4	37	-35
1,9,L		
-3	17	-13
-2	90	-81
-1	13	17
0	80	-81
1	5	5
2	51	-56
2,0,L		
-10	84	-95
-8	105	-108
-6	168	-163
-4	585	-560
-2	884	-869
0	698	-643
2	459	-497
4	190	-191
6	9	12
8	16	-19
2,1,L		
-10	11	11
-9	23	22
-8	8	-7
-7	164	167
-6	38	33
-5	185	178
-4	90	80
-3	68	-66
-2	181	164
-1	25	-15
0	233	263
1	182	195
2	169	170
3	113	110
4	22	-9
5	104	108
6	12	15
7	53	60
8	61	76
2,2,L		
-9	33	-31
-8	69	66
-7	53	-58
-6	142	129
-5	9	-7
-4	48	23
-3	129	-119
-2	131	-100
-1	306	-331
0	103	100
1	234	-256
2	210	215
3	248	-250
4	93	89
5	211	-225
6	-4	-1
7	81	-90
8	21	-23
2,3,L		
-9	10	-10
-8	37	-37
-7	79	-75
-6	46	37
-5	190	-131
-4	116	103
-3	280	-191
-2	10	-7
-1	199	-207
0	-3	5
1	125	-131
2	110	111
3	29	-29
4	79	77
5	50	-49
6	10	8
7	59	-66
8	10	8
2,4,L		
-9	6	1
-8	77	74
-7	-4	3
-6	98	95
-5	6	5
-4	385	389
-3	-4	-5
-2	384	348
-1	75	73
0	216	241
1	138	139
2	186	177
3	154	153
4	163	164
5	70	75
6	67	71
7	6	9
2,5,L		
-8	36	34
-7	47	-41
-6	78	-61
-5	43	-37
-4	181	-166
-3	11	10
-2	98	-89
-1	57	-61
0	9	-4
1	95	-108
2	50	-51
3	87	-87
4	69	-70
5	19	20
6	57	-65
7	8	-4
2,6,L		
-7	28	27
-6	42	-40
-5	65	-59
-4	115	-97
-3	11	-1
-2	180	-161
-1	159	155
0	141	-152
1	125	141
2	74	-75
3	61	58
4	17	-16
5	43	43
6	13	-14
2,7,L		
-6	12	-11
-5	87	83
-4	22	-23
-3	24	24
-2	26	24
-1	39	41
0	25	28
1	85	94
2	9	-7
3	69	76
4	-4	1
5	27	31
2,8,L		
-5	-3	-1
-4	70	-60
-3	13	-14
-2	83	-74
-1	56	-53
0	46	-42
1	66	-69
3	46	-43
2,9,L		
-2	16	19
-1	24	19
0	28	27
1	7	-1
3,0,L		
-10	13	12
-8	27	20
-6	57	57
-4	39	38
-2	198	197
0	449	480
2	262	281
4	93	97
6	52	58
3,1,L		
-10	66	76
-9	19	-18
-8	87	85
-7	39	-39
-6	179	160
-5	202	-179
-4	314	280
-3	363	-331
-2	380	314
-1	116	-123
0	230	234
1	11	-11
2	181	186
3	146	-161
4	62	69
5	146	-163
6	38	44
7	69	-78
3,2,L		
-9	50	-50
-8	16	15
-7	88	-85
-6	39	-38
-5	34	-30
-4	149	-153
-3	137	-127
-2	66	-65
-1	309	-309
0	110	106
1	134	-132
2	45	42
3	15	-13
4	78	-78
5	34	-35
6	63	-71
7	4	1
3,3,L		
-9	33	35
-8	12	12
-7	23	25
-6	138	133
-5	98	88
-4	287	309
-3	283	250
-2	49	36
-1	315	338
0	14	10
1	236	236
2	137	140
3	177	186
4	75	80
5	103	113
6	-4	0
7	58	58
3,4,L		
-9	17	-13
-8	60	-56
-7	7	0
-6	116	-106
-5	54	53
-4	24	-15
-3	85	79
-2	27	-16
-1	60	54
0	205	-198
1	32	29
2	185	-192
3	6	2
4	57	-57
5	27	-29
6	36	-37
3,5,L		
-8	90	-88
-7	32	-31
-6	194	-177
-5	6	5
-4	195	-174
-3	86	83
-2	72	-59
-1	31	30
0	90	-70
1	10	-12
2	175	-167
3	41	40
4	131	-134
5	47	48
6	27	-31
3,6,L		
-7	16	10
-6	11	12
-5	28	-4
-4	8	1
-3	118	112
-2	32	28
-1	175	179
0	109	98
1	40	39
2	107	108
3	55	-58
4	46	52
5	12	7
3,7,L		
-6	-4	0
-5	79	-72
-4	7	5
-3	160	-150
-2	86	28
-1	97	-98
0	13	-10
1	35	-28
2	51	-48
3	83	-73
4	12	-13
3,8,L		
-5	5	0
-4	9	7
-3	24	-26
-2	16	14
-1	60	-57
0	68	59
1	41	-38
2	43	38
4,0,L		
-10	7	10
-8	33	38
-6	237	234
-4	373	360
-2	258	266
0	281	309
2	56	56
4	50	-38
6	27	25
4,1,L		
-9	67	-72
-8	76	-78
-7	46	-48
-6	184	-188
-5	11	14
-4	110	-104
-3	20	-18
-2	134	-143
-1	11	12
0	405	-401
1	11	-8
2	118	-116
3	111	-110
4	84	-80
5	41	-48
6	49	-53
7	36	60
4,2,L		
-9	46	47
-8	80	-86
-7	77	75
-6	44	-43
-5	216	210
-4	57	-48
-3	260	271
-2	21	7
-1	233	243
0	33	31
1	358	346
2	59	-59
3	290	297
4	63	-66
5	120	128
6	5	8
4,3,L		
-9	31	35
-8	-17	-14
-7	35	32
-6	13	13
-5	72	63
-4	51	-50
-3	114	102
-2	189	-206
-1	49	41
0	125	-114
1	64	-54
2	32	28
3	12	-14
4	13	-7
5	18	19
6	61	-61
4,4,L		
-9	22	-24
-8	80	-79
-7	-4	0
-6	110	-101
-5	20	-17
-4	72	-55
-3	122	-119
-2	108	-111
-1	169	-163
0	243	-221
1	136	-121
2	125	-117
3	75	-70
4	36	34
5	45	-46
6	15	16
4,5,L		
-8	37	37
-7	10	-7
-6	79	83
-5	43	43
-4	125	122
-3	85	86
-2	150	156
-1	9	5
0	108	95
1	38	-30
2	23	19
3	33	32
4	62	60
5	38	37
4,6,L		
-7	29	-30
-6	30	28
-5	74	-68
-4	59	53
-3	78	-70
-2	86	72
-1	107	-92
0	83	69
1	195	-169
2	17	15
3	141	-128
4	27	-24
4,7,L		
-6	15	11
-5	47	-49
-4	19	-18
-3	44	-43
-2	22	-18
-1	20	20
0	16	-16
1	27	20
2	-4	-6
3	47	-41
4,8,L		
-4	32	28
-3	27	25
-2	31	30
-1	30	30
0	33	34
1	99	80
5,0,L		
-8	50	-55
-6	55	55
-4	107	-116
-2	373	-382
0	312	-293
2	127	-118
4	49	-50
6	11	-13
5,1,L		
-9	19	20
-8	124	-132
-7	141	151
-6	120	-121
-5	211	222
-4	4	5
-3	110	116
-2	-4	-4
-1	105	101
0	98	-98
1	171	164
2	23	-20
3	138	139
4	-5	11
5	95	100
6	6	2
5,2,L		
-9	10	-7
-8	35	38
-7	47	-49
-6	19	20
-5	44	42
-4	12	-7
-3	86	88
-2	39	26
-1	11	-10
0	53	45
1	8	-9
2	22	15
3	9	-4
4	20	20
5	55	-59
5,3,L		
-9	6	-12
-8	27	-29
-7	103	-104
-6	54	-56
-5	214	-219
-4	58	-59
-3	244	-246
-2	66	-72
-1	255	-232
0	-5	1
1	241	-219
2	63	55
3	126	-124
4	12	-15
5	61	-65
5,4,L		
-8	63	65
-7	25	23
-6	58	62
-5	22	-24
-4	82	91
-3	49	-50
-2	109	105
-1	7	3
0	90	80
1	72	70
2	129	116
3	53	51
4	129	125
5	-4	3
5,5,L		
-8	69	73
-7	7	-4
-6	64	64
-5	14	-11
-4	25	21
-3	27	-28
-2	25	24
-1	79	-76
0	30	24
1	64	-56
2	8	5
3	10	7
4	11	11
5,6,L		
-7	4	-2
-6	22	-25
-5	44	-41
-4	28	-31
-3	41	-37
-2	56	-54
-1	12	-2
0	77	-69
1	6	-6
2	65	-60
3	-4	6
5,7,L		
-5	90	88
-4	35	-30
-3	117	106
-2	11	10
-1	135	113
0	54	43
1	107	87
6,0,L		
-8	16	-21
-6	17	18
-4	105	-116
-2	170	-172
0	88	84
2	189	182
4	42	44
6,1,L		
-9	5	0
-8	7	-4
-7	14	15
-6	97	109
-5	21	-20
-4	206	227
-3	106	-114
-2	125	116
-1	47	-46
0	16	-10
1	69	65
2	55	53
3	-5	4
4	74	77
6,2,L		
-9	85	-103
-8	10	-9
-7	143	-163
-6	49	-53
-5	101	-110
-4	23	-20
-3	156	-159
-2	56	48
-1	321	-307
0	50	46
1	265	-260
2	24	-23
3	119	-122
4	39	-41
6,3,L		
-8	7	2
-7	43	-45
-6	15	20
-5	43	-41
-4	72	77
-3	78	84
-2	78	72
-1	144	132
0	60	59
1	51	47
2	51	46
3	18	16
4	8	6
6,4,L		
-8	34	38
-7	26	29
-6	9	-9
-5	35	36
-4	12	5
-3	86	77
-2	53	44
-1	140	125
0	9	4
1	109	99
2	29	-23
3	26	25
6,5,L		
-7	-3	-2
-6	65	-72
-5	33	-32
-4	96	-99
-3	23	-24
-2	74	-67
-1	8	-11
0	45	-44
1	-4	0
2	71	-68
6,6,L		
-6	16	-14
-5	69	71
-4	17	-13
-3	107	99
-2	6	-1
-1	145	124
0	20	16
1	88	80
6,7,L		
-3	85	-80
-2	25	19
-1	31	-36
7,0,L		
-8	84	88
-6	80	91
-4	72	69
-2	88	84
0	175	174
2	97	103
7,1,L		
-8	10	14
-7	81	-86
-6	33	38
-5	95	-93
-4	11	6
-3	115	-108
-2	187	-184
-1	94	-98
0	145	-139
1	68	-64
2	10	-8
3	88	-96
7,2,L		
-8	41	-50
-7	24	29
-6	15	-13
-5	69	78
-4	54	55
-3	48	50
-2	46	43
-1	20	-20
0	44	-41
1	55	53
2	73	-72
3	114	122
7,3,L		
-7	75	83
-6	15	-12
-5	156	163
-4	7	9
-3	235	230
-2	14	-13
-1	165	155
0	43	-38
1	30	32
2	14	-12
7,4,L		
-7	23	-25
-6	54	-61
-5	21	-25
-4	61	-61
-3	10	-11
-2	48	-44
-1	24	-23
0	87	-81
1	49	-48
2	78	-77
7,5,L		
-6	28	28
-5	5	2
-4	36	33
-3	31	32
-2	40	39
-1	49	48
0	43	36
7,6,L		
-3	32	-28
-2	45	42
8,0,L		
-6	10	-5
-4	52	-52
-2	112	-118
0	77	-81
8,1,L		
-7	35	40
-6	48	-53
-5	76	82
-4	63	-65
-3	37	37
-2	67	-68
-1	10	11
0	19	-18
1	35	40
8,2,L		
-7	56	66
-6	52	55
-5	89	101
-4	41	43
-3	130	138
-2	26	-26
-1	119	119
0	39	-38
1	111	124
8,3,L		
-6	59	-60
-5	43	-44
-4	18	-18
-3	96	-91
-2	5	-7
-1	113	-116
0	80	-84
8,4,L		
-5	41	-39
-4	11	6
-3	35	-36
-2	56	-56
-1	40	-38
9,0,L		
-4	29	-32
-2	35	-42
9,1,L		
-4	68	76
-3	27	31

Cl atom, at fractional coordinates (−0·25, 0·15, 0·25) and (0·29, 0·36, 0·01). The latter position gave more reasonable intermolecular Cl distances and was used in a phasing calculation. The Fourier map based on these phases indicated the position of the five C atoms in the asymmetric unit, which were related to the complete molecule by the operation of the centre of symmetry at (0, $\frac{1}{2}$, $\frac{1}{2}$). The positions were refined as shown in Table 1 using least-squares calculations first with isotropic and later with anisotropic temperature factors. The hydrogen positions were located and refined in the isotropic mode.

The weights used in the least-squares calculations were initially based only on counting statistics and the refinement converged at an R value of 9·6% with an average shift/error of 0·12 and maximum shift/error of 0·60. At this stage we wrote a new program for the analysis of $\omega\Delta^2$ as a function of $|F_o|$ and sin θ, which indicated that a more appropriate form of the weighting scheme would be:

$$\sigma^2(F) = A + BF + C/\omega + DF^2$$

where ω is the weighting factor.

The following parameters were chosen $A = 1{\cdot}20$, $B = 0{\cdot}50$, $C = 1{\cdot}00$, $D = 2 \times 10^{-4}$.

TABLE 5. MOLECULAR DIMENSIONS FOR ALL *cis*-1,6-DICHLORODECA-1,3,6,8-TETRAENE. INTERATOMIC DISTANCES AND STANDARD DEVIATIONS IN Å UNITS. BOND ANGLES IN DEGREES

Interatomic distances and standard deviations			
Cl(1)—C(1)	1·755 (6)	C(2)—H(1)	1·00
C(1)—C(2)	1·512 (6)	C(2)—H(2)	1·15
C(2)—C(3)	1·504 (7)	C(3)—H(3)	0·85
C(3)—C(4)	1·329 (8)	C(4)—H(4)	1·01
C(4)—C(5)	1·460 (9)	C(5)—H(5)	1·00
C(5)—C($\bar{1}$)	1·320 (7)	H(1)... H($\bar{1}$)	2·84
Bond angles			
C($\bar{5}$)—C(1)—C(2)	127·8	C(2)—C(3)—C(4)	125·7
Cl(1)—C(1)—C(2)	113·7	C(2)—C(3)—H(3)	118·4
Cl(1)—C(1)—C($\bar{5}$)	118·5	C(4)—C(3)—H(3)	115·4
C(1)—C(2)—C(3)	113·5	C(3)—C(4)—C(5)	127·4
H(1)—C(2)—C(3)	115·5	C(3)—C(4)—H(4)	117·8
H(1)—C(2)—C(1)	108·8	H(4)—C(4)—C(5)	114·6
H(2)—C(2)—C(1)	101·0	C(4)—C(5)—C($\bar{1}$)	125·8
H(2)—C(2)—C(3)	101·8	C(4)—C(5)—H(5)	112·8
H(2)—C(2)—H(1)	115·3	C($\bar{1}$)—C(5)—H(5)	121·4

The positional and thermal parameters were again refined to convergence to give an R-value of 9·0% for the 860 reflexions including the 25 unobserved reflexions. The reflexions 020, 110 and 200 had apparently been affected by extinction and were excluded from the refinement. The average shift/error was 0·07 and the maximum 0·47. The average standard deviation was 0·005Å for the carbon and 0·07Å for the hydrogen positions.

The final atomic positions are listed in Table 2 together with the individual standard deviations. The anisotropic temperature parameters for the C and Cl atoms are shown in Table 3. The final isotropic temperature factors for the H atoms were H(1) = 2·38, H(2) = 6·20, H(3) = 3·31, H(4) = 2·53, H(5) = 2·18Å^2. The observed and calculated structure factors are listed in Table 4.

Molecular geometry and description of the structure

The shape and dimensions of the molecule are illustrated in Figs 1 and 2 together with the numbering system used. The entire molecule can be defined in terms of two

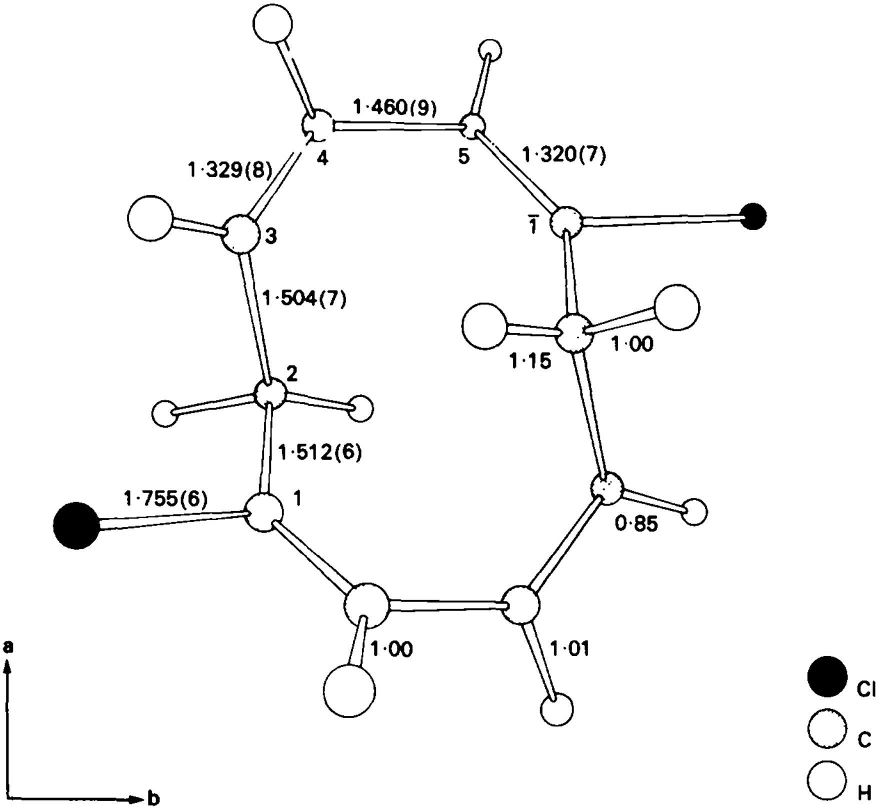

FIG. 1 Perspective view of all *cis*-1,6-dichlorodeca-1,3,6,8-tetraene and values of bond lenghts (Å).

sets of planes, the first defined by atoms C(2), C(3), C(4), C(5), H(4), H(3), which are coplanar to within 0·004Å (r.m.s.Δ) and the second by atoms C(4), C(5), $C(\bar{1})$, $C(\bar{2})$, H(5), Cl(1), which are coplanar to within 0·006Å (r.m.s.Δ). These planes are related to similar planes defining the second half of the molecule through the operation of the centre of symmetry.

In addition to the crystallographic centre of symmetry $\bar{1}(C_i)$ of the molecule as a whole, the symmetry of the 10-membered carbon ring skeleton approximates to a

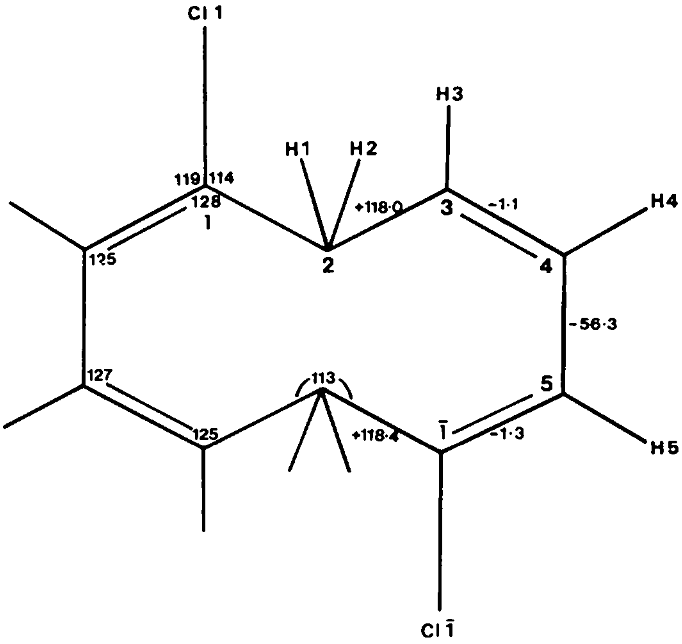

FIG. 2 Chemical formula for all *cis*-1,6-dichlorodeca-1,3,6,8-tetraene showing values of some of the bond and torsional angles (°).

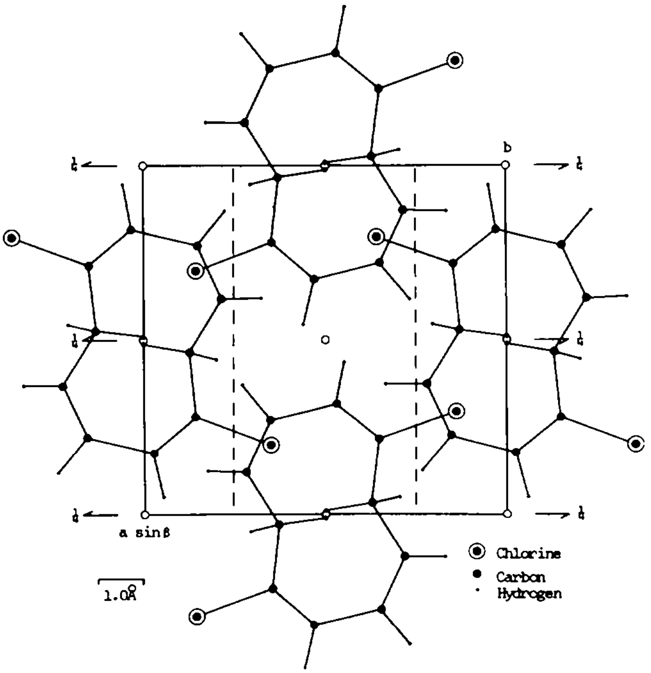

FIG. 3 Projection of the crystal structure of all *cis*-1,6-dichlorodeca-1,3,6,8-tetraene perpendicular to the crystallographic *c* axis.

symmetry of 2/m (C_{2h}). Bonds C(2)-C(3) and C(2)-C($\bar{1}$) are equivalent within experimental error and significantly shorter than bond C(4)-C(5). This shortening is unlikely to be due to a conjugation effect in view of the torsion angle of 56·3° about C(4)-C(5) (Fig. 2). The two bonds C(3)-C(4) and C($\bar{1}$)-C(5) are equivalent and in good agreement with the accepted value for a simple Sp^2-Sp^2 bond.

As discussed by Dunitz in a recent review[5] of the conformation of medium rings, the ring skeleton in 1,6-dichlorodeca-1,3,6,8-tetraene corresponds to an extreme distortion of the stable cyclodecane conformation in which the torsion angles about the four bonds C(3)-C(4), C(5)-C($\bar{1}$), C($\bar{3}$)-C($\bar{4}$) and C($\bar{5}$)-C(1) have been reduced to zero while the 2/m symmetry was preserved.

The resultant arrangement allows for a separation of 2·84Å between the intra-annular H atoms H(1) and H($\bar{1}$), a value considerably greater than the H . . . H distance calculated for cyclodecane.

The molecules are held in the crystal lattice by van der Waals forces only. No unusually close intermolecular approaches were found. The packing is illustrated in Fig. 3.

EXPERIMENTAL

Crystal data. All *cis*-1,6-dichlorocyclodeca-1,3,6,8-tetraene $C_{10}H_{10}Cl_2$; F.W. = 201·1; m.p. = 88–89° dec (green melt) Chunky, colourless prisms. Monoclinic a = 7·577Å, b = 7·878Å, c = 8·397Å, av. σ = 0·001Å, β = 109·05°, σ = 0·05° V = 471·07Å^3, Z = 2, D(calc) = 1·43 g.cm^{-3}. Space group $P2_1/c$ from absences. Unless the structure is disordered the molecule must possess a centre of symmetry in the crystal.

Dichlorocyclodecatetraene is unstable both in soln and in the solid state. The crystals show diagonal extinction on prominent diamond-shaped faces. By examining the crystals under plane polarized light and correlating the observations with X-ray photographs, it was shown that the *b*-direction of the crystal is the direction of higher refractive index. It was possible to cut one of the chunky prisms under the polarising microscope with its sides parallel to the *b* axis and seal it in a capillary tube filled with N_2. This crystal, which was used for the analysis, had dimensions of 0·15 × 0·3 × 0·8 mm and a mosaic spread, estimated from peak breadth, of 0·2°.

The cell dimensions were determined by measuring the θ value of a number of reflexions on the diffractometer and carrying out a least-squares calculation on these. The value of the wavelength used was 1·5418Å.

Intensity data were collected for 863 independent reflexions in the range $0 < 2\theta < 136{\cdot}5°$ with a Picker 4-circle diffractometer in the 2θ-scan mode using Ni-filtered CuKα radiation at 32 KV and 4 mA. A 2θ range of ±1·25° was scanned at a rate of 2°/min with 20-sec background counts at the extremes of the scan range. Only 25 reflexions were too weak to be of significant intensity. The diffractometer data were corrected for the usual factors other than absorption.

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