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The Crystal Structure of Octamethylcyclooctatetraene

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The crystal structure of octamethylcyclooctatetraene, $C_{16}H_{24}$, has been determined by the application of direct methods. Three-dimensional data were collected with Cu $K\alpha$ radiation on a Datex-automated General Electric diffractometer to a maximum 2θ value of 155°. The coordinates and the anisotropic temperature factors of the carbon atoms were refined by the method of least squares. The final R index is 0·086. The crystals are orthorhombic, space group *Pbcn* with $a=12{\cdot}774$, $b=9{\cdot}339$, and $c=12{\cdot}217$ Å. The molecule crystallizes in the 'tub' conformation with half a molecule per asymmetric unit. The two halves of the molecule are related by a twofold rotation. The structure is compared with that found for the parent compound, cyclooctatetraene, and for two other derivatives of this parent.

Introduction

The determination of the structure of octamethylcyclooctatetraene, $C_{16}H_{24}$, was undertaken to examine the possible effects of the presence of the methyl groups on the conformation of the eight-membered ring.

Experimental

Parameters for the orthorhombic unit cell were determined from measurements of precession photographs, which were calibrated by lines diffracted from powdered samples of sodium chloride. The values obtained for the unit-cell dimensions are: $a=12{\cdot}774$ (3), $b=9{\cdot}339$ (2), $c=12{\cdot}217$ (3) Å. The absence of $0kl$ reflections with k odd, of $h0l$ reflections with l odd, and of $hk0$ reflections with $h+k$ odd indicates that the space group is *Pbcn*.

The crystals, prepared in these laboratories, slowly sublimed at room temperature and all of the crystals used in this investigation were sealed in glass capillaries. While mounting the crystals it was apparent that they were of lower density than that usually encountered for organic compounds. The density calculated for these crystals, assuming four molecules per unit cell, is 0·98 g.cm^{-3}. This assumption requires that there be a half molecule per asymmetric unit. The two halves of the molecules could be related by either a center of symmetry or a twofold rotation.

Intensity data were collected by the θ–2θ scan method on a Datex-automated General Electric diffractometer using Cu $K\alpha$ radiation. Two sets of data were collected and corrected for Lorentz and polarization factors. No correction for absorption was made. The initial set of data was collected with a scan speed of 2°min^{-1} and a background count was collected for 10 sec at both the beginning and the end of the scan. This set of data consisted of 765 reflections with 2θ values less than 101° and was used for the determination and initial refinement of the structure. The data were placed on an approximate absolute scale by Wilson's (1942) statistical method. The normalized structure factors, $|E|$ (Karle & Karle, 1966), were calculated using an overall temperature parameter of 2·6 Å^2.

We were unsatisfied when the R index could not be reduced below 0·08. The second set of data was, therefore, collected from the same crystal with a scan speed of 1°min^{-1} and background counts of 20 sec at both ends of the scan. The second set of data was expanded to include all reflections with 2θ values less than 155°: these numbered 1550. Among this set, 353 reflections had intensities less than one standard deviation above background. These 'unobserved' reflections were set equal to zero and were excluded from the R index and from the least-squares calculations. The background observed in the second set of data, which was collected on another Datex-automated General Electric diffractometer, was much higher than for the first set. Indeed, a comparison of the standard deviations for the two sets of data showed that despite the slower scan speed, the second data set was very nearly equal in quality to the first; and a weighted average (based on the standard deviations of the observations) of the two sets was used in the final cycles of least-squares refinement.

Sign determination

The general method of sign determination described by Karle & Karle (1966), based on the relationship:

$$sE_{\mathbf{h}} \simeq s \sum_{\mathbf{k}_r} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} ,$$

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Table 1. *Observed and calculated structure factors*

Within each group, the columns contain h, $10F_o$, and $10F_c$. The asterisks indicate those reflections whose intensities were less than one standard deviation above background and were omitted from the R index and from the least-squares calculations.

H	0	0
2	572	563
4	449	453
6	175	-171
8	15	-9
10	52	-44
12	278	-272
14	83	-80
16	-9	2
H	1	0
1	588	-549
3	405	419
5	134	-132
7	25	35
9	128	-131
11	74	73
13	112	109
15	10	15
H	2	0
0	40	-37
2	147	151
4	31	-35
6	81	80
8	70	-69
10	23	15
12	-17	-11
14	35	-34
H	3	0
1	48	48
3	197	-208
5	25	-15
7	81	86
9	155	162
11	24	1
13	36	31
15	12	14
H	4	0
0	19	1
2	20	-23
4	35	29
6	39	-36
8	56	-49
10	32	-29
12	33	-31
14	15	-7
H	5	0
1	142	-141
3	-12	-7
5	12	-14
7	25	16
9	38	-34
11	56	57
13	-8	-2
H	6	0
0	22	-19
2	60	54
4	91	91
6	39	34
8	29	25
10	69	-63
12	19	-10
H	7	0
1	119	-125
3	275	-274
5	73	-77
7	25	26
9	155	152
11	41	46
13	10	-5
H	8	0
0	171	-172
2	27	29
4	63	61
6	18	13
8	61	-65
10	23	-30
H	9	0
1	101	97
3	-6	18
5	-12	-3
7	8	-2
9	-18	-4
H	10	0
0	52	52
2	-19	9
4	1	-17
6	21	-22
8	13	-1
H	11	0
1	14	5
3	33	34
5	30	25
H	1	1
1	590	544
2	270	283
3	418	-418
4	239	247
5	113	-114
6	200	198
7	95	-99
8	35	42
9	119	121
10	73	70
11	89	-88
12	26	-20
13	44	-46
14	15	5
15	-9	14
16	8	-6
H	2	1
0	71	-70
1	140	143
2	850	771
3	57	59
4	410	414
5	68	-58
6	94	93
7	-11	9
8	198	-202
9	75	-73
10	146	-147
11	-15	2
12	17	26
13	7	-9
14	23	-15
15	-7	-12
H	3	1
1	16	3
2	116	-118
3	202	-202
4	280	281
5	91	-87
6	26	22
7	34	36
8	113	113
9	75	76
10	11	-15
11	73	66
12	17	-16
13	13	-5
14	8	16
15	18	16
H	4	1
0	13	9
1	301	301
2	74	-73
3	22	11
4	14	18
5	29	31
6	28	-21
7	18	0
8	48	48
9	16	-13
10	36	-37
11	57	56
12	17	-5
13	-20	-12
14	-15	14
15	6	-1
H	5	1
1	154	158
2	80	-78
3	35	-30
4	33	24
5	14	-8
6	23	-23
7	39	-31
8	8	10
9	36	41
10	27	-25
11	2	17
12	-6	-17
13	24	-20
14	16	2
H	6	1
0	37	-36
1	9	-7
2	194	190
3	20	19
4	137	136
5	9	5
6	56	29
7	28	23
8	92	-102
9	-13	0
10	91	-91
11	4	4
12	10	2
13	-6	3
H	7	1
1	68	-68
2	10	7
3	125	-127
4	-9	-7
5	40	-38
6	-11	3
7	35	31
8	19	10
9	65	69
10	23	22
11	-6	4
12	4	3
H	8	1
0	65	64
1	-9	-26
2	-17	6
3	73	-72
4	-14	-3
5	65	-64
6	10	13
7	51	-52
8	43	31
9	30	-28
10	20	20
11	-11	-7
H	9	1
1	197	-189
2	-8	5
3	31	-30
4	22	5
5	-9	9
6	-17	5
7	14	2
8	-14	10
9	-14	-7
10	-8	2
H	10	1
0	100	101
1	9	-14
2	39	35
3	17	-13
4	25	-21
5	17	-8
6	13	-14
7	13	-8
8	-2	4
H	11	1
1	12	2
2	18	17
3	-2	7
4	15	2
5	-7	5
H	0	2
1	18	12
2	480	-468
3	91	90
4	150	147
5	112	-114
6	179	172
7	123	126
8	117	-115
9	-10	-4
10	71	71
11	93	93
12	165	163
13	36	34
14	64	61
15	18	-19
16	3	-11
H	1	2
1	411	402
2	650	-619
3	42	-14
4	280	-285
5	188	-187
6	308	-305
7	63	57
8	89	-83
9	69	67
10	61	-64
11	71	-73
12	54	-54
13	63	-66
14	42	37
15	22	-16
H	2	2
0	189	195
1	580	576
2	130	-132
3	168	-172
4	24	-26
5	97	95
6	13	-17
7	9	-10
8	15	8
9	-13	-9
10	18	6
11	77	77
12	15	0
13	44	-39
14	29	23
15	9	-17
H	3	2
1	170	177
2	109	-102
3	311	309
4	213	223
5	95	98
6	21	31
7	72	-72
8	118	121
9	119	-123
10	44	-44
11	26	-29
12	15	19
13	30	-26
14	9	10
15	24	-26
H	4	2
0	300	-295
1	67	-68
2	222	-213
3	25	18
4	113	-110
5	10	18
6	8	15
7	7	-1
8	64	67
9	-4	3
10	44	50
11	36	-33
12	40	38
13	-18	-1
14	6	20
15	-12	-1
H	5	2
1	32	21
2	164	164
3	64	-65
4	70	-76
5	-7	5
6	11	-1
7	21	16
8	82	-88
9	25	31
10	46	39
11	26	-20
12	-21	2
13	13	-9
14	5	-8
H	6	2
0	44	-40
1	60	-62
2	25	-18
3	104	113
4	51	-48
5	141	147
6	26	-29
7	117	122
8	-17	15
9	44	46
10	33	36
11	25	-20
12	16	15
13	18	4
H	7	2
1	35	30
2	39	44
3	128	122
4	-13	0
5	78	76
6	18	-20
7	47	-52
8	14	-19
9	100	-103
10	24	-15
11	10	-23
12	-9	7
H	8	2
0	129	128
1	5	1
2	19	24
3	13	12
4	60	-59
5	42	45
6	19	-11
7	28	23
8	58	59
9	31	31
10	4	10
11	0	-8
H	9	2
1	53	-49
2	10	11
3	22	-4
4	22	-23
5	18	14
6	8	-3
7	8	-5
8	13	-10
9	15	2
10	21	17
H	10	2
0	49	-50
1	44	-39
2	21	-17
3	44	-36
4	3	8
5	49	-41
6	14	8
7	24	-21
8	9	-3
H	11	2
1	-4	20
2	11	2
3	16	-13
4	-4	0
5	18	-17
H	1	3
1	437	-433
2	348	-351
3	144	-142
4	210	-211
5	250	239
6	270	-266
7	130	-127
8	64	-59
9	8	-21
10	92	-90
11	55	55
12	42	33
13	53	50
14	20	4
15	3	2
H	2	3
0	317	320
1	13	-17
2	389	385
3	164	-160
4	199	-197
5	32	41
6	33	-34
7	25	30
8	147	149
9	58	62
10	3	-6
11	21	-9
12	29	-25
13	9	3
14	-13	-14
15	-6	16
H	3	3
1	309	298
2	232	230
3	73	73
4	145	-150
5	103	104
6	92	-89
7	88	-87
8	146	-147
9	73	-74
10	60	62
11	23	-24
12	16	16
13	29	-26
14	24	-25
15	8	2
H	4	3
0	75	-75
1	344	-343
2	95	93
3	28	-22
4	34	31
5	38	31
6	58	-59
7	122	128
8	6	-11
9	17	0
10	28	-28
11	85	-81
12	28	20
13	21	17
14	17	2
H	5	3
1	142	136
2	66	62
3	60	65
4	63	-63
5	120	122
6	65	-69
7	20	-7
8	46	-49
9	29	-25
10	44	36
11	30	-24
12	20	17
13	23	-19
14	2	-2
H	6	3
0	164	-159
1	38	31
2	142	-139
3	33	-37
4	167	-169
5	-11	-6
6	18	-15
7	20	-18
8	100	106
9	19	10
10	52	58
11	3	10
12	28	24
13	2	-4
H	7	3
1	37	-36
2	52	-53
3	24	30
4	27	-27
5	36	36
6	28	-32
7	24	-33
8	39	-34
9	-9	-22
10	54	-50
11	-8	-1
12	-4	-5
H	8	3
0	14	-13
1	37	36
2	11	-8
3	114	114
4	26	26
5	101	100
6	-9	16
7	79	77
8	13	-16
9	52	46
10	-8	-4
11	11	9
H	9	3
1	53	54
2	-5	-4
3	11	-11
4	-19	-14
5	41	-42
6	-16	-1
7	21	17
8	12	-13
9	7	11
10	3	-3
H	10	3
0	69	-68
1	25	19
2	43	-42
3	20	27
4	12	11
5	-2	11
6	20	6
7	11	4
8	13	-5
H	11	3
1	13	7
2	35	-39
3	5	8
4	15	-17
5	11	1
H	0	4
0	541	-545
1	250	254
2	224	225
3	219	-218
4	515	-490
5	46	41
6	-1	-11
7	35	29
8	130	126
9	39	-37
10	50	-53
11	40	-34
12	12	-17
13	17	-27
14	33	-33
15	15	18
H	1	4
1	199	-194
2	214	214
3	136	-137
4	330	319
5	240	236
6	46	38
7	98	-96
8	74	67
9	31	32
10	75	72
11	20	32
12	20	24
13	16	17
14	15	-22
15	14	4
H	2	4
0	140	-147
1	317	-313
2	32	-30
3	272	-266
4	89	93
5	166	-161
6	-6	0
7	18	16
8	21	15
9	104	-102
10	-12	-18
11	62	-67
12	16	11
13	32	29
14	-10	-1
15	34	36
H	3	4
1	259	-249
2	186	186
3	260	-257
4	26	34
5	161	-157
6	24	-20
7	66	66
8	18	-15
9	61	57
10	83	82
11	51	48
12	-11	1
13	15	7
14	-18	-11
15	31	28
H	4	4
0	275	265
1	41	41
2	239	236
3	11	11
4	95	95
5	39	-36
6	-13	-7
7	57	-63
8	56	-57
9	27	-28
10	54	-53
11	23	5
12	20	-29
13	-13	-6
14	32	-25
H	5	4
1	93	89
2	56	-53
3	106	104
4	129	127
5	49	51
6	178	181
7	56	-57
8	117	119
9	19	-26
10	44	-43
11	28	-21
12	-16	-8
13	17	17
14	-11	1
H	6	4
0	72	69
1	56	55
2	-15	-4
3	28	10
4	19	-19
5	87	-92
6	21	3
7	111	-115
8	28	-32
9	22	12
10	-10	0
11	27	31
12	19	-16
13	-7	1
H	7	4
1	44	54
2	45	-47
3	43	38
4	63	-64
5	49	-52
6	-10	13
7	59	56
8	-15	-8
9	-14	17
10	-11	-8
11	10	0
12	-5	-6
H	8	4
0	31	-29
1	31	-22
2	46	-44
3	23	0
4	49	54
5	37	-31
6	11	0
7	25	-30
8	37	-33
9	20	-13
10	14	6
11	10	6
H	9	4
1	11	-4
2	8	-7
3	21	-12
4	6	9
5	11	-15
6	20	25
7	-15	8
8	21	15
9	-8	-2
H	10	4
0	34	35
1	27	25
2	18	24
3	25	26
4	1	-2
5	15	10
6	6	5
7	18	-1
H	11	4
1	33	-33
2	5	-8
3	-6	-3
4	7	-3
H	1	5
1	191	190
2	129	125
3	94	99
4	29	22
5	118	-118
6	54	48
7	125	121
8	32	19
9	30	-37
10	13	16
11	-12	-5
12	25	-16
13	45	-41
14	30	-26
15	11	1
H	2	5
0	82	-87
1	93	-91
2	248	-248
3	127	123
4	98	99
5	-15	11
6	46	-45
7	45	-39
8	12	-16
9	38	35
10	35	31
11	8	12
12	12	12
13	20	17
14	23	15
15	-8	-7
H	3	5
1	205	-198
2	227	-220
3	83	-88
4	211	-214
5	23	30
6	118	119
7	23	21
8	7	3
9	22	22
10	62	-64
11	7	10
12	7	-5
13	25	22
14	10	19
H	4	5
0	-11	-2
1	38	29
2	10	13
3	24	28
4	89	-88
5	226	-224
6	21	24
7	250	-255
8	42	41
9	13	10
10	33	27
11	19	26
12	9	-15
13	-7	0
14	2	-11
H	5	5
1	117	-118
2	11	14
3	36	-34
4	59	63
5	47	-39
6	183	189
7	23	10
8	62	67
9	5	0
10	10	-4
11	22	21
12	-25	0
13	22	18
H	6	5
0	77	76
1	40	-34
2	19	-3
3	12	12
4	80	82
5	19	6
6	-17	-14
7	-16	-12
8	46	-45
9	29	-25
10	10	-17
11	38	-31
12	12	-14
H	7	5
1	45	54
2	87	86
3	23	14
4	65	65
5	22	-21
6	38	42
7	22	26
8	41	41
9	-13	-1
10	43	42
11	8	-2
H	8	5
0	16	-18
1	-12	-17
2	21	0
3	39	-48
4	31	-21
5	39	-42
6	11	-12
7	19	-28
8	14	3
9	16	-23
10	-3	0
H	9	5
1	9	0
2	-19	1
3	21	13
4	19	19
5	21	24
6	9	3
7	24	-21
8	20	2
9	-9	-4
H	10	5
0	43	-40
1	-15	-4
2	25	29
3	14	-20
4	11	1
5	8	-2
6	13	3
H	11	5
1	-11	2
2	48	45
H	0	6
0	59	60
1	61	-62
2	38	-46
3	70	67
4	123	119
5	17	9
6	83	-85
7	36	-44
8	21	19
9	23	13
10	26	-5
11	-15	-8
12	9	2
13	11	14
14	-8	5
H	1	6
1	18	26
2	58	-51
3	33	-31
4	116	-115
5	43	37
6	61	60
7	-16	3
8	30	-32
9	31	-30
10	29	-36
11	26	13
12	-24	-8
13	12	-5
14	7	9
H	2	6
0	20	13
1	117	110
2	135	137
3	417	415
4	93	-94
5	119	121
6	16	-13
7	58	53
8	40	36
9	127	129
10	-7	-6
11	40	40
12	9	-9
13	-7	-8
14	20	-17
H	3	6
1	-13	8
2	142	-139
3	26	25
4	125	-126
5	82	81
6	38	38
7	62	-62
8	78	-75
9	25	-10
10	60	-62
11	25	-12
12	33	-24
13	15	15
14	19	19
H	4	6
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1	-14	-9
2	7	4
3	34	-29
4	17	25
5	40	38
6	19	18
7	72	71
8	-13	0
9	-9	29
10	-20	4
11	11	14
12	-18	-4
13	-5	3
H	5	6
1	-12	-20
2	-13	-6
3	21	-28
4	97	-100
5	87	-87
6	247	-243
7	48	45
8	76	-70
9	-12	17
10	8	22
11	20	15
12	20	25
13	-9	-8
H	6	6
0	15	-15
1	36	-40
2	27	-21
3	106	-102
4	42	48
5	13	25
6	15	12
7	35	38
8	14	-22
9	49	-45
10	-7	-9
11	31	-32
12	10	6
H	7	6
1	-21	0
2	27	32
3	23	-5
4	44	48
5	17	3
6	13	6
7	5	-4
8	16	17
9	17	17
10	21	17
11	-1	-4
H	8	6
0	20	-17
1	-20	15
2	17	-7
3	9	6
4	17	-25
5	7	6
6	-11	11
7	21	20
8	-12	1
9	6	0
10	-5	1
H	9	6
1	-11	-5
2	-25	-8
3	-12	3
4	-15	-13
5	-10	-7
6	46	-43
7	8	1
8	15	-20
H	10	6
0	10	-10
1	14	-6
2	8	-12
3	-4	-15
4	11	10
5	21	15
H	1	7
1	7	1
2	65	-66
3	33	32
4	82	-82
5	-8	-3
6	49	50
7	21	-2
8	41	-41
9	24	14
10	-10	-4
11	6	-9
12	-9	0
13	18	9
14	25	24
H	2	7
0	79	-79
1	13	-19
2	100	-97
3	16	1
4	13	-17
5	24	-24
6	35	33
7	15	-2
8	41	-34
9	-19	-7
10	24	14
11	-7	-8
12	7	-1
13	15	-9
14	12	11
H	3	7
1	15	1
2	156	157
3	18	13
4	132	128
5	107	-104
6	71	-72
7	57	54
8	28	26
9	16	27
10	18	19
11	6	4
12	28	15
13	13	-7
H	4	7
0	13	17
1	27	19
2	53	-59
3	15	-23
4	108	107
5	240	244
6	38	33
7	173	173
8	47	-50
9	25	14
10	25	-2
11	-6	-20
12	-5	0
13	16	-5
H	5	7
1	28	-23
2	24	11
3	40	-34
4	53	-55
5	77	-80
6	114	-115
7	16	16
8	38	-38
9	-10	18
10	17	-2
11	-9	3
12	7	7
H	6	7
0	46	56
1	22	0
2	53	49
3	23	25
4	28	24
5	31	-23
6	7	14
7	16	-7
8	19	-19
9	13	20
10	-14	-9
11	15	16
H	7	7
1	10	-8
2	58	-59
3	-3	5
4	36	-42
5	19	6
6	-20	-3
7	12	-9
8	29	-28
9	-7	-3
10	25	-23
H	8	7
0	28	20
1	20	20
2	20	9
3	-2	20
4	-14	-4
5	19	25
6	-9	-6
7	18	23
8	-10	2
9	14	13
H	9	7
1	19	8
2	11	-5
3	-7	6
4	-9	-12
5	20	9
6	23	-22
7	1	2
H	10	7
0	-5	4
1	-19	2
2	-5	7
3	15	6
4	-7	-1
H	0	8
0	36	41
1	67	-70
2	35	-37
3	103	100
4	99	99
5	42	-38
6	29	31
7	24	-29
8	37	-46
9	30	23
10	15	11
11	21	-15
12	17	0
13	4	-3
H	1	8
1	90	95
2	74	78
3	42	40
4	16	13
5	82	-85
6	69	70
7	34	29
8	12	19
9	-9	-2
10	22	23
11	17	-11
12	25	12
13	16	-20
H	2	8
0	36	-39
1	80	-84
2	68	-64
3	219	-220
4	39	38
5	47	-49
6	-14	0
7	58	-59
8	34	-34
9	58	-54
10	-29	0
11	32	-34
12	14	14
13	12	14
H	3	8
1	115	113
2	60	65
3	66	62
4	40	24
5	18	6
6	70	-70
7	15	12
8	29	24
9	-10	-9
10	23	20
11	23	-22
12	22	16
13	27	-24
H	4	8
0	106	-104
1	10	6
2	87	-89
3	17	21
4	55	-52
5	23	-15
6	12	-6
7	23	-21
8	30	28
9	6	-5
10	36	31
11	-13	0
12	17	19
H	5	8
1	51	-50
2	28	-28
3	-11	-2
4	51	47
5	38	38
6	129	131
7	-25	-3
8	22	23
9	16	-13
10	-5	-12
11	-12	-1
12	23	-26
H	6	8
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1	28	35
2	-15	7
3	34	37
4	47	-43
5	43	-43
6	2	-6
7	14	-16
8	40	39
9	-21	10
10	15	14
11	26	23
H	7	8
1	43	-36
2	16	-19
3	20	-9
4	12	7
5	27	26
6	33	-23
7	13	-23
8	1	0
9	19	-15
10	-7	-3
H	8	8
0	-4	5
1	-9	0
2	17	10
3	26	-29
4	20	-18
5	-19	-1
6	16	-7
7	11	-6
8	15	11
H	9	8
1	13	8
2	9	14
3	-10	9
4	30	25
5	23	13
6	35	27
H	10	8
0	7	-4
1	6	11
2	3	-4
H	1	9
1	56	-55
2	84	84
3	27	-22
4	112	113
5	37	40
6	16	-14
7	14	-27
8	59	54
9	10	12
10	28	23
11	22	0
12	6	7
13	16	17
H	2	9
0	66	61
1	42	40
2	60	56
3	46	-47
4	47	-52
5	35	32
6	18	-2
7	32	21
8	17	18
9	18	-26
10	17	7
11	-10	-2
12	17	-4
H	3	9
1	33	32
2	69	-65
3	77	81
4	19	16
5	41	43
6	33	24
7	21	-24
8	23	13
9	44	-46
10	13	-8
11	20	-21
12	10	-9
H	4	9
0	59	63
1	43	39
2	-22	-1
3	15	13
4	49	-50
5	99	-100
6	20	-28
7	52	-51
8	22	13
9	14	-7
10	16	16
11	34	31
H	5	9
1	19	24
2	23	-24
3	51	56
4	35	35
5	54	54
6	21	14
7	14	-13
8	14	7
9	21	-25
10	12	-12
11	9	-16
H	6	9
0	46	-45
1	-4	7
2	23	-24
3	29	-26
4	45	-46
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8	34	28
9	-13	-5
10	11	19
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5	-7	3
6	19	-16
7	-8	-4
8	12	14
9	-12	1
H	8	9
0	14	-18
1	21	-19
2	14	-9
3	29	-30
4	8	12
5	44	-39
6	15	2
7	40	-36
H	9	9
1	19	17
2	-4	-6
3	-12	0
4	13	-1
H	0	10
0	127	126
1	11	-4
2	83	82
3	94	-96
4	54	-57
5	24	24
6	13	8
7	27	28
8	-15	1
9	8	-13
10	9	-3
11	-5	-1
12	34	-37
H	1	10
1	99	-100
2	23	-28
3	-9	7
4	26	-23
5	18	16
6	83	-81
7	-13	-8
8	16	-18
9	-17	-5
10	10	-12
11	7	7
12	8	6
H	2	10
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1	47	51
2	15	-17
3	49	49
4	12	8
5	21	9
6	27	2
7	-4	8
8	7	4
9	21	13
10	9	13
11	16	17
12	19	-20
H	3	10
1	74	-80
2	30	-25
3	34	-32
4	31	30
5	32	-28
6	51	55
7	28	31
8	28	20
9	25	12
10	4	-9
11	25	26
H	4	10
0	30	31
1	7	-5
2	46	45
3	-12	-8
4	20	17
5	-4	-3
6	-15	-6
7	-11	-3
8	16	-18
9	16	-4
10	21	-25
11	12	-7
H	5	10
1	25	32
2	24	31
3	16	-14
4	15	-15
5	-12	4
6	26	-40
7	20	-16
8	12	-13
9	17	13
10	17	13
H	6	10
0	29	-24
1	-8	-10
2	14	19
3	23	15
4	17	27
5	34	39
6	8	7
7	17	21
8	16	-16
9	4	0
H	7	10
1	3	4
2	18	-1
3	27	-32
4	-12	-2
5	31	-27
6	25	23
7	15	17
H	8	10
0	5	-3
1	10	10
2	-12	8
3	24	27
4	34	28
5	12	-2
H	1	11
1	48	50
2	75	-75
3	-9	-6
4	32	-38
5	39	-34
6	10	-6
7	23	7
8	9	-4
9	12	-5
10	24	-23
11	14	-4
H	2	11
0	-15	1
1	-9	22
2	49	38
3	9	19
4	69	63
5	34	-28
6	-24	0
7	8	-20
8	29	-21
9	0	2
10	29	-28
11	10	14
H	3	11
1	19	-14
2	11	0
3	61	-65
4	16	-11
5	19	-2
6	15	-1
7	-17	-3
8	17	-4
9	43	38
10	23	13
H	4	11
0	61	-59
1	33	-24
2	16	21
3	-17	-6
4	7	0
5	12	8
6	16	13
7	26	13
8	2	0
9	11	-13
H	5	11
1	16	13
2	16	-3
3	21	-25
4	18	-8
5	-16	-9
6	3	-2
7	-11	0
8	16	4
9	15	19
H	6	11
0	-1	10
1	23	13
2	26	16
3	13	7
4	30	31
5	17	-21
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7	18	-22
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1	12	-18
2	16	-19
3	18	-15
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5	14	-6
6	10	7
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2	-13	5
3	15	16
H	0	12
0	142	-143
1	74	67
2	74	-76
3	30	37
4	20	6
5	7	-1
6	6	5
7	-11	-10
8	8	1
9	11	3
10	5	14
H	1	12
1	43	45
2	32	-34
3	13	-8
4	8	13
5	-15	-3
6	15	12
7	18	3
8	8	13
9	7	13
10	8	-10
H	2	12
0	18	-18
1	10	-10
2	15	13
3	12	2
4	-8	-13
5	-16	0
6	-13	2
7	23	10
8	-16	-1
9	10	-7
H	3	12
1	25	29
2	-10	14
3	19	21
4	17	-13
5	-6	14
6	21	-20
7	21	-23
8	27	-13
9	-2	-13
H	4	12
0	16	-12
1	18	1
2	13	-14
3	14	2
4	10	-4
5	-9	8
6	-17	4
7	-2	5
8	-8	9
H	5	12
1	-11	1
2	3	-7
3	9	5
4	-10	7
5	-10	-3
6	-13	11
7	4	9
H	6	12
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1	12	-3
2	-21	-11
3	18	-6
4	-8	-12
5	9	-6
6	-10	-9
H	7	12
1	21	17
2	-8	11
3	37	34
H	1	13
1	39	-36
2	24	33
3	8	4
4	13	-8
5	11	16
6	6	-8
7	7	-1
8	21	-16
H	2	13
0	14	-12
1	36	-34
2	24	-27
3	11	-7
4	33	-32
5	13	12
6	-7	-2
7	12	21
8	22	25
H	3	13
1	11	16
2	14	10
3	-5	11
4	-16	-7
5	-9	6
6	-12	-11
7	-7	-6
H	4	13
0	-10	2
1	-2	0
2	-15	3
3	5	-2
4	-6	8
5	-7	2
6	-13	-5
H	5	13
1	-23	-8
2	11	10
3	9	1
4	13	0
5	15	6
H	6	13
0	-20	-12
1	4	-14
2	26	-22
3	-11	0
H	0	14
0	52	59
1	29	-35
2	28	31
3	-6	-17
4	7	-4
5	20	-2
6	11	-8
H	1	14
1	9	-9
2	23	32
3	8	0
4	4	12
5	11	9
6	5	3
H	2	14
0	29	-21
1	-17	-2
2	15	2
3	8	-10
4	-16	5
5	-12	-6
6	4	1
H	3	14
1	-26	-8
2	16	-6
3	14	-22
4	10	3
5	17	-6
H	4	14
0	19	20
1	2	0
2	22	12
3	-7	0
4	17	6
H	1	15
1	10	22
2	10	-6
3	-4	-1
H	2	15
0	-13	-1
1	12	11
2	9	5

Table 2. *Carbon atom parameters and their standard deviations*

The values have been multiplied by 10^5. The temperature factor is in the form:

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

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	54659(12)	28959(16)	28645(13)	943(14)	1241(19)	929(15)	-360(29)	97(24)	-90(32)
C(2)	62168(12)	19232(17)	27860(13)	688(12)	1389(22)	921(15)	-407(30)	51(25)	245(33)
C(3)	61520(12)	7222(16)	19995(13)	613(10)	1391(22)	945(14)	28(28)	277(25)	55(32)
C(4)	54046(10)	-2608(15)	20622(13)	638(11)	1120(19)	1016(15)	193(25)	127(23)	-116(31)
C(5)	54771(15)	41118(18)	36768(18)	1562(21)	1621(28)	1516(21)	-384(41)	-30(35)	-944(44)
C(6)	72109(13)	19871(21)	34576(15)	928(15)	2456(40)	1328(17)	-576(40)	-233(30)	130(43)
C(7)	70071(12)	6735(21)	11457(16)	961(16)	2547(36)	1335(18)	-307(34)	752(30)	-195(45)
C(8)	53294(12)	-15131(17)	12737(17)	1028(16)	1523(25)	1505(20)	171(34)	222(30)	-335(41)

where s means 'the sign of', was used throughout the analysis. A listing of the $\sum_2$ relationships for the 75 normalized structure factors whose magnitudes exceeded 1·5 was prepared. Three reflections were then chosen to fix the origin and were given the following signs:

h	k	l	E	Sign
2	2	1	3·44	+
6	5	6	3·79	−
5	4	7	3·47	+

In addition, three reflections could be given signs by inspection. For example, among the 10 relationships for the reflection 12,0,0 eight were pairs involving reflections of the type $6kl$ and $6\bar{k}\bar{l}$, with k odd. For reflections of space group *Pbcn* with $h+k$ odd, $E(hkl) = -E(h\bar{k}\bar{l})$ and, therefore, all of these pairs indicate a minus sign for the 12,0,0 reflection. In a like manner, both the 0,8,0 and 0,0,12 reflections were assigned minus signs.

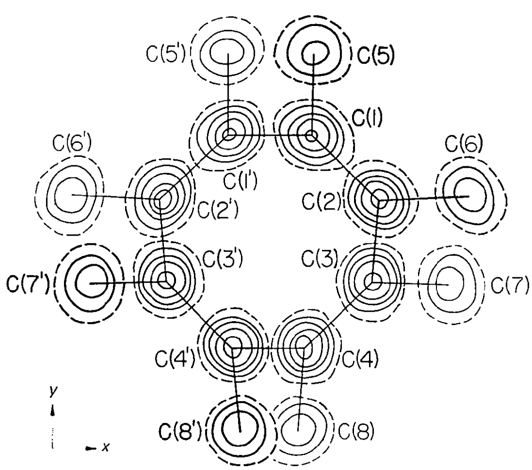

Fig. 1. A composite of sections of a three-dimensional electron density map through each of the carbon atoms, viewed down the c axis. The dashed contour is at 2 e.Å^{-3}. The successive contours are at 3, 4, 5,..... e.Å^{-3}.

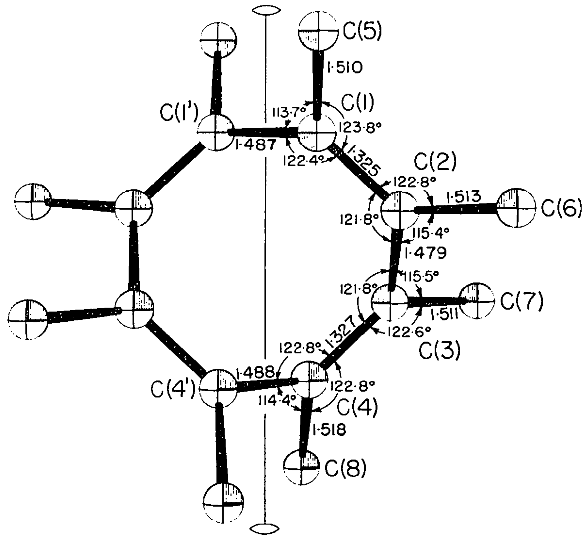

Fig. 2. Bond distances and angles for the carbon atoms.

Beginning with these six reflections it was possible to generate in a short time, by hand, the signs for 72 of the 75 largest E values. At the conclusion of the structure refinement a survey showed that 66 of these derived signs were correct.

These 72 reflections were used to calculate an E map. The positions of the atoms of the octatetraene ring were clearly evident in this map; and there were also strong indications of the positions of the methyl groups.

Refinement of the structure

All calculations described below were carried out on an IBM 360/75 computer with subprograms operating under the *CRYM* system. This system is a conversion of the *CRYRM* system (Duchamp, 1964) which was written for the IBM 7094 computer. The atomic scattering factor for C was taken from *International Tables for X-ray Crystallography* (1962). The atomic scattering factor for H is that given by Stewart, Davidson & Simpson (1965). The least-squares routine minimizes the quantity $\sum w(F_o^2 - F_c^2)^2$. The weights, w, used through out the refinement of the structure, were set equal to $1/\sigma^2(F_o^2)$; here, $\sigma^2(F_o^2)$ was based on the variance of the intensity calculated by the formula:

$$\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2 ,$$

where S is the total counts collected during the scan, B_1 and B_2 are the numbers of counts collected for each background, α is the scan time to total background time ratio, and d is an empirical constant of 0·02.

After several cycles of refinement of the positional and anisotropic temperature parameters of the carbon atoms, the R index had been reduced to 0·131. Difference electron density maps were then calculated in those planes expected to contain the methyl hydrogen atoms. No definite positions for the hydrogen atoms could be assigned from these maps, since the electron density was distributed nearly uniformly around a circle in each of the planes. As an approximation to this apparent disorder in the methyl hydrogen atoms, 12 hydrogen atoms with population factors of 0·25 were placed at 30° intervals around these circles, 1·00 Å from the methyl carbon atoms. All of the hydrogen atoms were assigned isotropic temperature factors of 9·5 Å². During the remainder of the calculations, the contributions of the hydrogen atoms were included in the structure factors, but their parameters were excluded from the least-squares refinement. In the final stages of refinement, a secondary extinction factor was included; the expression used is $F^2_{\text{corrected}} = (F_{\text{cal}})^2/[1+g\beta(F_{\text{cal}})^2]$ (Larson, 1967). The final value obtained for the factor g is $26\ (\pm 2)\times 10^{-6}$. The final R index, $\sum ||F_o|-|F_c||/\sum |F_o|$, is 0·086; the weighted R index, $\sum w(F_o^2-F_c^2)^2/\sum wF_o^4$, is 0·007; and the 'goodness of fit', $\sum w(F_o^2-F_c^2)^2/(m-s)$ (where m is the number of observations and s is the number of parameters refined), is 1·4. The observed and calculated structure factors, F_o and F_c, are listed in Table 1.

The final coordinates and anisotropic temperature factors for the carbon atoms and their standard deviations, calculated from the least-squares residuals, are given in Table 2. The assigned positional parameters for the quarter hydrogen atoms are given in Table 3. The shifts calculated for the parameters in the final cycle of least-squares refinement were all less than one-tenth of the standard deviation.

Table 3. *Assigned coordinates of the quarter hydrogen atoms*

A fixed isotropic temperature factor of 9·5 Å² was assigned to all hydrogen atoms. The values have been multiplied by 10⁴.

Hydrogen atoms on C(5)			Hydrogen atoms on C(6)		
x	y	z	x	y	z
4749	4388	3870	7032	2065	4252
4848	4720	3578	7086	2562	4138
5117	4961	3363	7233	2907	3881
5485	5046	3283	7434	3010	3550
5853	4955	3357	7635	2845	3235
6122	4710	3568	7782	2454	3020
6221	4376	3858	7836	1941	2962
6122	4044	4150	7782	1444	3076
5853	3803	4365	7635	1099	3333
5485	3718	4445	7434	996	3664
5117	3809	4371	7233	1161	3979
4848	4054	4160	7086	1552	4194

Hydrogen atoms on C(7)			Hydrogen atoms on C(8)		
x	y	z	x	y	z
6695	630	400	4575	−1747	1136
6763	130	494	4674	−2075	1430
6949	−225	711	4943	−2329	1636
7204	−342	993	5311	−2439	1698
7459	−191	1265	5679	−2379	1602
7645	188	1454	5948	−2163	1372
7713	698	1510	6047	−1849	1068
7645	1198	1416	5948	−1521	774
7459	1554	1199	5679	−1267	568
7204	1671	917	5311	−1157	506
6949	1520	645	4943	−1217	602
6763	1140	456	4674	−1433	832

Description of the structure

The two halves of the molecule are related by a two-fold axis parallel to the b axis. A composite of the final electron density map viewed along the c axis is shown in Fig. 1.

The bond distances and angles involving the carbon atoms are shown in Fig. 2. [Figs. 2 and 3 were drawn on a *CALCOMP* plotter controlled by an IBM 360/75 computer using the *ORTEP* program (Johnson, 1965)]. The standard deviations in the atomic coordinates (Table 2) correspond to positional uncertainties of approximately 0·0018 Å. On this basis, the standard deviations in the bond distances should be about 0·0025 Å and in the bond angles about 0·2°.

A stereoscopic view down the c axis showing the 'tub' conformation of the molecule and the packing of the molecules is given in Fig. 3. The shortest intermolecular carbon–carbon contact is 3·83 Å between atom 5 of the molecule at x,y,z, and atom 5 of the molecule at $1\text{-}x,1\text{-}y,1\text{-}z$.

Comparison of related compounds

The crystal structures of three related compounds have been determined: cyclooctatetraene (COT) (Bregman

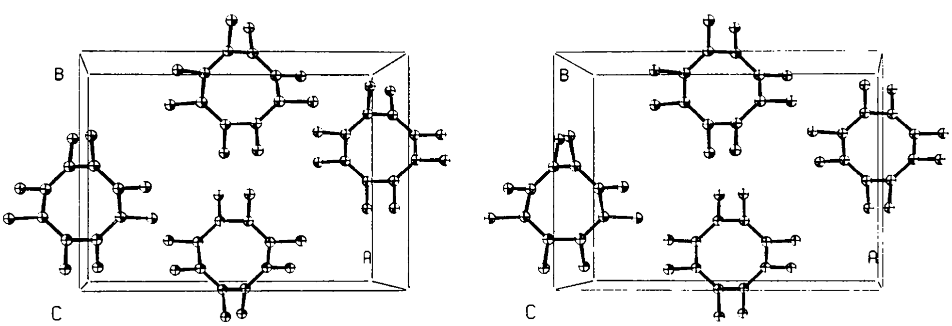

Fig. 3. A stereoscopic view down the c axis showing the packing of the molecules in the unit cell.

& Post, private communication), cyclooctatetraene-carboxylic acid (COT acid) (Shoemaker, Kindler, Sly & Srivastava, 1965), and calcium 2,4,6,8-cyclooctatetraene-1,2-dicarboxylate (CaCOT) (Wright, Shoemaker & Seff, private communication). The four molecules are shown in Fig. 4. Earlier and less precise investigations of the crystal structures of cyclooctatetraene (Kaufman, Fankuchen & Mark, 1948) and silver cyclooctatetraene nitrate (Mathews & Lipscomb, 1959) are not included in our study.

An attempt to interpret the thermal vibrational parameters of the ring carbon atoms of the four compounds under consideration in terms of rigid-body motion (Schomaker & Trueblood, 1968) was successful only for cyclooctatetraene and octamethylcyclooctatetraene (8MeCOT). The resulting rigid-body parameters for COT and 8MeCOT are shown in Table 4. The r.m.s. discrepancies between the observed and calculated U_{ij} are:

Compound	$(\overline{\Delta U_{ij}^2})^{1/2}$(Å^2)	e.s.d. in U_{ij}
COT	0·0021	0·0023*
COT acid	0·0036	0·0022*
CaCOT	0·0037	0·0020
8MeCOT	0·0007	0·0013

* These values were estimated on the basis of the reported standard deviations of the positional parameters.

An analysis including all 16 carbon atoms in 8MeCOT resulted in a discrepancy of 0·0037 Å^2. Values of the discrepancy of this size indicate considerable internal motion.

In both COT and 8MeCOT the translational motion is small and reasonably isotropic. Apparently only the principal axes ($T3$ in COT and $T2$ in 8MeCOT), which are of necessity parallel to crystallographic twofold axes, correlate with an inertial axis of the molecules.

Table 4. *Rigid-body thermal parameters of cyclooctatetraene rings*

Axes of reference are *a*, *b*, *c*. E.s.d.'s of components of *L* are given in parentheses.

	COT			8MeCOT		
L(°)^2	23·8 (3·2)	−6·2 (3·4)	0·0	25·8 (1·9)	0·0	0·1 (0·7)
		16·6 (3·6)	0·0		19·8 (1·8)	0·0
			19·1 (5·4)			19·4 (0·7)

Principal axes of **L**

	r.m.s. amplitude	Direction cosines (×10^3)			r.m.s. amplitude	Direction cosines (×10^3		
L1	5·2°	867	−498	0	5·1	1000	0	10
L2	4·4	0	0	1000	4·5	0	1000	0
L3	3·6	498	867	0	4·4	10	0	1000

Principal axes of reduced **T**

	R.m.s. amplitude	Direction cosines (×10^3)			R.m.s. amplitude	Direction cosines (×10^3)		
T1	0·22 Å	339	−941	0	0·24 Å	514	0	858
T2	0·21	941	339	0	0·21	0	1000	0
T3	0·20	0	0	1000	0·21	858	0	−514

Displacement of libration axes from intersecting (Å)

	COT	8MeCOT
Parallel to **L**i	0·0	0·0
Parallel to **L**2	0·353	0·872
Parallel to **L**3	0·0	0·0

Effective screw translations (Å)

	COT	8MeCOT
Parallel to **L**1	0·009	0·021
Parallel to **L**2	−0·044	−0·042
Parallel to **L**3	0·040	0·019

Table 5. *Average structural components of the cyclooctatetraene rings*

The r.m.s. deviations from the averages are shown in parentheses.

	Compound	Double bond	Single bond	Bond angle	Torsion angle	Standard diviation	Standard
	COT*	1·334 Å	1·462 Å	126·46°		0·001 Å	0·23°
(I)	COT	1·330 (±0·006)	1·456 (±0·012)	126·8 (±1·9)	55·7 (±3·9)°	0·009	0·5
(II)	COT acid	1·322 (±0·008)	1·470 (±0·017)	126·4 (±0·8)	57·1 (±0·6)	0·007	0·5
(III)	CaCOT	1·335 (±0·003)	1·464 (±0·022)	126·4 (±1·1)	57·1 (±2·5)	0·0035–0·007	0·3–0·6
(IV)	8MeCOT	1·326 (±0·001)	1·483 (±0·005)	122·2 (±0·5)	66·6 (±4·3)	0·0025	0·2

* Values from an electron diffraction study of cyclooctatetraene in the gas phase by Bastiansen, Hedberg & Hedberg (1957).

The librational motions are also small and nearly isotropic. In COT, one principal axis, $l2$, is required by symmetry to parallel the c axis. Of the two remaining principal axes, $L3$ makes an angle of 13° with the pseudo-twofold axis which passes through the midpoints of the bonds C(3)–C(4) and C(3′)–C(4′), and $L1$, therefore, nearly parallels a second pseudo-twofold axis 'perpendicular' to the ring. In 8MeCOT, $L2$ is required to parallel the b axis; $L1$ makes an angle of only 5° with the pseudo-twofold axis which passes through the midpoints of the bonds C(2)–C(3) and C(2′)–C(3′); and $L3$ closely parallels the pseudo-twofold axis 'perpendicular' to the ring.

The bond distances and angles in the cyclooctatetraene rings are shown in Fig. 4 for all four compounds. In addition, the torsion angle and its standard deviation (Stanford & Waser, to be published) about each bond is given. The average values for the structural components are summarized in Table 5.

It is apparent from Fig. 4 and Table 5 that the addition of substituents to the ring produces a significant flattening of the ring. In particular, the decrease in the bond angles and the increase in the torsion angles should be noted.

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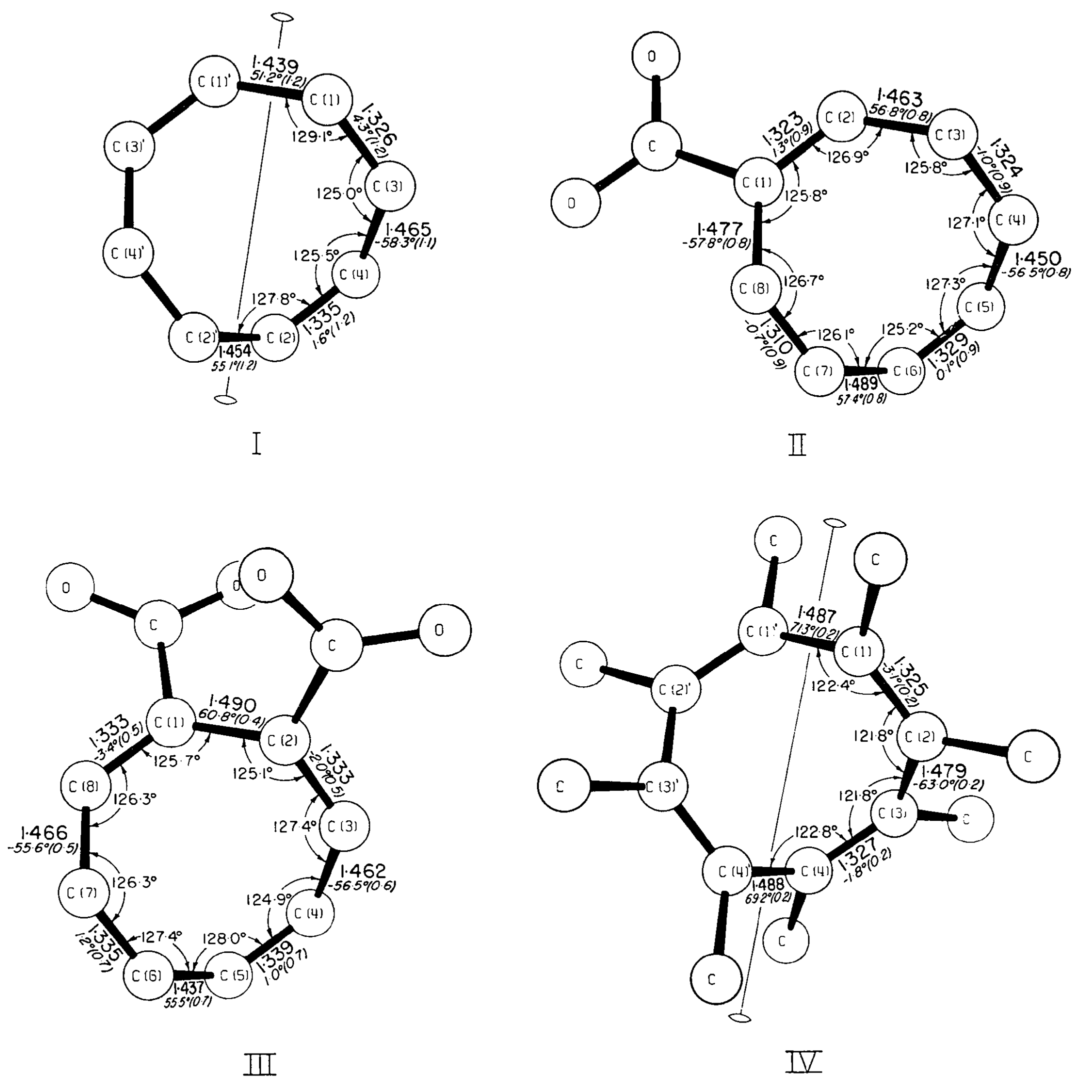

Fig. 4. Bond distances, bond angles, and torsion angles in the cyclooctatetraene rings of (I) cyclooctatetraene, (II) cyclooctatetraenecarboxylic acid, (III) calcium cyclooctatetraene-dicarboxylate and (IV) octamethylcyclooctatetraene. The standard deviations in the torsion angles are shown in parentheses.

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The Crystal and Molecular Structure of *N*-(1-methyl-3-oxo-butyliden)-*N*′-(1-methyl-2-isonitroso-3-oxobutyliden)ethylenediaminecopper(II), Cu(II) ($C_{12}H_{17}N_3O_3$)

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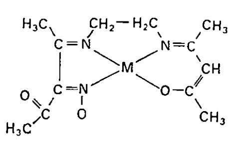
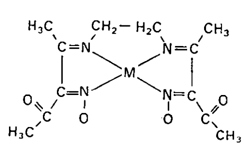
The crystal structure of *N*-(1-methyl-3-oxobutyliden)-*N*′-(1-methyl-2-isonitroso-3-oxobutyliden)ethylenediaminecopper(II), Cu(II) ($C_{12}H_{17}N_3O_3$), has been determined from 2538 independent reflexions, measured with Cu $K\alpha$ radiation by a single-crystal diffractometer and refined by the least-squares methods to $R = 5{\cdot}1$ %. The triclinic ($P\overline{1}$) unit cell of dimensions $a = 12{\cdot}11$ (1), $b = 8{\cdot}15$ (1), $c = 7{\cdot}92$ (1) Å, $\alpha = 102{\cdot}1$ (1)°, $\beta = 109{\cdot}6$ (1)°, $\gamma = 105{\cdot}6$ (1)°, contains two complex molecules, where copper coordinates to two oxygen [Cu–O(1) = 1·887 (6) Å, Cu–O(2) = 1·926 (13) Å] and two nitrogen atoms [Cu–N(1) = 1·937 (14) Å, Cu–N(2) = 1·937 (7) Å] in a planar arrangement. The nitric oxide does not behave as a free ligand, but interacts with the organic molecule forming an oxime group which coordinates to metal through oxygen.

Introduction

The reaction of nitric oxide with bis(acetylacetone)-ethylenediimine metal-complexes was studied by Masuda, Tamaki & Shinra (1969), who found, from spectroscopic evidence, that the nitric oxide does not coordinate to metal as a free ligand in complexes containing Ni(II), Cu(II) and Pd(II). On the contrary, the NO group interacts with the organic ligand giving complex compounds for which they suggest the structural formulae:



(I)



(II)

(I) obtained by partial reaction, (II) by complete reaction of NO. The conclusion reached by these authors is quite right as far as the direct coordination of NO to the metal is concerned, but the role of the nitrous group, as given in their formulae, is not convincing. Therefore, to define this point, an X-ray analysis of (I) with M = Cu(II) was undertaken, also in connexion with a general programme, in progress in this laboratory, concerning structures of metal complexes of polydentate ligands containing nitrogen.

Experimental

Dark red-violet crystals of the compound were prepared by treatment of bis(acetylacetone)ethylenediimine-Cu(II) with nitric oxide as described by Masuda, Tamaki & Shinra (1969). The crystals are flattened prisms elongated along [001] showing pleochroic effects: observed perpendicularly to the flattening, they appear red or pinky-yellow depending on whether the electric vector vibrates perpendicular or parallel to the elongation.

The unit-cell dimensions, determined from rotation and Weissenberg photographs and refined by an