The Crystal Structure of 1,4-Ethyleno-2,8-dihydroxy-2,4,6,8-tetramethyl-octahydronaphthal-5-en-3,7-dione

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The crystal structure of 1,4-ethyleno-2,8-dihydroxy-2,4,6,8-tetra-methyl-octahydronaphthal-5-en-3,7-dione, $C_{16}H_{20}O_4$, has been determined by three-dimensional single crystal X-ray diffraction methods. The monoclinic unit cell, $P2_1/c$, has lattice parameters $a = 8.470$, $b = 12.080$, $c = 14.995$ Å, $\beta = 108.69°$. The intensities of 2804 independent reflexions were measured by using the $\theta - 2\theta$ scan mode with a Siemens automatic diffractometer and monochromatized $CuK\alpha$ radiation. The structure was solved by direct methods and refined to an R value of 0.066 for 2076 observed independent reflexions.

The compound is a Diels-Alder dimer of 2,6-dimethyl-o-quinol obtained by periodate oxidation of 2,6-dimethylphenol. The rather strained structure has $C(sp^3) - C(sp^3)$ bond lengths of 1.589 and 1.554 Å, respectively, for the bonds $C(4) - C(4a)$ and $C(4a) - C(8a)$.

Oxidation of certain xylenols with sodium periodate results in the formation of o-quinols which undergo Diels-Alder dimerisation to yield substituted 1,4-ethylenonaphthalenes. Several isomeric dimers can arise but usually only one is observed. The steric orientation of these substituted 1,4-ethylenonaphthalenes have been discussed by Adler et al.[1,2] and structures have been proposed on the basis of chemical and spectral evidence as well as from considerations of steric requirements.

An X-ray analysis of the title compound has been undertaken as part of a program concerning crystal structure studies of Diels-Alder dimerisation of o-quinols.

EXPERIMENTAL

Crystal data from X-ray photographs and diffractometer measurements are summarized in Table 1. One molecule constitutes the asymmetric unit. Intensity data were collected on a Siemens four circle diffractometer with graphite-monochromatized $CuK\alpha$ radiation by a $\theta - 2\theta$ scan technique in which the scan width was 150 steps of 0.01° in

θ and 0.02° in 2θ, at 0.6 sec per step. The reflexions were measured twice. Stationary background counts were taken for 90 sec at each end of the scan. By this method 2804 reflexions were measured out to $\theta = 70°$. The net intensities, I_{net}, and their estimated standard deviations, $\sigma(I_{net})$, based on counter statistics, were calculated. Only the 2076 most significant reflexions with $\sigma(I_{net})/I_{net} \leq 0.25$ were used in the subsequent calculations. The data were corrected for Lorentz and polarization factors but no correction for absorption was made. Two irregular crystals of approximate volumes 0.011 mm^3 and 0.0053 mm^3 were mounted with the b axis coincident with the ϕ axis of the diffractometer. The crystals deteriorated in the X-ray beam during the data collection. Three monitor reflexions measured at intervals of 40 reflexions showed a deviation of about 15 % in intensity on both crystals. Individual reflexions were corrected for this loss by fitting a linear function of time to the intensity of the monitor reflexions.

Table 1. Crystallographic data (estimated standard deviations in parentheses).

Space group $P2_1/c$
$a = $ 8.470(5) Å
$b = $ 12.080(7) Å
$c = $ 14.995(6) Å
$\beta = 108.69(7)$ °
$Z = 4$

Graphite-monochromatized Cu$K\alpha$ radiation, 1.5418 Å.
Chemical formula $C_{16}H_{20}O_4$.
Calculated density 1.261 g cm^{-3}.

STRUCTURE DETERMINATION AND REFINEMENT

The absolute scale and the overall temperature factor for calculation of normalized structure factor magnitudes $|E|$ were estimated by Wilson's method.[3] The structure was solved by use of the MULTAN system.[4] Four combinations of signs of two reflexions as variables (in addition to three origin determining reflexions) were used to calculate probable phases for the 187 reflexions whose $|E|$ values were ≥ 1.90. The starting set of phases is given in Table 2. One combination of signs was better than the rest. This solution had a consistency index of 0.79. The E map of this best $|E|$ set yielded the coordinates of 17 out of the 20 non-hydrogen atoms in the asymmetric unit. The remaining three atoms were located from a difference Fourier synthesis. Introduction of anisotropic thermal parameters for all the non-hydrogen atoms

Table 2. Starting phase set.

h			$|E_h|$	Starting phase value	Correct phase value
2	3	-6	3.18	0	0
5	6	3	3.67	0	0
3	10	-6	3.12	0	0
9	5	-9	3.02	$0,\pi$	0
3	8	-7	3.27	$0,\pi$	0

Table 3. Observed and calculated structure amplitudes. The columns contain the index k, $10|F_o|$ and $10|F_c|$. The reflexions marked with an asterisk were not included in the refinement.

Table 3. Continued.

6	42	46
7	73	74
8	45	43
9	137	145
10	59	65
11	43	45
12	47	44
H=	6	L= -2
0	131	125
1	92	86
2	151	153
3	103	102
4	65	57
5	55	52
6	31	26
7	72	81
8	84	96
9	63	59
10	33	29
H=	7	L= -2
0	83	77
1	119	128
2	34	26
3	18	7
4	47	44
5	89	94
6	86	90
7	18	16
10	26	21
H=	8	L= -2
0	26	29
2	69	74
4	53	59
5	56	46
6	16	15
8	25	24
9	12	10
H=	9	L= -2
0	40	41
1	18	9
2	65	58
5	26	21
H=	10	L= -2
0	78	52
1	28	23
H=	1	L= -1
1	24	10
2	528	531
3	371	369
4	37	41
5	38	48
6	444	425
7	24	18
8	64	59
9	25	20
10	85	74
11	146	150
12	32	26
H=	2	L= -1
1	1137	1167
2	160	143
3	268	250
4	290	280
5	338	327
6	244	244
7	236	213
8	42	30
9	30	20
10	86	76
11	27	23
H=	3	L= -1
1	456	487
2	400	409
3	303	305
4	323	309
5	191	175
*6	32	0
7	28	27
8	63	66
9	43	41
10	84	85
11	74	87
12	43	38
14	11	10
H=	4	L= -1
1	144	152
2	40	43
3	296	294
4	196	190
6	50	42
7	87	81
8	105	115
9	64	69
H=	5	L= -1
1	198	214
2	252	261
3	41	38
4	36	38
5	156	155
6	68	61
7	61	57
8	41	38
9	69	73
11	28	19
H=	6	L= -1
1	118	127
2	64	55
3	156	160
4	224	218
5	77	71
6	111	119
8	43	45
10	25	14
H=	7	L= -1
1	106	107
2	137	125
3	113	111
4	101	88
6	24	28
7	31	33
8	32	33
9	39	38
10	14	12
H=	8	L= -1
2	72	67
7	45	33
8	77	69
H=	9	L= -1
1	54	45
2	39	32
3	23	18
4	59	52
6	34	28
H=	0	L= 0
2	294	264
4	269	247
6	289	273
8	175	151
10	43	33
12	81	87
H=	1	L= 0
0	533	548
1	950	993
2	975	1068
3	99	97
4	318	360
5	26	27
6	423	394
7	176	164
8	79	60
9	130	125
10	57	59
12	118	138
H=	2	L= 0
0	667	717
1	338	322
2	228	233
3	153	148
4	358	358
5	441	448
6	259	261
7	54	56
8	43	45
9	32	35
10	38	38
12	64	74
13	55	53
H=	3	L= 0
0	1015	1117
1	403	383
2	294	306
3	201	181
4	88	66
5	123	112
6	47	47
7	144	149
8	108	115
10	53	51
11	24	26
14	29	27
H=	4	L= 0
0	578	601
1	562	564
2	188	211
3	167	170
4	86	85
5	37	25
7	156	152
8	55	58
9	70	69
10	28	22
11	33	38
12	47	44
H=	5	L= 0
0	144	166
1	47	32
2	281	296
3	106	101
4	103	113
6	27	34
7	24	18
8	25	18
9	67	73
11	22	15
H=	6	L= 0
0	63	68
1	61	65
3	141	149
6	32	24
7	67	62
8	31	35
H=	7	L= 0
0	85	82
1	46	60
2	131	141
4	28	23
5	22	15
8	35	33
9	50	45
H=	8	L= 0
0	125	137
2	28	19
4	22	18
5	33	33
7	59	56
8	35	40
H=	9	L= 0
3	45	37
4	35	31
H=	0	L= 1
1	161	142
2	344	347
3	44	44
4	309	285
5	203	182
6	48	38
7	104	100
8	50	51
10	23	33
11	105	109
12	68	81
H=	1	L= 1
1	1008	1017
2	375	382
3	118	131
4	126	120
5	88	91
6	180	192
7	184	177
8	127	133
10	122	121
12	119	125
14	50	26
H=	2	L= 1
1	661	712
2	72	78
3	210	233
4	314	324
5	80	69
6	154	139
7	29	30
8	140	138
9	31	36
10	181	174
12	64	68
13	48	60
H=	3	L= 1
1	163	166
3	394	401
4	142	158
5	70	67
6	104	101
7	61	71
8	23	26
9	74	73
10	49	54
11	90	94
12	64	64
H=	4	L= 1
1	90	96
2	76	78
3	82	93
4	147	151
6	24	19
7	137	128
8	76	75
9	30	29
11	80	75
H=	5	L= 1
1	245	256
2	82	76
3	37	34
4	43	52
5	205	217
6	129	121
7	122	124
8	30	27
11	34	38
H=	6	L= 1
1	93	92
3	40	50
6	52	54
7	84	86
8	42	42
10	40	42
11	55	48
H=	7	L= 1
1	43	45
2	24	12
4	40	39
5	43	51
6	61	58
8	29	31
H=	8	L= 1
1	30	40
2	31	37
3	21	10
7	42	45
H=	9	L= 1
3	27	30
H=	0	L= 2
0	312	268
1	965	949
2	30	18
3	188	201
4	126	116
5	116	125
6	155	142
7	195	191
8	38	45
9	151	148
10	49	47
11	150	138
12	109	114
13	34	37
H=	1	L= 2
0	70	83
1	32	25
2	69	73
4	354	363
5	111	112
6	187	187
7	153	146
8	39	28
9	28	26
10	66	62
13	79	82
H=	2	L= 2
0	55	53
1	394	414
2	102	73
3	376	354
5	335	327
6	282	255
7	105	106
8	59	58
9	170	171
10	33	33
12	93	89
*14	37	1
H=	3	L= 2
0	437	414
1	512	534
2	29	23
3	85	99
4	146	131
5	49	48
7	32	28
9	118	108
12	52	45
13	15	18
H=	4	L= 2
0	268	283
1	223	250
2	81	71
3	74	85
5	60	59
6	66	68
7	110	115
8	55	55
9	72	74
10	42	33
12	25	28
13	36	47
H=	5	L= 2
0	66	58
1	108	107
2	32	28
3	99	97
4	99	108
5	127	139
6	124	126
7	87	84
8	57	64
9	27	28
10	40	38
11	38	39
12	31	28
H=	6	L= 2
2	121	118
3	70	70
4	90	98
5	45	46
6	37	41
7	22	24
8	45	41
11	30	31
H=	7	L= 2
0	34	30
1	99	101
2	29	31
6	22	19
H=	8	L= 2
0	70	75
4	28	19
5	35	33
7	21	14
H=	0	L= 3
2	443	451
3	846	847
4	290	272
5	159	170
6	77	69
7	75	92
8	182	179
9	121	130
11	131	127
12	27	25
H=	1	L= 3
1	109	120
2	326	328
3	449	421
4	105	95
5	285	272
6	135	123
7	32	31
8	45	43
9	54	57
10	58	50
11	40	42
12	21	24
13	37	35
H=	2	L= 3
1	55	45
2	452	441
3	434	432
4	121	114
5	63	52
6	24	28
7	60	72
8	69	75
9	58	59
10	98	90
11	48	48
12	54	62
14	21	26
H=	3	L= 3
1	62	68
3	104	95
4	118	130
5	49	48
6	31	27
7	82	75
8	105	114
9	114	108
11	135	140
13	27	21
H=	4	L= 3
1	124	121
2	71	59
3	151	156
4	185	188
5	220	216
6	65	66
7	171	174
8	84	78
9	43	36
10	67	73
11	27	31
12	12	12
H=	5	L= 3
1	49	44
2	93	90
3	80	81
4	126	114
6	279	279
7	27	26
8	28	27
9	53	59
10	101	101
11	71	66
H=	6	L= 3
1	70	62
2	38	39
4	88	88
5	30	27
6	79	80
7	30	33
8	38	42
9	36	38
10	26	21
H=	7	L= 3
2	67	81
3	42	47
6	51	58
8	48	52
9	23	25
H=	8	L= 3
1	28	31
5	23	13
6	81	66
H=	9	L= 3
1	30	23
H=	0	L= 4
0	113	134
1	89	88
2	519	500
3	444	434
4	127	128
5	40	43
6	75	74
7	90	82
8	85	71
9	151	153
11	54	54
12	44	49
H=	1	L= 4
0	53	56
1	43	43
2	209	203
3	87	96
4	82	55
5	85	81
6	144	132
8	137	141
9	188	181
10	171	173
11	28	25
12	80	78
H=	2	L= 4
0	433	423
1	80	69
2	204	168
3	248	249
4	19	14
5	165	169
6	32	36
7	183	178
8	127	130
9	42	43
10	48	41
12	47	46
13	17	17
H=	3	L= 4
0	397	380
1	348	346
2	165	158
3	130	142
4	242	242
6	58	55
7	89	82
9	106	99
10	44	52
11	38	36
12	32	31
13	99	85
H=	4	L= 4
0	222	216
1	68	51
3	146	137
4	83	81
6	201	211
7	42	39
8	81	82
10	53	54
11	65	62
12	71	69
H=	5	L= 4
0	152	149
1	49	51
2	60	55
3	86	87
4	93	97
5	84	80
7	132	135
8	123	121
9	48	43
11	23	22
H=	6	L= 4
1	31	30
2	74	68
5	58	60
6	64	73
7	35	29
9	21	19
10	64	64
H=	7	L= 4
0	75	70
1	106	109
6	36	34
7	43	39
H=	8	L= 4
0	22	21
1	26	22
5	23	24
H=	0	L= 5
1	209	193
2	391	373
3	577	534
4	295	291
6	193	190
7	130	123
8	177	162
9	120	113
11	27	30
12	26	28
13	46	47
H=	1	L= 5
1	139	137
2	101	84
3	162	171
5	50	31
6	85	83
7	106	103
8	178	169
9	77	77
10	60	59
11	83	83
H=	2	L= 5
1	20	7
2	197	181
4	138	132
5	189	191
7	31	27
8	54	57
9	74	86
10	98	104
11	32	36
H=	3	L= 5
1	60	47
2	104	101
3	201	190
4	228	224
5	24	18
6	25	24
7	52	52
8	127	135
9	45	43
10	36	37
11	31	32
12	34	33
H=	4	L= 5
1	71	72
2	142	154
3	146	145
4	169	168
5	51	46
6	138	129
7	64	61
8	43	47
9	36	35
10	70	64
12	39	44
H=	5	L= 5
2	24	16
3	35	34
4	99	108
5	143	142
7	24	26
H=	6	L= 5
7	65	68
9	18	17
H=	7	L= 5
1	43	43
3	21	23
4	25	19
5	44	41
7	30	30
H=	0	L= 6
0	521	529
1	304	309
2	125	120
3	681	655
4	167	155
5	288	243
6	38	40
8	24	31
9	98	99
11	34	39
13	65	68
H=	1	L= 6
0	145	146
1	29	21
2	166	183
3	185	177
4	299	275
5	33	42
6	161	169
7	24	26
8	49	39
9	168	165
10	35	38
11	39	50
13	21	18
H=	2	L= 6
0	93	102
1	187	192
2	241	226
3	66	57
4	77	76
5	111	106
6	87	93
8	132	126
9	172	176
10	121	126
11	37	40
12	25	28
13	12	19
H=	3	L= 6
0	44	39
2	119	112
3	190	203
4	94	90
6	77	75
7	22	32
9	76	24
10	84	92
12	73	72
H=	4	L= 6
0	92	92
1	76	73
2	44	39
3	52	46
5	41	48
6	114	116
8	54	51
9	22	14
11	48	52
H=	5	L= 6
0	89	97
1	71	72
3	45	39
4	71	72
5	57	55
6	25	25
7	59	67
8	50	51
9	62	59
10	36	37
H=	6	L= 6
0	85	94
1	25	14
2	42	45
5	26	26
6	27	30
7	23	26
8	29	26
H=	7	L= 6
2	27	25
3	21	20
6	41	45
H=	8	L= 6
0	25	24
2	19	18
H=	0	L= 7
1	186	184
2	94	93
3	35	29
5	119	104
6	103	99
7	178	184
8	236	231
9	52	45
H=	1	L= 7
1	483	465
2	134	135
3	100	91
5	147	151
6	112	113
7	93	90
8	71	65
9	152	153
10	90	101
11	25	26
13	10	8
H=	2	L= 7
1	27	30
2	229	215
3	134	121
4	28	25
5	42	35
6	62	67
7	81	87
8	86	75
11	39	33
*12	76	1
H=	3	L= 7
1	61	68
2	145	136
3	45	36
4	165	153
5	71	71
6	98	99
7	34	30
8	41	35
11	32	30
H=	4	L= 7
1	136	142
2	76	71
4	74	69
5	30	36
6	49	56
7	41	41
8	49	49
10	44	39
H=	5	L= 7
1	84	80
2	89	91
5	42	42
6	41	46
H=	6	L= 7
1	42	40
2	35	30
6	29	22
7	20	26
H=	7	L= 7
2	25	27
5	31	31
H=	0	L= 8
0	68	58
1	126	127
2	144	139
3	222	200
4	118	95
5	43	47
6	46	40
7	199	198
8	115	109
9	22	25
10	47	48
11	21	19
12	122	109
H=	1	L= 8
0	20	20
1	63	51
3	41	36
6	82	84
7	57	50
8	214	202
9	99	101
10	100	111
11	28	28
12	49	43
H=	2	L= 8
0	171	162
1	66	69
2	252	243
3	66	64
4	68	73
5	45	38
6	72	70
7	45	46
8	80	82
9	99	102
10	102	102
12	29	24
H=	3	L= 8
0	109	99
1	35	39
3	109	113
4	53	54
7	25	19
8	57	59
H=	4	L= 8
0	90	94
2	46	47
3	21	19
4	80	85
9	21	19
H=	5	L= 8
0	99	101
1	78	87
3	51	48
5	47	42
6	30	30
7	40	36
H=	6	L= 8
0	100	112
2	22	22
4	21	20
5	24	11
H=	7	L= 8
0	25	25
1	29	27
2	30	37
H=	0	L= 9
1	225	211
2	83	74
4	26	28
5	64	60
6	101	89
8	82	87
9	64	67
12	45	47
H=	1	L= 9
2	95	91
3	88	87
4	28	32
5	39	46
6	51	52
7	44	40
8	30	30
11	41	37
*12	73	10
H=	2	L= 9
1	52	52
2	225	233
3	95	96
4	87	74
5	76	79
6	86	87
8	59	61
10	38	36
H=	3	L= 9
2	185	186
3	33	30
4	200	207
6	119	126
8	45	44
9	57	60
H=	4	L= 9
1	89	99
2	128	133
3	45	50
4	58	72
H=	5	L= 9
2	43	39
3	46	54
5	51	44
6	27	30
8	20	21
H=	6	L= 9
1	55	48
2	35	30
3	33	30
4	42	40
5	42	45
H=	0	L= 10
0	241	233
1	151	149
2	109	118
3	77	78
4	53	52
5	183	181
7	38	36
8	81	84
10	27	30
11	48	46
12	19	13
H=	1	L= 10
0	57	53
1	139	140
2	66	70
3	34	34
4	165	155
6	29	30
7	21	13
8	82	84
9	66	74
10	50	54
11	20	20
H=	2	L= 10
0	73	74
3	41	38
4	106	103
5	52	57
7	30	29
8	45	41
9	36	32
10	19	22
H=	3	L= 10
0	134	130
1	124	124
2	37	37
3	93	95
4	30	35
6	39	41
9	34	33
H=	4	L= 10
0	81	75
1	71	78
2	38	35
3	64	71
4	52	51
5	25	24
8	22	23
H=	5	L= 10
0	43	46
1	43	36
2	48	40
3	46	42
6	23	18
H=	6	L= 10
0	39	41
1	34	32
2	21	15
3	40	40
H=	0	L= 11
1	142	143
2	118	114
4	82	74
5	56	57
9	27	32
11	12	9
H=	1	L= 11
1	45	46
2	160	154
3	84	80
6	121	124
8	35	39
10	30	29
H=	2	L= 11
1	220	207
2	54	47
3	85	82
4	124	129
5	128	131
6	76	80
7	29	28
10	21	17
H=	3	L= 11
1	42	39
2	43	47
3	98	106
4	22	16
5	66	72
9	18	20
H=	4	L= 11
1	25	20
2	32	26
3	65	62
4	42	43
5	23	18
7	27	20
H=	5	L= 11
1	84	77
2	64	61
3	30	25
5	37	40
H=	0	L= 12
0	431	431
2	66	61
4	71	66
5	32	28
6	61	63
8	50	54
9	34	32
H=	1	L= 12
0	93	98
1	138	133
2	34	37
4	24	20
5	58	56
7	47	45
8	59	61
10	23	26
H=	2	L= 12
0	96	91
1	79	82
3	55	63
4	20	20
7	32	33
9	17	13
H=	3	L= 12
0	102	111
1	22	23
2	52	52
3	45	55
4	25	19
6	25	24
7	19	17
H=	4	L= 12
0	66	61
3	23	18
5	60	56
6	19	22
H=	5	L= 12
0	26	17
1	34	34
2	33	31
H=	0	L= 13
1	78	70
2	44	44
6	29	29
8	62	60
H=	1	L= 13
1	42	45
2	59	60
3	34	30
4	21	21
5	42	46
6	72	65
7	44	47
8	26	27
9	16	18
H=	2	L= 13
1	43	45
2	46	47
3	32	29
4	56	50
5	23	21
7	38	37
H=	3	L= 13
1	26	22
2	35	35
H=	4	L= 13
2	51	51
3	16	17
H=	0	L= 14
1	85	91
4	40	40
6	51	48
7	21	25
8	39	40
H=	1	L= 14
2	27	29
3	27	24
4	29	28
5	39	37
6	27	27
7	49	45
H=	2	L= 14
3	34	33
H=	3	L= 14
1	27	23
H=	0	L= 15
1	49	48
3	34	35
4	79	75
5	41	37
6	68	63
H=	1	L= 15
2	44	42
3	48	47
4	60	59
5	81	77
6	66	61
H=	2	L= 15
1	19	19
3	31	35
H=	0	L= 16
1	57	61
2	42	45
3	24	25
4	32	35
5	105	99
H=	1	L= 16
0	60	60
1	19	17
H=	0	L= 17
1	27	31
2	24	25

into the fullmatrix least-squares refinement reduced R to 0.117. The scattering factors of Freeman[5] were used for all atoms except hydrogens for which the scattering factors were those of Stewart, Davidson and Simpson.[6] All 20 hydrogen atoms showed well defined peaks in a difference Fourier synthesis. The hydrogens, given fixed isotropic thermal parameters equal to those of their parent atoms, were included in the refinement. 2076 reflexions were used in the refinement and Hughes'[7] weighting procedure with $F_{o,min} = 1.5$ was applied. The R value reduced to 0.066.

RESULTS

Observed and calculated structure factors are presented in Table 3, atomic coordinates and thermal parameters in Tables 4 and 5 and bond distances and angles involving the non-hydrogen atoms in Tables 6 and 7. Correction for thermal motion was not applied in the calculation of bond lengths and

Table 4. Positional and anisotropic thermal parameters of the non-hydrogen atoms. The β-values refer to the temperature factor expression $\exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})\right]$. Estimated standard deviations are given in parentheses.

	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
C(1)	8992(4)	1867(2)	4475(2)	167(5)	51(2)	35(2)	2(4)	58(4)	8(3)
C(2)	9724(4)	3040(3)	4711(2)	180(5)	59(2)	40(2)	−15(5)	71(4)	−11(3)
C(3)	9523(4)	3603(3)	3759(2)	183(5)	54(2)	48(2)	−21(5)	93(4)	−11(3)
C(4)	8930(4)	2846(2)	2908(2)	195(5)	56(2)	39(2)	−25(5)	88(4)	−3(3)
C(4a)	7108(4)	2473(3)	2867(2)	156(5)	59(2)	45(2)	42(5)	48(4)	20(3)
C(5)	6504(4)	1664(4)	2067(3)	197(6)	121(4)	40(2)	−63(7)	32(5)	6(4)
C(6)	6203(4)	599(3)	2132(3)	170(6)	102(3)	58(2)	−50(6)	46(5)	−39(4)
C(7)	6296(4)	153(3)	3059(3)	153(5)	66(3)	66(2)	−33(5)	26(5)	−11(3)
C(8)	6079(4)	973(3)	3777(2)	161(5)	86(3)	53(2)	−46(6)	67(5)	11(3)
C(8a)	7158(4)	2015(3)	3844(2)	146(5)	57(2)	46(2)	11(4)	81(4)	−4(3)
C(9)	9983(4)	1294(3)	3929(2)	144(5)	58(2)	55(2)	28(5)	44(4)	−6(3)
C(10)	9980(4)	1805(3)	3152(2)	149(5)	73(2)	54(2)	3(5)	86(4)	−34(3)
C(11)	11552(5)	3046(4)	5324(3)	211(7)	89(3)	58(2)	−50(7)	47(6)	−19(4)
O(12)	8737(3)	3615(2)	5168(2)	260(5)	74(2)	57(2)	−49(4)	137(4)	−46(2)
O(13)	9757(4)	4580(2)	3695(2)	406(7)	57(2)	64(2)	−88(5)	152(5)	−15(2)
C(14)	8996(6)	3429(4)	2018(3)	332(9)	78(3)	49(2)	−64(8)	142(7)	−1(4)
C(15)	5818(8)	−189(5)	1310(4)	321(11)	159(6)	78(3)	−159(12)	80(9)	−97(7)
O(16)	6394(4)	−833(2)	3234(3)	334(7)	76(2)	100(2)	−38(6)	10(6)	−9(3)
C(17)	4239(5)	1303(4)	3468(4)	175(7)	131(4)	113(4)	−57(8)	150(8)	−28(6)
O(18)	6508(4)	462(3)	4677(2)	317(6)	122(3)	67(2)	−158(7)	112(5)	34(3)

angles. Conformationally significant least-squares planes are given in Table 8, and intermolecular distances shorter than 3.8 Å in Table 9. Fig. 1 shows the numbering convention and all bond lengths of the non-hydrogen atoms. Fig. 2 is a perspective view[8] of the molecule. Fig. 3 is a projection of the crystal structure along the b axis.

Table 5. Positional and isotropic thermal parameters of the hydrogen atoms, with estimated standard deviations in parentheses.

	$x \times 10^3$	$y \times 10^3$	$z \times 10^3$	$B \times 10^2 \; Å^2$
H(C1)	903(3)	155(3)	500(2)	273
H(C4a)	657(4)	302(3)	273(2)	336
H(C5)	634(4)	194(3)	150(3)	441
H1(C8)	381(6)	165(4)	289(3)	647
H2(C8)	413(6)	170(4)	397(3)	647
H3(C8)	350(4)	61(3)	352(2)	647
H(C8a)	672(4)	256(3)	409(2)	287
H(C9)	1054(4)	62(3)	414(2)	331
H(C10)	1055(4)	154(3)	276(2)	345
H1(C11)	1194(5)	382(3)	545(3)	467
H2(C11)	1167(5)	267(3)	589(3)	467
H3(C11)	1220(5)	260(3)	505(3)	467
H(O12)	924(5)	405(3)	547(3)	391
H1(C14)	881(4)	299(3)	154(3)	431
H2(C14)	1016(4)	385(3)	213(3)	431
H3(C14)	804(5)	392(3)	181(3)	431
H1(C15)	589(6)	27(4)	68(3)	678
H2(C15)	465(6)	−34(4)	118(3)	678
H3(C15)	658(6)	−74(4)	143(4)	678
H(O18)	624(5)	−18(4)	458(3)	544

Table 6. Bond distances (Å) involving the non-hydrogen atoms, with estimated standard deviations in parentheses.

C(1)−C(2)	1.542(4)	C(4a)−C(5)	1.505(4)
C(1)−C(8a)	1.549(4)	C(4a)−(8a)	1.554(4)
C(1)−C(9)	1.515(4)	C(5)−C(6)	1.321(5)
C(2)−C(3)	1.539(4)	C(6)−C(7)	1.470(4)
C(2)−C(11)	1.528(4)	C(6)−C(15)	1.507(6)
C(2)−O(12)	1.420(3)	C(7)−C(8)	1.517(4)
C(3)−C(4)	1.519(4)	C(7)−O(16)	1.217(4)
C(3)−O(13)	1.205(3)	C(8)−C(8a)	1.540(4)
C(4)−C(4a)	1.589(4)	C(8)−C(17)	1.531(5)
C(4)−C(10)	1.517(4)	C(8)−O(18)	1.420(4)
C(4)−C(14)	1.526(4)	C(9)−C(10)	1.318(4)

DISCUSSION

The structural and conformational features of the dimer are illustrated in Fig. 2. The result is in agreement with the stereochemical considerations discussed by Adler *et al.*[1] A review of the theory concerning Diels-Alder dimerisation, in conjunction with results from X-ray structure determinations, has been presented by Karlsson *et al.*[9] Most bond lengths in this structure are in agreement with usually observed values.[10] C(4)−C(4a) (1.589 Å) and C(4a)− C(8a) (1.554 Å) are, however, significantly longer (∼ 5σ and ∼ 13σ, respec-
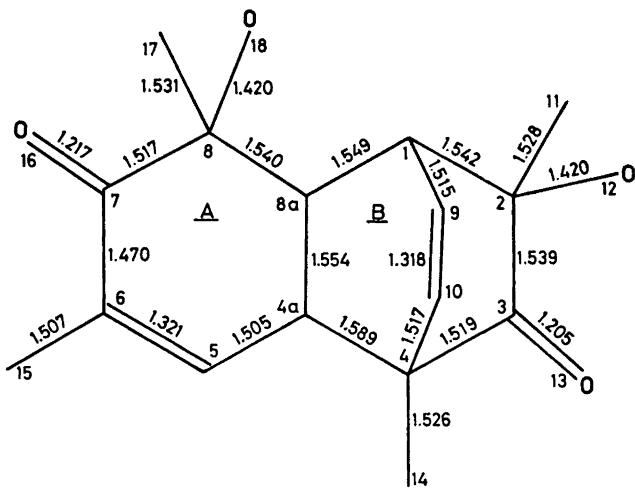
Fig. 1. Bond distances in the molecule

tively) than the average value, 1.536 Å, of the other $C(sp^3) - C(sp^3)$ bonds in the structure. This is probably due to internal strain in the molecule. Effects of conjugation are apparent in the $C(6) - C(7)$ bond adjacent to double bonds. The average value of the $C(sp^2) - C(sp^3)$ bonds is 1.517 Å; $\sim 4\sigma$ longer than the accepted value of 1.50 Å.[11] This can probably be explained by the fact that

Table 7. Bond angles (°) involving non-hydrogen atoms, with estimated standard deviations in parentheses.

C(2) − C(1) − C(8a)	106.6	(2)	C(5) − C(4a) − C(8a)	114.9	(3)
C(2) − C(1) − C(9)	107.0	(3)	C(4a) − C(5) − C(6)	126.7	(3)
C(8a) − C(1) − C(9)	110.1	(2)	C(5) − C(6) − C(7)	118.3	(3)
C(1) − C(2) − C(3)	106.1	(2)	C(5) − C(6) − C(15)	123.4	(4)
C(1) − C(2) − C(11)	113.5	(3)	C(7) − C(6) − C(15)	118.3	(4)
C(1) − C(2) − O(12)	107.7	(3)	C(6) − C(7) − C(8)	116.8	(3)
C(3) − C(2) − C(11)	110.2	(3)	C(6) − C(7) − O(16)	122.8	(3)
C(3) − C(2) − O(12)	108.9	(3)	C(8) − C(7) − O(16)	120.1	(3)
C(11) − C(2) − O(12)	110.3	(3)	C(7) − C(8) − C(8a)	112.1	(3)
C(2) − C(3) − C(4)	114.9	(3)	C(7) − C(8) − C(17)	107.3	(3)
C(2) − C(3) − O(13)	122.3	(3)	C(7) − C(8) − O(18)	109.8	(3)
C(4) − C(3) − O(13)	122.7	(3)	C(8a) − C(8) − C(17)	109.4	(3)
C(3) − C(4) − C(4a)	105.0	(3)	C(8a) − C(8) − O(18)	109.1	(3)
C(3) − C(4) − C(10)	106.6	(3)	C(17) − C(8) − O(18)	109.1	(3)
C(3) − C(4) − C(14)	111.2	(3)	C(1) − C(8a) − C(4a)	109.7	(2)
C(4a) − C(4) − C(10)	105.2	(2)	C(1) − C(8a) − C(8)	113.8	(3)
C(4a) − C(4) − C(14)	113.8	(3)	C(4a) − C(8a) − C(8)	113.1	(3)
C(10) − C(4) − C(14)	114.2	(3)	C(1) − C(9) − C(10)	114.8	(3)
C(4) − C(4a) − C(5)	107.1	(3)	C(4) − C(10) − C(9)	115.9	(3)
C(4) − C(4a) − C(8a)	109.3	(2)			

Table 8. Least-squares planes and deviations. The planes are described in terms of axes (m, n, p) having $m \parallel a^*$, $n \parallel b$ and $p \parallel c$. The atoms indicated with asterisks were omitted from the calculations of the least-squares planes. Deviation in Å.

Plane A[a]		Plane B1[b]		Plane B2[c]		Plane B3[d]	
Atom	Deviation	Atom	Deviation	Atom	Deviation	Atom	Deviation
C(4a)	0.035	C(1)*	0.786	C(1)*	−0.736	C(1)*	0.627
C(5)	−0.035	C(2)	0.048	C(2)	0.034	C(4)*	0.752
C(6)	0.015	C(3)	−0.048	C(3)	−0.035	C(4a)	−0.040
C(7)	0.004	C(4)*	0.735	C(4)*	−0.628	C(8a)	0.040
C(8)*	−0.575	C(4a)	0.048	C(9)	−0.040	C(9)	−0.047
C(8a)	−0.018	C(8a)	−0.048	C(10)	0.040	C(10)	0.047

[a] Plane A : $0.9584m - 0.2400n - 0.1545p = 4.3480$.
[b] Plane B1: $0.9911m + 0.1331n - 0.0004p = 8.1852$.
[c] Plane B2: $0.3899m + 0.8450n + 0.3660p = 5.6554$.
[d] Plane B3: $0.5878m - 0.7254n - 0.3582p = 0.2892$.

Table 9. Intermolecular distances (Å) shorter than 3.8 Å, with estimated standard deviations in parentheses.

	Code for symmetry related atoms.		
Superscript	Coordinates	Superscript	Coordinates
none	x, y, z	v	$2 - x, 1 - y, 1 - z$
i	$1 + x, y, z$	vi	$x, \frac{1}{2} - y, -\frac{1}{2} + z$
ii	$1 - x, -y, -z$	vii	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
iii	$1 - x, -y, 1 - z$	viii	$2 - x, \frac{1}{2} + y, \frac{1}{2} - z$
iv	$2 - x, -y, 1 - z$		

C(10) − C(17[i])	3.537(5)	C(11) − O(13[v])	3.559(4)
C(15) − C(15[ii])	3.754(10)	O(12) − O(13[v])	2.811(3)
C(17) − O(18[iii])	3.716(6)	C(14) − O(12[vi])	3.667(4)
O(18) − O(18[iii])	3.209(6)	C(14) − O(18[vi])	3.719(4)
C(9) − O(18[iv])	3.706(4)	C(4a) − O(16[vii])	3.547(4)
C(11) − O(16[iv])	3.529(5)	O(13) − C(15[viii])	3.761(7)
C(2) − O(13[v])	3.675(3)		

many of the bonds involve a highly substituted carbon atom. The C−H bond distances range from 0.73 to 1.11 Å, mean value 0.92 Å, in good agreement with values found in some precisely determined X-ray structures.[6] The best plane for the ring A (Fig. 1) contains the atoms C(4a), C(5), C(6), C(7), and C(8a) which are coplanar within ± 0.035 Å. Atom C(8) deviates by 0.575 Å from the plane (Table 8). The rather strained ring system B consists of three boat-shaped rings, for which least-squares planes and deviations are given in Table 8. The A ring and the B ring system are connected in accordance with the *endo* rule.[12]
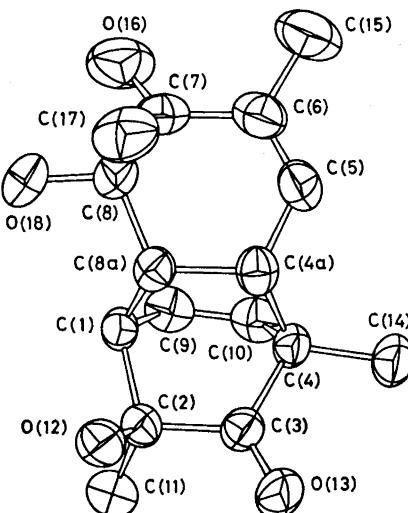
Fig. 2. A perspective view of the molecule.

An interaction, within the range of a possible intramolecular hydrogen bond, is observed between the hydroxyl group (18) and the ketone (16). The O(16)···H(O18) and O(16)···O(18) distances are 2.211 and 2.646 Å, respectively, and the O(16)···H(O18) − O(18) angle is 113.9°. The packing arrangement of the crystal viewed along the b axis is shown in Fig. 3. Those pairs of molecules related to each other by centers of symmetry at 0,0,0 and 0,$\frac{1}{2}$,$\frac{1}{2}$ form hydrogen bonded dimers. The O(13^v)···H(O12) distance is 2.091 Å and the O(12) − H(O12)···O(13^v) angle is 169.4°. The intermolecular distances between the hydrogen bonded dimers are all longer than the sum of the van der Waals radii as shown in Table 9.
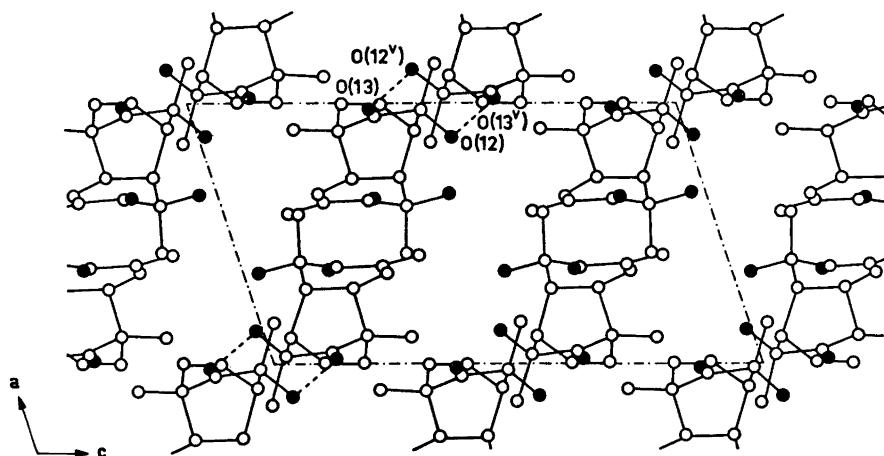
Fig. 3. Projection of the unit cell looking down the b axis. The dotted lines are hydrogen bonds. ○ carbon; ● oxygen.

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