Acta Cryst. (1971). B27, 1073

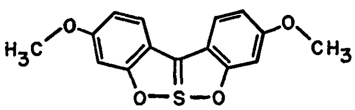
The Crystal Structure of an Oxygen Analogue of a Thiathiaphthene, $C_{15}H_{12}SO_4$

By Richard D. Gilardi and Isabella L. Karle

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C., 20390, *U.S.A.*

(*Received* 15 *June* 1970)

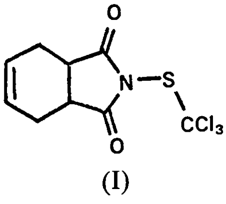
A colorimetric determination for residues of the fungicide, Captan, is based on the production of a stable red pigment of previously unknown structure. The X-ray diffraction analysis of a methoxy derivative of this pigment ($C_{15}H_{12}SO_4$) has revealed its molecular structure,



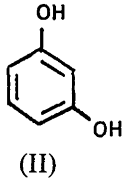
The molecule has a twofold symmetry axis (not required by the space group) and is almost planar. Unusual features in the bonding are a planar sulfur environment, an almost linear[176·1 (±1)°] oxygen–sulfur–oxygen arrangement, and extremely long [1·879 (±2)Å] sulfur–oxygen bonds. The heterocyclic nucleus of this compound has not been previously reported, but is related to the classes of polysulfur compounds known as thiathiaphthenes and thiafurophthenes. The derivative studied forms yellow crystals in space group $P2_1/c$, with cell parameters $a = 4{\cdot}005\ (\pm 5)$, $b = 24{\cdot}32\ (\pm 3)$, $c = 13{\cdot}64\ (\pm 2)$ Å, $\beta = 107{\cdot}05\ (\pm 5)$, $Z = 4$ and a density of 1·503 g.cm^{-3}. The 2190 X-ray diffraction intensities were measured with an automatic diffractometer and refined to an agreement factor, R, of 5·0%. The structure was solved using the symbolic addition procedure for phase determination.

Introduction

The fusion of *N*-trichloromethylthio-4-cyclohexene-1,2-dicarboximide (Captan, I) with resorcinol (II) produces an intense red pigment. Captan is a common agricultural fungicide and this fusion reaction provides a colorimetric method for determining its residue on foods (Kittleson, 1952). The chromogenic product was reported to be very stable at the time of its discovery, but was not at that time isolated and characterized. The pigment was recently isolated and partially characterized by non-crystallographic means (Pomerantz, Miller, Lustig, Mastbrook, Hansen, Barron, Oates & Chen, 1969). A dimethylated derivative of the pigment, obtained by treatment with diazomethane, provided well-formed yellow crystals for a crystallographic investigation. The diffraction analysis was undertaken with no preliminary hypotheses concerning the possible structural arrangement. The resultant structure (Fig. 1) displayed a unique planar fused ring system consisting of two phenyl rings bridged by a pair of unusual five-membered heterocyclic rings.



(I)



(II)

Experimental

The crystals used for the X-ray measurements were obtained from Dr I. Pomerantz of the Food and Drug Administration. They were yellow elongated prisms with well-formed faces. Precession and Weissenberg photographs indicated that the crystal was monoclinic. The systematic absences, $h0l$ with l odd and $0k0$ with k odd, fixed the space group to be $P2_1/c$. Cell constants and other physical data are in Table 1.

Table 1. *Physical data*

Molecular formula	$C_{15}H_{12}SO_4$
Molecular weight	288·32
Habit	Acicular prism
Crystal size	1·0 × 0·14 × 0·24 mm ($a \times b \times c$)
Space group	$P2_1/c$
a	4·005 ± 0·005 Å
b	24·32 ± 0·03
c	13·64 ± 0·02
β	107·05 ± 0·05°
Volume	1270 Å^3
Density (calc.)	1·503 g.cm^{-3}
Radiation	Cu $K\alpha$ (1·54178 Å)
Number of independent reflections	2190
Molecules per unit cell	4
Linear absorption coefficient	23 cm^{-1}

Integrated intensities for the reflections were collected on a four-circle automatic diffractometer using the θ, 2θ scan technique with a $2{\cdot}0° + 2\theta(\alpha_2) - 2\theta(\alpha_1)$ scan over 2θ. Lorentz and polarization corrections were

Table 2. *Observed and calculated structure factors for* $C_{15}H_{12}SO_4$

The columns are the index l, $|F_o| \times 10$, and $F_c \times 10$. Asterisks indicate those reflections omitted from final refinement (see text).

0	0	L
* 2	677	784
4	479	508
* 6	797	-848
8	235	-243
10	78	86
12	171	157
14	97	98
0	1	L
1	407	-421
2	624	707
3	107	109
4	500	-532
5	86	73
6	260	-257
7	389	399
8	145	-137
9	205	208
10	54	47
11	161	157
12	219	212
13	59	63
14	35	30
15	150	-153
0	2	L
0	517	-567
1	108	-114
* 2	830	-970
* 3	823	909
4	350	369
5	107	107
6	25	21
7	404	417
8	367	383
9	84	-91
10	50	-48
11	38	-37
12	275	-272
13	73	74
14	164	-161
15	26	-19
0	3	L
1	341	386
2	488	551
3	508	539
4	485	519
5	447	-467
6	350	-355
7	487	-511
8	343	-337
9	338	-340
10	9	8
11	389	-397
12	79	75
13	66	63
14	44	-46
15	139	139
0	4	L
0	372	-431
1	443	-495
2	392	-413
3	116	-122
4	75	69
5	135	-138
6	86	80
7	29	-22
8	11	6
9	308	312
10	152	150
11	325	324
12	228	224
13	54	53
14	42	36
15	79	77
0	5	L
1	129	-133
2	58	56
3	180	178
4	441	458
5	640	668
6	238	223
7	369	380
8	217	215
9	58	47
10	165	-156
11	116	116
12	131	-121
13	42	-39
14	125	-126
15	62	-65
0	6	L
0	16	-5
1	183	182
2	379	-397
3	278	-290
4	196	190
5	145	-138
6	132	-130
7	164	151
8	225	-225
9	72	-71
10	273	-274
11	103	-99
12	63	-66
13	25	-27
14	130	128
15	6	-1
0	7	L
1	184	-193
2	133	-140
3	102	-103
4	236	-246
5	247	-235
6	25	-18
7	240	-232
8	145	127
9	23	21
10	219	233
11	76	76
12	251	247
13	39	30
14	136	135
0	8	L
0	162	-170
1	186	-185
2	274	-283
3	132	145
4	113	-103
5	265	269
6	272	-258
7	252	254
8	244	241
9	237	-242
10	43	45
11	320	-316
12	145	145
13	197	-192
14	78	-72
0	9	L
1	174	177
2	152	-148
3	486	-496
4	72	56
5	68	-71
6	121	-118
7	281	-287
8	53	59
9	89	74
10	32	18
11	157	-154
12	26	21
13	49	46
14	37	33
0	10	L
0	455	-450
1	117	-117
2	104	97
3	141	-142
4	278	272
5	370	-396
6	182	174
7	20	-20
8	94	92
9	127	-119
10	239	-241
11	204	199
12	0	-14
13	51	45
14	81	-82
0	11	L
1	179	-184
2	188	-173
3	475	-494
4	511	540
5	88	-87
6	84	-86
7	107	105
8	158	164
9	397	407
10	347	-368
11	92	92
12	179	-182
13	77	-78
14	166	-168
0	12	L
* 0	778	856
1	24	-15
2	496	527
3	148	137
4	71	-66
5	269	-254
6	267	-259
7	43	32
8	194	-194
9	24	-13
10	35	-19
11	303	303
12	100	101
13	82	-81
0	13	L
1	136	170
2	278	-289
3	179	166
4	189	-200
5	181	181
6	338	-343
7	142	136
8	40	32
9	103	-100
10	66	-61
11	101	106
12	107	107
13	46	-44
0	14	L
0	614	-638
1	274	267
2	269	-266
3	487	522
4	126	-123
5	72	75
6	241	242
7	134	137
8	235	230
9	195	-196
10	125	122
11	40	-40
12	97	-97
13	27	-26
0	15	L
1	288	299
2	170	163
3	303	311
4	62	63
5	177	-178
6	64	-68
7	326	-330
8	67	-68
9	241	-258
10	17	14
11	142	-144
12	7	-7
13	38	38
0	16	L
0	285	-292
1	252	-243
2	87	82
3	180	-180
4	3	-1
5	203	-200
6	5	-2
7	153	-154
8	48	-50
9	49	46
10	23	24
11	142	139
12	61	56
0	17	L
1	167	-162
2	20	-16
3	16	24
4	295	301
5	450	468
6	242	242
7	319	322
8	126	125
9	89	109
10	23	-17
11	17	-10
12	100	-101
0	18	L
0	313	319
1	7	5
2	126	122
3	71	69
4	104	105
5	24	-23
6	110	101
7	77	68
8	135	-137
9	68	-65
10	78	-80
11	73	-73
0	19	L
1	130	-130
2	228	-226
3	80	-81
4	382	-394
5	185	-179
6	7	20
7	94	-89
8	170	165
9	53	-54
10	47	72
11	66	65
0	20	L
0	33	30
1	186	-181
2	28	36
3	193	198
4	216	-217
5	80	72
6	204	-202
7	226	226
8	107	105
9	34	26
10	63	68
11	106	-104
0	21	L
1	32	-33
2	178	175
3	11	1
4	134	134
5	86	-72
6	20	23
7	51	-48
8	170	-176
9	36	-36
10	17	12
0	22	L
0	82	-79
1	257	-259
2	128	128
3	46	-45
4	97	-100
5	154	-153
6	162	162
7	75	-62
8	12	11
9	80	79
0	23	L
1	71	73
2	216	217
3	116	-113
4	64	63
5	34	29
6	26	28
7	34	29
8	80	-82
9	60	64
0	24	L
0	222	-221
1	87	88
2	58	57
3	45	44
4	88	-81
5	20	21
6	20	-9
7	17	16
8	128	-131
0	25	L
1	59	-69
2	89	-89
3	44	36
4	165	-162
5	12	12
6	79	-76
7	17	17
0	26	L
0	167	-163
1	18	13
2	77	-72
3	33	33
4	18	19
5	64	65
6	74	72
0	27	L
1	133	139
2	21	14
3	49	50
4	7	11
5	47	-44
0	28	L
0	10	8
1	83	-77
2	37	29
3	102	-106
1	0	L
-16	46	-47
-14	232	-232
-12	335	-348
-10	134	-125
-8	238	-218
-6	643	701
-4	557	607
-2	278	282
* 0	728	-910
2	356	-351
4	633	-645
6	115	106
8	266	-271
10	385	-405
12	97	96
14	47	-45
1	1	L
-16	102	-102
-15	105	104
-14	41	-36
-13	77	77
-12	4	-4
-11	40	40
-10	436	465
-9	75	67
-8	418	423
-7	204	-209
-6	29	-18
-5	287	306
-4	249	-250
* -3	1111	-1226
* -2	861	-900
-1	427	-423
0	626	-683
1	567	-570
2	123	117
3	461	454
4	221	209
5	147	133
6	262	274
7	56	-49
8	312	320
9	217	-209
10	146	-141
11	45	-39
12	236	-239
13	60	-65
14	85	-82
1	2	L
-16	34	-33
-15	63	66
-14	246	254
-13	65	-63
-12	225	223
-11	216	-217
-10	37	39
-9	510	-547
-8	125	116
-7	307	-312
-6	86	-94
-5	35	-29
-4	460	484
* -3	1485	1862
* -2	845	895
-1	105	101
0	58	37
1	400	391
2	312	333
3	183	-169
4	130	125
5	71	45
6	7	-8
7	102	105
8	82	84
9	119	-124
10	60	53
11	14	-2
12	23	-11
13	111	111
14	0	5
1	3	L
-15	55	-53
-14	128	126
-13	136	-135
-12	211	215
-11	90	-90
-10	62	63
-9	196	183
-8	298	-279
-7	227	232
-6	29	31
-5	397	441
-4	115	116
-3	327	345
* -2	1137	1302
* -1	1236	1502
0	587	623
1	473	-488
2	397	-402
3	171	155
4	373	-368
5	489	-494
6	75	-61
7	60	52
8	21	20
9	275	275
10	111	107
11	185	177
12	118	-119
13	109	107
1	4	L
-15	162	-163
-14	35	34
-13	21	-10
-12	134	131
-11	137	140
-10	28	31
-9	219	220
-8	34	32
-7	389	413
-6	382	-416
-5	0	5
-4	342	-371
-3	425	-444
* -2	945	-1049
-1	408	-436
0	116	105
1	121	-109
2	60	-51
3	219	197
4	177	171
5	649	664
6	89	85
7	371	370
8	18	-21
9	168	165
10	91	-84
11	76	76
12	77	-75
13	185	-180
1	5	L
-15	82	-84
-14	183	-187
-13	29	-23
-12	107	-103
-11	30	25
-10	19	8
-9	20	23
-8	265	-260
-7	325	-338
-6	46	-47
-5	54	-54
-4	219	-223
-3	315	-326
-2	339	367
-1	430	461
0	401	419
1	269	282
2	396	411
3	145	-126
4	8	-7
5	321	-300
6	119	-121
7	37	-37
8	371	-386
9	165	-160
10	196	-197
11	104	-103
12	32	30
13	87	-81
1	6	L
-15	83	85
-14	147	-146
-13	11	12
-12	279	-285
-11	154	-150
-10	49	47
-9	31	27
-8	51	-47
-7	42	-26
-6	79	-69
-5	163	159
-4	130	-120
-3	78	75
-2	102	-99
-1	64	-61
0	70	57
1	278	272
2	443	-452
3	226	214
4	532	-560
5	418	-424
6	197	-189
7	127	-118
8	308	312
9	167	-169
10	240	237
11	42	37
12	215	213
13	55	59
1	7	L
-15	42	39
-14	58	57
-13	152	148
-12	76	-74
-11	106	-105
-10	230	231
-9	24	20
-8	93	90
-7	65	-70
-6	255	264
-5	73	-71
-4	189	-189
-3	61	55
-2	78	-91
-1	106	-103
0	75	-80
1	111	104
2	50	-47
3	604	618
4	179	180
5	235	218
6	245	249
7	132	132
8	479	514
9	83	-80
10	279	282
11	85	-85
12	26	-27
13	48	-47
1	8	L
-15	110	113
-14	26	22
-13	140	139
-12	77	-79
-11	25	-15
-10	143	140
-9	189	-188
-8	44	36
-7	161	157
-6	227	220
-5	113	-107
-4	321	-342
-3	325	333
-2	172	-175
-1	50	56
0	116	108
1	78	77
2	248	252
3	366	362
4	442	447
5	232	-239
6	130	127
7	253	-248
8	67	-70
9	403	-410
10	75	-73
11	20	18
12	102	-102
13	39	36
1	9	L
-15	94	-99
-14	15	-22
-13	76	-77
-12	273	-281
-11	24	-12
-10	61	-61
-9	179	-177
-8	75	-75
-7	41	38
-6	274	268
-5	54	57
-4	193	-195
-3	205	201
-2	259	-265
-1	158	142
0	36	28
* 1	692	-700
2	150	135
3	228	-223
4	42	-30
5	283	-286
6	52	-53
7	304	304
8	153	-151
9	81	80
10	66	56
11	288	284
12	0	-7
13	83	90
1	10	L
-15	40	-45
-14	178	185
-13	80	-83
-12	8	15
-11	206	206
-10	82	-86
-9	15	7
-8	302	-302
-7	154	149
-6	61	53
-5	205	-201
-4	168	164
-3	312	-312
-2	322	319
-1	500	-551
0	398	414
1	411	-415
2	362	359
3	161	-147
4	142	152
5	21	-12
6	86	-96
7	305	303
8	219	-209
9	160	155
10	72	73
11	18	17
12	50	-46
13	125	-123
1	11	L
-14	108	109
-13	109	109
-12	108	103
-11	113	106
-10	80	-75
-9	59	53
-8	305	-317
-7	140	-143
-6	173	-160
-5	236	-236
-4	32	27
-3	71	-75
-2	337	348
-1	388	-402
0	22	-17
1	254	-238
2	88	75
3	236	228
4	406	-413
5	195	198
6	20	9
7	251	246
8	396	-409
9	131	-126
10	34	37
11	113	-113
12	0	3
1	12	L
-14	166	-173
-13	133	-133
-12	212	-211
-11	34	35
-10	23	-24
-9	51	-55
-8	81	81
-7	160	151
-6	356	376
-5	251	-259
-4	218	233
-3	12	-8
-2	90	-75
-1	277	272
0	264	-251
1	87	79
2	289	-296
3	101	97
4	155	-158
5	96	-96
6	129	-130
7	13	-18
8	32	25
9	120	116
10	18	10
11	58	57
12	129	126
1	13	L
-14	37	42
-13	124	124
-12	76	77
-11	75	-73
-10	285	294
-9	87	-86
-8	249	251
-7	183	-183
-6	78	81
-5	66	58
-4	142	-152
-3	25	-10
-2	289	-300
-1	134	-132
0	545	-565
1	372	-362
2	20	-17
3	44	-55
4	45	50
5	126	131
6	312	320
7	210	-216
8	51	-45
9	152	-155
10	24	-27
11	90	-94
12	136	-138
1	14	L
-14	40	40
-13	37	-37
-12	197	204
-11	19	8
-10	113	109
-9	252	-257
-8	85	85
-7	266	-273
-6	105	-107
-5	155	-157
-4	298	-302
-3	410	434
-2	52	-52
-1	178	181
0	54	28
1	107	-99
2	24	-16
3	130	-119
4	162	157
5	228	-227
6	70	70
7	156	161
8	127	129
9	28	-25
10	79	-74
11	31	-35
12	56	-57
1	15	L
-13	126	-132
-12	109	-112
-11	132	-130
-10	74	-69
-9	212	209
-8	291	-292
-7	391	407
-6	48	42
-5	334	350
-4	103	98
-3	387	406
-2	217	206
-1	191	190
0	100	92
1	40	27
2	54	-57
3	189	-184
4	206	-209
5	121	-117
6	75	-75
7	104	-101
8	9	2
9	207	215
10	41	41
11	111	112
1	16	L
-13	19	26
-12	117	123
-11	183	185
-10	0	-8
-9	167	171
-8	25	26
-7	226	219
-6	225	-224
-5	50	55
-4	204	-202
-3	240	-240
-2	28	-40
-1	87	-80
0	57	-57
1	227	-226
2	126	120
3	61	61
4	50	54
5	205	207
6	36	-36
7	164	159
8	23	-21
9	18	-9
10	30	-33
11	10	13
1	17	L
-12	65	-68
-11	152	155
-10	119	-119
-9	31	33
-8	46	-40
-7	232	-240
-6	166	166
-5	299	-305
-4	95	-95
-3	235	-230
-2	133	137
-1	90	93
0	39	35
1	266	268
2	217	224
3	183	-183
4	154	157
5	160	-161
6	88	92
7	68	-70
8	114	-116
9	113	-111
10	11	11
1	18	L
-12	86	-89
-11	82	-81
-10	50	-55
-9	30	32
-8	95	-92
-7	58	-55
-6	205	216
-5	44	40
-4	177	178
-3	27	-18
-2	198	196
-1	96	96
0	156	-157
1	225	220
2	262	-260
3	22	18
4	395	-425
5	220	-220
6	63	-55
7	172	-176
8	32	32
9	0	-9
10	76	75
1	19	L
-12	23	-16
-11	8	-7
-10	122	127
-9	27	34
-8	108	99
-7	51	54
-6	57	58
-5	30	-31
-4	55	-54
-3	94	-95
-2	12	6
-1	255	-252
0	228	-227
1	135	129
2	201	196
3	117	115
4	34	-38
5	249	252
6	80	84
7	5	1
8	132	131
9	23	21
10	54	57
1	20	L
-11	39	-45
-10	36	40
-9	4	2
-8	46	36
-7	62	63
-6	24	-14
-5	23	-22
-4	71	-68
-3	61	54
-2	245	253
-1	80	-84
0	25	19
1	256	257
2	250	245
3	125	118
4	325	323
5	78	80
6	86	88
7	108	-113
8	9	-9
9	125	-119
1	21	L
-10	11	-13
-9	54	-58
-8	10	-16
-7	153	156
-6	112	110
-5	112	113
-4	130	-131
-3	118	122
-2	146	147
-1	212	-214
0	92	90
1	153	-151
2	0	-2
3	179	-170
4	7	-13
5	13	-5
6	61	-64
7	54	-53
8	52	-45
1	22	L
-10	122	-119
-9	80	-82
-8	123	-122
-7	17	11
-6	74	-73
-5	88	86
-4	73	68
-3	95	99
-2	141	-148
-1	142	-127
0	9	4
1	166	-160
2	86	-84
3	200	-195
4	17	17
5	202	204
6	50	43
7	139	136
8	60	-58
1	23	L
-9	64	-64
-8	115	-116
-7	107	-107
-6	126	-121
-5	172	-176
-4	32	-30
-3	39	-41
-2	158	162
-1	32	-30
0	35	34
1	178	176
2	11	13
3	50	49
4	154	-154
5	93	87
6	70	-76
7	26	27
1	24	L
-8	95	99
-7	84	-86
-6	34	39
-5	60	57
-4	89	89
-3	57	-58
-2	67	-79
-1	8	-9
0	25	-16
1	31	24
2	86	-82
3	49	51
4	55	-46
5	16	3
6	44	-45
1	25	L
-7	16	18
-6	11	6
-5	55	-57
-4	27	-23
-3	196	196
-2	17	-11
-1	93	94
0	170	-168
1	100	94
2	50	-51
3	16	-16
4	23	18
5	15	-12
1	26	L
-6	76	-79
-5	0	3
-4	208	-207
-3	31	-32
-2	36	-36
-1	108	113
0	66	63
1	0	3
2	80	86
3	25	-28
4	64	62
1	27	L
-5	79	82
-4	38	-38
-3	64	57
-2	55	-55
-1	73	-75
0	38	37
1	67	-67
2	9	0
3	83	-88
1	28	L
-2	8	-7
-1	135	-138
0	35	34
2	0	L
-14	15	-20
-12	251	247
-10	432	445
-8	264	260
-6	46	-48
-4	28	-24
-2	73	-68
0	60	53
2	271	252
4	90	-94
6	317	322
8	150	144
10	44	45
2	1	L
-15	55	54
-14	213	214
-13	15	-19
-12	93	93
-11	17	-3
-10	47	44
-9	50	-50
-8	46	39
-7	195	-195
-6	243	-238
-5	269	-258
-4	89	-83
-3	55	44
-2	78	70
-1	146	137
0	31	-14
1	174	152
2	260	236
3	189	-177
4	16	-0
5	216	-215
6	45	-46
7	29	33
8	80	80
9	114	111
10	110	-111
11	76	70
2	2	L
-15	178	-181
-14	17	6
-13	137	-135
-12	208	-209
-11	160	-159
-10	226	-223
-9	187	177
-8	117	-110
-7	269	260
-6	299	291
-5	297	291
-4	109	-105
-3	72	-63
-2	242	232
-1	34	-28
0	309	-314
1	115	-111
2	165	-147
3	142	125
4	222	-220
5	136	-139
6	253	-257
7	111	-113
8	167	-166
9	205	213
10	49	48
11	120	121
2	3	L
-15	124	-125
-14	31	30
-13	52	48
-12	61	56
-11	203	204
-10	22	19
-9	127	121
-8	112	109
-7	78	76
-6	148	-138
-5	309	-307
-4	245	-227
-3	325	-328
-2	391	-393
-1	327	-336
0	182	173
1	284	-286
2	48	44
3	9	6
4	115	-106
5	283	284
6	257	-260
7	118	122
8	346	-357
9	81	-82
10	80	-82
11	97	-97
2	4	L
-15	88	84
-14	46	48
-13	26	-19
-12	103	-99
-11	184	180
-10	16	9
-9	73	-73
-8	284	-281
-7	169	161
-6	264	253
-5	209	-195
-4	401	-401
-3	382	-384
-2	66	-50
-1	135	135
0	154	-143
1	237	228
2	399	381
3	244	240
4	42	35
5	69	71
6	27	16
7	22	15
8	151	-142
9	100	-96
10	15	-11
11	101	-103
2	5	L
-15	88	89
-14	69	66
-13	128	-128
-12	82	-81
-11	101	-93
-10	130	-123
-9	90	-89
-8	99	98
-7	161	152
-6	325	312
* -5	694	734
* -4	1010	1096
-3	466	487
-2	67	-59
-1	294	294
0	289	-269
1	36	16
2	465	-450
3	19	-14
4	207	-208
5	150	-152
6	243	255
7	39	-39
8	113	112
9	118	-119
10	149	172
11	104	101
2	6	L
-15	116	119
-14	100	100
-13	97	-93
-12	197	195
-11	142	139
-10	163	157
-9	60	-59
-8	56	58
-7	200	196
-6	196	-175
-5	229	-216
-4	142	-135
-3	240	237
-2	27	12
-1	72	60
0	591	-597
1	92	74
2	258	247
3	43	-42
4	152	155
5	181	-177
6	508	547
7	79	-72
8	198	202
9	28	23
10	12	-3
11	72	-72
2	7	L
-15	126	130
-14	13	0
-13	14	-12
-12	160	159
-11	108	-101
-10	21	20
-9	147	-138
-8	16	-6
-7	19	-8
-6	448	-461
-5	183	176
-4	411	-406
-3	92	87
-2	26	-16
-1	227	230
0	28	-0
1	49	44
2	352	350
3	130	132
4	150	148
5	105	-110
6	132	177
7	229	-222
8	214	-216
9	18	17
10	114	-115
11	24	-15
2	8	L
-15	92	-96
-14	139	-140
-13	45	-40
-12	9	-6
-11	22	21
-10	131	-127
-9	161	-154
-8	38	-35
-7	97	96
-6	43	-38
-5	72	-57
-4	172	166
-3	184	172
-2	415	442
-1	147	-137
0	208	201
1	394	-408
2	21	-19
3	461	-479
4	313	-318
5	52	-49
6	141	-140
7	171	-171
8	128	-128
10	34	28
11	55	58
2	9	L
-15	58	-58
-14	77	-77
-13	0	-5
-12	48	-47
-11	180	183
-10	97	-94
-9	99	95
-8	5	-8
-7	78	81
-6	25	-23
-5	190	-180
-4	249	235
-3	462	-472
-2	294	290
-1	358	-362
0	112	101
1	48	40
2	44	-38
3	40	39
4	177	-177
5	419	454
6	184	184
7	161	157
8	146	148
9	71	64
10	99	97
11	67	-67
2	10	L
-14	18	-18
-13	99	102
-12	87	-82
-11	199	198
-10	58	-49
-9	35	26
-8	84	84
-7	196	-192
-6	127	123
-5	188	-187
-4	106	110
-3	27	-24
-2	213	204
-1	17	26
0	239	234
1	429	446
2	97	83
3	283	285
4	119	-115
5	206	214
6	169	-168
7	21	27
8	36	-31
9	105	-105
10	41	-43
2	11	L
-14	79	-81
-13	48	-50
-12	25	-25
-11	92	-89
-10	36	37
-9	14	-8
-8	143	143
-7	44	-43
-6	95	92
-5	163	-156
-4	123	118
-3	140	138
-2	292	-290
-1	117	119
0	63	-59
1	146	136
2	114	-112
3	21	16
4	27	-25
5	138	-144
6	77	-76
7	125	-126
8	11	1
9	33	34
10	80	74
2	12	L
-14	10	-5
-13	125	-129
-12	92	90
-11	238	-236
-10	281	278
-9	242	-236
-8	224	-217
-7	71	68
-6	69	-90
-5	40	41
-4	112	-109
-3	99	94
-2	107	-107
-1	33	-33
0	92	-86
1	114	-110
2	54	51
3	115	-115
4	32	25
5	87	83
6	197	193
7	84	76
8	151	155
9	74	64
10	44	39
2	13	L
-14	111	113
-13	21	-20
-12	68	67
-11	24	-26
-10	173	-168
-9	129	-123
-8	79	-81
-7	0	6
-6	157	-155
-5	121	115
-4	217	-213
-3	9	4
-2	58	-50
-1	86	84
0	53	48
1	23	21
2	140	140
3	30	34
4	122	115
5	137	-137
6	112	-114
7	30	22
8	91	-84
9	62	-59
10	87	-81
2	14	L
-13	29	-31
-12	29	-27
-11	16	14
-10	113	-108
-9	174	165
-8	317	-324
-7	184	182
-6	99	-95
-5	105	102
-4	9	5
-3	114	112
-2	41	35
-1	257	-256
0	22	20
1	74	76
2	245	-246
3	28	21
4	132	-133
5	139	137
6	21	-25
7	15	-11
8	93	-96
9	149	148
2	15	L
-13	68	69
-12	34	-34
-11	80	74
-10	82	82
-9	52	52
-8	134	132
-7	142	141
-6	17	2
-5	133	-128
-4	159	-159
-3	17	-13
-2	63	53
-1	199	-201
0	153	149
1	236	-241
2	249	256
3	51	-54
4	138	-138
5	13	-10
6	61	-65
7	46	45
8	6	-16
9	22	-21
2	16	L
-12	85	-91
-11	112	112
-10	25	-21
-9	187	-192
-8	70	-65
-7	138	-134
-6	40	38
-5	169	-167
-4	106	-106
-3	58	61
-2	263	-266
-1	23	-20
0	9	1
1	185	187
2	20	16
3	56	-61
4	272	281
5	99	98
6	99	-97
7	131	-132
8	63	-68
9	146	-147
2	17	L
-12	19	-25
-11	49	-49
-10	18	-16
-9	32	-38
-8	88	88
-7	13	11
-6	163	162
-5	39	37
-4	162	154
-3	316	324
-2	40	-36
-1	40	-41
0	119	-115
1	81	80
2	273	-272
3	36	-42
4	87	-80
5	10	-7
6	138	137
7	60	54
8	74	76
2	18	L
-12	7	8
-11	60	64
-10	85	81
-9	12	-0
-8	121	121
-7	97	96
-6	107	104
-5	98	-102
-4	145	143
-3	144	145
-2	287	-289
-1	13	3
0	15	16
1	32	-24
2	64	-62
3	78	-85
4	120	126
5	100	-98
6	86	85
7	14	-13
8	64	90
2	19	L
-11	0	-2
-10	11	1
-9	33	-30
-8	64	-68
-7	90	-87
-6	190	-188
-5	198	-196
-4	73	74
-3	58	-66
-2	19	27
-1	0	5
0	76	76
1	62	63
2	128	120
3	16	18
4	175	178
5	49	-48
6	12	-8
7	35	-34
2	20	L
-10	113	-116
-9	33	34
-8	13	-9
-7	69	73
-6	72	-78
-5	88	90
-4	104	95
-3	52	57
-2	134	131
-1	82	-81
0	165	162
1	213	-201
2	144	-143
3	171	-165
4	62	-61
5	28	-32
6	164	-161
2	21	L
-10	27	-26
-9	75	75
-8	18	-12
-7	40	39
-6	58	61
-5	70	-69
-4	32	26
-3	117	-111
-2	7	-8
-1	42	-38
0	13	-3
1	58	-54
2	166	-166
3	13	-6
4	92	-93
5	70	70
6	16	-4
2	22	L
-9	18	15
-8	20	-13
-7	70	-72
-6	56	55
-5	90	-95
-4	64	68
-3	118	-119
-2	57	59
-1	75	64
0	166	160
1	278	272
2	51	56
3	187	186
4	0	4
5	69	67
2	23	L
-8	62	68
-7	53	-58
-6	35	35
-5	46	50
-4	41	37
-3	133	127
-2	63	-61
-1	130	127
0	26	-28
1	144	144
2	14	-9
3	0	9
4	37	-39
2	24	L
-7	107	109
-6	9	-10
-5	20	-14
-4	88	-91
-3	40	41
-2	149	-148
-1	87	-91
0	133	-133
1	39	-37
2	42	38
3	40	-41
2	25	L
-5	131	129
-4	53	-52
-3	17	14
-2	11	-1
-1	18	15
0	10	-8
1	71	-76
2	26	L
-2	77	81
3	0	L
-14	38	40
-12	31	-26
-10	6	-1
-8	79	-71
-6	59	-52
-4	20	-21
-2	106	-96
0	124	-128
2	180	169
4	164	157
6	12	7
8	120	-121
3	1	L
-14	55	-59
-13	77	-81
-12	97	-104
-11	88	-78
-10	157	-150
-9	103	-94
-8	9	-1
-7	39	34
-6	34	-30
-5	14	6
-4	129	117
-3	31	-24
-2	191	172
-1	214	-200
0	93	-92
1	22	-17
2	193	-185
3	19	18
4	230	-229
5	91	85
6	148	-150
7	34	33
8	49	-51
3	2	L
-14	72	-77
-12	44	45
-11	137	131
-10	25	-25
-9	0	4
-8	114	106
-7	17	10
-6	37	36
-5	50	-45
-4	14	-6
-3	102	-88
-2	202	179
-1	114	-109
0	36	29
1	73	-70
2	24	-25
3	179	166
4	134	-129
5	267	261
6	53	-50
7	129	125
8	53	53
3	3	L
-14	7	-5
-13	142	148
-12	77	78
-11	95	91
-10	54	-52
-9	132	-120
-8	29	-28
-7	209	-189
-6	59	55
-5	39	-29
-4	58	-52
-3	94	86
-2	84	70
-1	110	110
0	84	-87
1	204	203
2	75	-76
3	53	46
4	40	-40
5	257	244
6	72	68
7	92	-92
8	10	-5
3	4	L
-14	100	-108
-13	47	-50
-12	21	-11
-11	43	-40
-10	55	-56
-9	51	38
-8	111	102
-7	179	-166
-6	69	52
-5	100	99
-4	0	3
-3	215	201
-2	123	-119
-1	98	93
0	48	-44
1	42	37
2	32	-30
3	335	-338
4	57	-50
5	42	-40
6	160	155
7	27	-22
8	129	128
3	5	L
-14	21	21
-13	93	-104
-12	68	65
-11	10	4
-10	26	19
-9	127	113
-8	44	-37
-7	227	208
-6	170	-151
-5	32	27
-4	284	-261
-3	231	214
-2	270	-263
-1	157	-155
0	168	-168
1	19	-15
2	131	130
3	353	-348
4	83	77
5	160	-156
6	107	-103
7	51	-47
8	60	56
3	6	L
-14	113	123
-13	49	54
-12	114	120
-11	70	-68
-10	20	-15
-9	94	90
-8	232	-214
-7	272	-256
-6	468	-454
-5	62	-62
-4	272	-249
-3	41	-43
-2	62	60
-1	10	8
0	265	267
1	14	-2
2	164	164
3	134	-126
4	154	149
5	35	-30
6	205	-202
7	73	-68
8	146	-149
3	7	L
-14	83	-88
-13	47	-50
-12	17	-19
-11	3	-1
-10	137	-133
-9	176	164
-8	229	216
-7	315	305
-6	211	192
-5	190	-179
-4	200	188
-3	9	-9
-2	79	79
-1	164	-160
0	152	148
1	24	18
2	34	-36
3	62	-56
4	87	81
5	64	-62
6	81	-78
7	9	8
8	43	42
3	8	L
-14	64	-69
-13	105	108
-12	89	-92
-11	58	57
-10	65	59
-9	63	56
-8	94	82
-7	112	105
-6	410	406
-5	118	118
-4	251	241
-3	287	-274
-2	62	-55
-1	36	-34
0	171	-168
1	43	-38
2	222	-219
3	160	157
4	13	7
5	166	163
6	84	85
7	14	3
8	38	42
3	9	L
-13	123	131
-12	22	-18
-11	100	97
-10	67	-58
-9	116	-109
-8	76	78
-7	309	-296
-6	129	-120
-5	103	-95
-4	41	37
-3	15	-16
-2	98	-97
-1	181	180
0	80	80
1	272	269
2	66	64
3	119	117
4	47	47
5	29	25
6	12	2
7	26	-17
3	10	L
-13	137	-147
-12	62	65
-11	172	-171
-10	50	47
-9	71	-73
-8	22	20
-7	69	-63
-6	135	122
-5	99	94
-4	54	54
-3	123	124
-2	7	-0
-1	29	-29
0	101	-93
1	21	-17
2	88	-81
3	132	-127
4	112	-106
5	195	-194
6	22	-22
7	94	-91
3	11	L
-13	45	-47
-12	84	85
-11	121	-125
-10	106	98
-9	45	-37
-8	32	33
-7	59	50
-6	64	-60
-5	22	27
-4	26	-26
-3	69	66
-2	110	-104
-1	129	-124
0	80	-76
1	252	-250
2	42	43
3	25	-24
4	44	40
5	25	15
6	92	89
7	44	39
3	12	L
-13	30	33
-12	24	-23
-11	124	130
-10	128	-125
-9	60	60
-8	82	-76
-7	69	69
-6	102	-98
-5	45	-45
-4	58	55
-3	50	47
-2	19	-23
-1	237	230
0	20	-17
1	183	176
2	48	44
3	84	82
4	140	140
5	153	155
6	28	-26
7	14	17
3	13	L
-12	22	24
-11	77	84
-10	118	-115
-9	59	56
-8	66	-63
-7	102	98
-6	39	-36
-5	60	-58
-4	219	214
-3	64	-68
-2	228	222
-1	30	-31
0	164	159
1	104	102
2	162	-161
3	18	-15
4	145	-142
5	49	-42
6	95	-93
3	14	L
-12	24	23
-11	33	38
-10	33	31
-9	41	36
-8	41	38
-7	55	53
-6	73	-69
-5	0	6
-4	48	47
-3	140	-129
-2	79	-79
-1	117	-115
0	105	97
1	155	-149
2	22	9
3	122	116
4	11	-6
5	70	67
6	67	58
3	15	L
-11	13	-18
-10	5	2
-9	47	-46
-8	41	42
-7	13	-15
-6	189	-185
-5	51	47
-4	96	96
-3	33	-30
-2	105	-106
-1	160	151
0	0	4
1	52	49
2	85	-87
3	61	59
4	24	25
5	59	58
3	16	L
-11	121	-131
-10	64	-65
-9	74	-75
-8	93	91
-7	23	-21
-6	107	-103
-5	163	159
-4	101	-96
-3	40	41
-2	27	-20
-1	63	61
0	32	-21
1	15	8
2	49	52
3	29	-29
4	39	-34
5	123	-121
3	17	L
-10	69	66
-9	0	-2
-8	57	57
-7	86	-88
-6	24	22
-5	117	114
-4	48	-40
-3	7	-7
-2	146	-144
-1	58	55
0	9	9
1	201	-206
2	19	-11
3	55	-56
4	133	130
3	18	L
-9	42	50
-8	69	-68
-7	64	-58
-6	140	-141
-5	83	-87
-4	19	-14
-3	64	-62
-2	91	90
-1	22	-24
0	147	142
1	9	-5
3	66	-64
3	19	L
-9	18	-14
-8	15	-17
-7	27	28
-6	30	27
-5	28	28
-4	0	-7
-3	101	-96
-2	50	45
-1	16	-15
0	0	31
1	66	-59
2	41	40
3	121	118
3	20	L
-8	115	112
-7	23	17
-6	101	103
-5	64	-61
-4	109	106
-3	81	-73
-2	34	-30
-1	59	-59
0	92	-91
1	16	-8
2	123	-121
3	21	L
-6	6	11
-5	28	-28
-4	28	-24
-3	15	-10
-2	37	-41
-1	116	113
0	6	9
3	22	L
-4	10	-3
-3	91	90
-2	65	-64
4	0	L
-12	15	20
-10	34	-33
-8	44	-47

Table 2 (*cont.*)

-6	120	115	-3	33	31	-5	89	-86	-7	64	61	-8	89	-92	-8	36	-25	-8	9	18	-8	25	23	-8	22	-16	-7	77	-87	-5	95	104	-2	16	-21	4	13	L	-2	24	-30
-4	204	207	-2	9	-0	-4	34	-37	-6	48	-50	-7	127	127	-7	6	-2	-7	30	-26	-7	27	-23	-7	100	-103	-6	62	-69	-4	110	-117	-1	113	121	-8	22	23	-1	53	56
-2	115	116	-1	28	25	-3	24	-28	-5	85	86	-6	130	-128	-6	70	-74	-6	104	107	-6	102	109	-6	84	-87	-5	45	44	-3	19	25	0	28	-28	-7	45	-51	4	15	L
0	27	-26	0	48	-56	-2	73	-76	-4	65	-64	-5	115	118	-5	33	34	-5	16	-13	-5	28	-20	-5	11	-11	-4	9	6	-2	138	-153	1	40	43	-6	112	119	-5	127	133
2	185	-147	1	143	153	-1	83	90	-3	55	52	-4	21	-17	-4	37	37	-4	88	95	-4	80	-81	-4	7	1	-3	35	36	-1	53	-59	4	12	L	-5	6	11	-4	22	-21
4	89	-45	2	174	-189	0	74	87	-2	106	-115	-3	29	-24	-3	71	-73	-3	10	17	-3	44	-46	-3	13	8	-2	144	161	0	26	26	-9	23	22	-4	49	-48	-3	100	102
4	1	1	3	36	37	1	175	194	-1	35	-35	-2	73	-74	-2	92	95	-2	66	77	-2	63	-66	-2	77	-87	-1	0	-11	1	60	-67	-8	12	-3	-3	85	-88			
-12	12	-11	4	38	-40	2	20	-19	0	52	59	-1	82	-95	-1	51	-54	-1	9	-2	-1	19	18	-1	45	50	0	67	77	2	43	46	-7	110	-123	-2	82	-95			
-11	43	-47	4	2	L	3	109	117	1	50	-56	0	87	97	0	123	138	0	46	-53	0	96	-109	0	18	-26	1	10	-1	4	11	L	-6	72	74	-1	38	-33			
-10	72	74	-12	34	37	4	112	121	2	46	-49	1	115	-134	1	53	-60	1	29	-32	1	66	-73	1	32	36	2	15	11	-9	18	-15	-5	10	12	0	106	-115			
-9	28	28	-11	56	-55	4	3	L	3	38	-43	2	13	-3	2	153	164	2	6	-6	2	119	-130	2	0	-1	4	10	L	-8	43	50	-4	71	72	4	14	L			
-8	30	30	-10	70	79	-12	54	-56	4	15	17	3	32	31	3	57	63	3	80	84	3	75	-73	3	93	-99	-10	104	111	-7	27	-19	-3	95	-106	-7	12	-11			
-7	9	2	-9	101	-102	-11	36	-35	4	4	L	4	5	L	4	6	L	4	7	L	4	8	1	4	9	L	-9	145	223	-6	45	54	-2	144	155	-6	10	1			
-6	31	26	-8	57	66	-10	7	-4	-11	10	-5	-11	25	21	-11	14	-11	-11	26	22	-11	55	-59	-10	66	70	-8	179	208	-5	47	-52	-1	43	54	-5	12	2			
-5	118	-117	-7	66	-67	-9	7	-12	-10	10	12	-10	47	-46	-10	103	-111	-10	109	115	-10	51	-56	-9	99	-108	-7	60	69	-4	12	11	0	8	2	-4	21	-24			
-4	63	60	-6	27	-25	-8	29	-26	-9	89	89	-9	50	55	-9	24	-28	-9	22	24	-9	147	-160	-8	92	-108	-6	67	-71	-3	17	10	1	3	2	-3	5	-3			

applied and normalized structure factors, E, were calculated for use in the phase determination.

The symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1963; 1966) was used to determine the phases for 267 reflections of high $|E|$ value. The $\sum_2$ relationship was used to expand a starting set of six reflections, all of whose $|E|$ values exceeded 2·7. Three reflections were assigned zero phases to fix the origin ($25\bar{4}$, $12\bar{3}$, 2,22,1) and three were assigned symbolic phases (266, $25\bar{5}$, 178). The phase determination indicated that the three symbolic phases were probably zero. An E map computed with this assumption revealed the 20 non-hydrogen atoms of the structure.

The atomic coordinates and thermal vibration parameters for the 20 atoms were refined by full-matrix least-squares methods. The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1952). Initially, each reflection intensity was given a weight of unity, and the function minimized was $\sum w(F_o-F_c)^2$. Anisotropic refinement brought the agreement factor, R, down to 0·09. At this point, a difference map revealed all of the 12 hydrogen atoms of the molecule. A statistical examination of the magnitude of the remaining discrepancies suggested the weighting function

$$\frac{1}{W}=1\cdot0+\left(\frac{|F_o|-8}{16}\right)^2,$$

which gives a distribution of weights consistent with the distribution of errors expected in counter diffractometry. Such errors include instrumental factors which limit the reliability of very intense and also very weak intensity measurements. At this point in the refinement systematic errors which were probably due to secondary extinction were apparent. To minimize the effects of this error source, the 16 reflections with $|F_o|>65\cdot0$ were removed, leaving 2174 reflections in the refinement. This type of treatment can significantly diminish the slight structural errors attributable to extinction (Åsbrink & Werner, 1966). Errors due to absorption are negligible for low values of the index h because of the small cross-section of the needle-shaped crystal ($\mu r \simeq 0\cdot25$ for $h=0$). The h index runs only to 4 in this data set, and the slight errors which may be present for the higher h values would primarily affect the reliability of the B_{11} parameters. No distortion of the thermal ellipsoids in this direction was apparent.

After the elimination of some of the secondary extinction errors, further refinement led to an R of 4·6% including 'unobserved' (zero intensity) reflections. Recalculation of the R value on the full data set *including* those reflections with secondary extinction errors gave a value of 5·0%. The positions of the hydrogen atoms were allowed to vary, and all converged satisfactorily. The thermal vibration of each hydrogen atom was set equal to that of the carbon to which it was attached.

Table 3(*a*). *Fractional coordinates and thermal parameters**

Standard deviations are in parentheses.

$$T=\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*)\right].$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	1·30992 (14)	0·16952 (2)	0·56235 (4)	3·63 (3)	3·41 (3)	1·94 (2)	−0·07 (2)	0·04 (2)	0·46 (2)
O(1)	1·08430 (42)	0·10131 (6)	0·53036 (11)	4·23 (7)	3·56 (7)	2·56 (6)	−0·28 (6)	0·20 (5)	0·70 (5)
O(2)	0·25089 (45)	0·01975 (7)	0·23979 (13)	4·79 (8)	3·43 (7)	3·72 (7)	−1·01 (6)	0·74 (6)	−0·38 (6)
C(3)	0·87146 (54)	0·10139 (9)	0·43595 (15)	3·27 (8)	3·45 (9)	2·53 (8)	0·39 (7)	0·79 (7)	0·35 (7)
C(4)	0·86398 (50)	0·15069 (8)	0·38110 (15)	2·93 (8)	2·77 (8)	2·47 (8)	0·21 (6)	0·76 (6)	0·02 (6)
C(5)	0·63947 (54)	0·15416 (9)	0·27963 (16)	3·56 (9)	3·23 (9)	2·47 (8)	0·17 (7)	0·59 (7)	0·22 (7)
C(6)	0·44400 (56)	0·10966 (9)	0·23725 (17)	3·53 (9)	3·62 (10)	2·66 (9)	−0·22 (7)	0·43 (7)	−0·14 (7)
C(7)	0·45929 (57)	0·06031 (9)	0·29315 (17)	3·41 (9)	3·15 (9)	3·24 (9)	−0·19 (7)	1·07 (7)	−0·38 (7)
C(8)	0·66996 (56)	0·05576 (9)	0·39246 (17)	3·71 (9)	3·09 (9)	3·25 (9)	0·02 (7)	1·00 (7)	0·27 (7)
C(9)	0·23832 (81)	−0·03113 (10)	0·29158 (24)	5·16 (13)	3·38 (10)	5·06 (13)	−0·87 (9)	1·29 (11)	0·05 (9)
C(10)	1·09262 (48)	0·19093 (8)	0·44004 (14)	2·84 (7)	3·17 (8)	2·05 (7)	0·50 (6)	0·57 (6)	0·04 (6)
O(11)	1·51847 (42)	0·23941 (7)	0·58550 (11)	4·32 (7)	3·81 (7)	2·13 (6)	−0·35 (6)	−0·28 (5)	0·25 (5)
O(12)	1·49131 (42)	0·40481 (6)	0·39181 (12)	4·29 (7)	3·04 (7)	3·70 (7)	−0·52 (5)	0·34 (6)	0·07 (5)
C(13)	1·41572 (51)	0·27008 (9)	0·50257 (15)	3·02 (8)	3·45 (9)	2·15 (8)	0·39 (7)	0·35 (6)	−0·02 (6)
C(14)	1·17491 (49)	0·24482 (8)	0·41752 (15)	2·90 (7)	2·88 (8)	2·24 (8)	0·41 (6)	0·50 (6)	−0·17 (6)
C(15)	1·05811 (56)	0·27518 (9)	0·32509 (16)	3·60 (9)	3·09 (9)	2·25 (8)	0·18 (7)	0·22 (7)	−0·03 (7)
C(16)	1·17106 (58)	0·32738 (9)	0·32069 (17)	3·84 (9)	3·31 (9)	2·51 (9)	0·28 (7)	0·27 (7)	0·14 (7)
C(17)	1·40942 (52)	0·35201 (8)	0·40796 (16)	3·11 (8)	2·97 (8)	3·07 (9)	0·10 (6)	0·82 (7)	−0·25 (7)
C(18)	1·53290 (55)	0·32386 (9)	0·49827 (17)	3·10 (8)	3·47 (9)	2·67 (9)	−0·13 (7)	0·31 (7)	−0·51 (7)
C(19)	1·73515 (71)	0·43304 (11)	0·47388 (22)	4·39 (11)	3·61 (11)	4·63 (12)	−0·92 (9)	0·76 (9)	−0·71 (9)

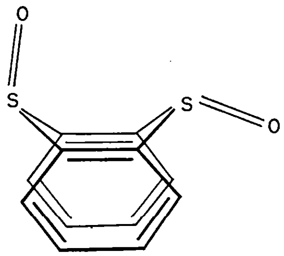
Tables 3(*a*) and 3(*b*) list the coordinates and thermal parameters of each atom; the observed and calculated structure factors are compared in Table 2.

Table 3(*b*). *Fractional coordinates, hydrogen atoms*

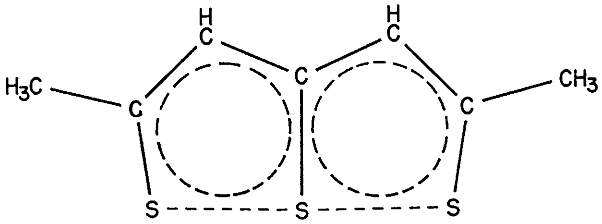
	x	*y*	*z*
H(5)	0·617	0·188	0·241
H(6)	0·282	0·109	0·168
H(8)	0·694	0·021	0·436
H(9*a*)	0·152	−0·021	0·356
H(9*b*)	0·072	−0·057	0·239
H(9*c*)	0·462	−0·052	0·312
H(15)	0·909	0·257	0·266
H(16)	1·113	0·350	0·264
H(18)	1·686	0·340	0·551
H(19*a*)	1·962	0·411	0·493
H(19*b*)	1·667	0·436	0·534
H(19*c*)	1·776	0·471	0·448
Standard deviations	0·010	0·0013	0·0025

Discussion

A striking feature of this molecule is its planarity to within ±0·06 Å, Fig. 3, except for the hydrogen atoms on the CH_3 groups. The characteristic geometry of sulfur, bonded to three substituents, is pyramidal (Abrahams, 1956). This is usually the case even if one of the substituents is doubly bonded to the sulfur atom as in β-thianthrene dioxide which is a markedly non-planar molecule with pyramidal sulfur atoms (Hosoya, 1966):



The unusual environment about the sulfur atom in this molecule can be related to structural results reported for two special classes of polysulfur compounds, the thiathiaphthenes and the thiafurophthenes, which have been discussed in a recent review article (Salmond, 1968). The structure of the thiathiaphthene skeleton was discovered through X-ray diffraction studies (Bezzi, Mammi & Garbuglio, 1958; Mammi, Bardi, Garbuglio & Bezzi, 1960) on a substance found to be 2,5-dimethylthiathiaphthene:



The thiathiaphthene system is planar and exhibits an approximately linear arrangement of the three sulfur atoms. The S–S bond lengths for the above thiathiaphthene system were reported to be 2·35 Å, about 0·25 Å longer than any previously reported S–S single bonds. The corresponding S–O bond lengths reported in this work are 1·879(±2) Å (Fig. 1), about 0·28 Å longer than a normal S–O single bond. The 2,5-dimethylthiathiaphthene molecule was reported to be symmetrical by the early investigators, but this was questioned later (Johnson, Newton, Paul, Beer & Cartwright, 1967), with the suggestion that a disordered asymmetric molecule might also be consistent with the limited two-dimensional data observed by Bezzi *et al.* (1958). An anisotropic refinement of a complete three-dimensional data set has recently corroborated the earlier results (Leung & Nyburg, 1969). The molecule reported in this investigation has no symmetry imposed on it by the crystal-

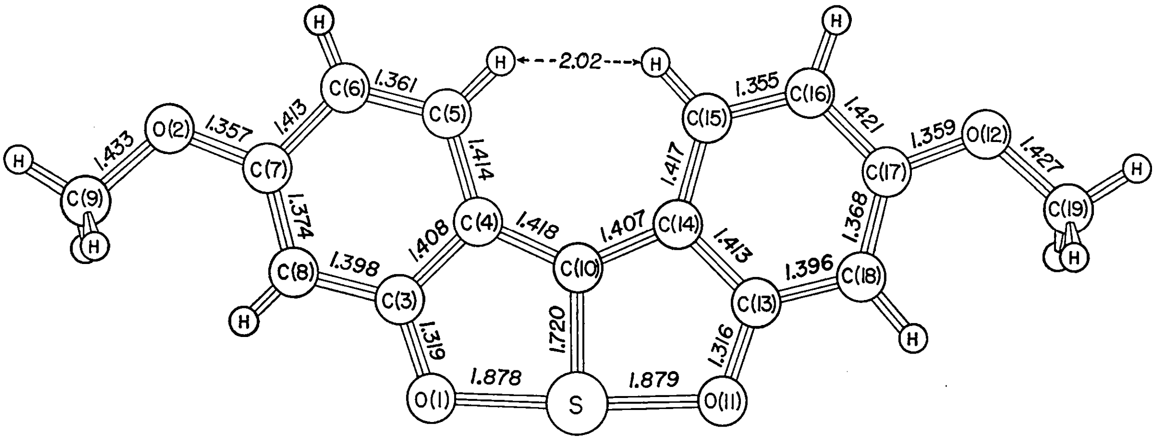


Fig. 1. Numbering scheme and bond distances for $C_{15}H_{12}SO_4$. Estimates of the standard deviations of the individual bond lengths are obtained solely from the least-squares refinement of the structural parameters. These estimates are: ±0·002 Å for bonds involving sulfur; ±0·003 to 0·004 Å for all bonds involving carbon or oxygen atoms, and ±0·05 Å for the hydrogen–hydrogen nonbonded distance illustrated.

lographic space group, but displays a twofold axis of symmetry which is virtually exact to within the limits of error (see Figs. 1 and 2).

The C–C ring bonds of 2,5-dimethylthiathiaphthene are 1·37 and 1·38 Å, within the range of aromatic bonds. In the present molecule, the C(4)–C(10) distance of 1·418(±4) Å is also more typical of an aromatic bond than a normal single or double bond. The C(3)–C(4) bond is, of course, part of a benzene ring and displays a typical aromatic distance. The C(3)–O(1) distance, as well as the C(13)–O(11) distance, is 1·318(±4) Å, which could also be called an 'aromatic' type distance, for it lies between the normal single(1·40–1·45 Å) and double. (1·18–1·25 Å) bond ranges. The bond lengths of 2,5-dimethylthiathiaphthene have been discussed by several authors from a theoretical point of view (Giacometti & Rigatti, 1959; Maeda, 1960, 1961*a*,*b*; Gleiter & Hoffmann, 1968) and their conclusions would seem to apply, at least qualitatively, to the system reported here. However, structures have been reported since these publications which may disrupt some of their conclusions. Johnson & Paul (1969*a*) described the structure of 3,4-diphenylthiathiaphthene, which is symmetrically substituted with phenyl groups. The thiathiaphthene nucleus is planar but asymmetric, with S–S distances of 2·23 and 2·43 Å. A smaller but probably significant asymmetry has also been reported for the structure of symmetrically substituted 2,5-diphenylthiathiaphthene (Hordvik, 1968).

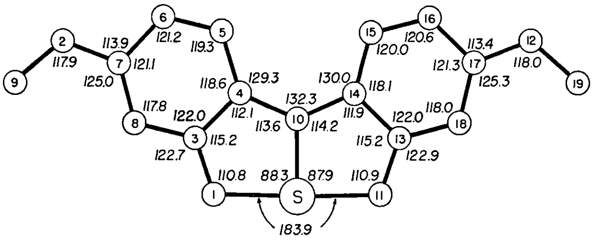


Fig. 2. Bond angles for $C_{15}H_{12}SO_4$. Standard deviations estimated from the least-squares refinement are 0·10° for the angles surrounding the sulfur atom, and 0·15° to 0·20° for all other angles.

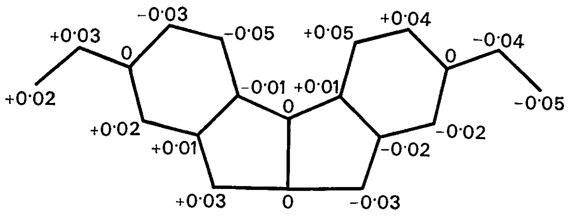
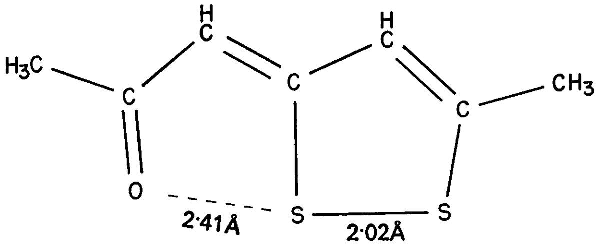


Fig. 3. Deviations from a least-squares plane.

It is possible to replace one of the end S atoms of thiathiaphthene with an oxygen atom. This system, called the dithiafurophthene (also referred to in the literature as thiafurophthene and furothiaphthene) system, is structurally dissimilar to the symmetric 2,5-dimethylthiathiaphthene and the di-oxygenated molecule under discussion. The symmetry of the doubly heterocyclic system is apparently easily disrupted, as in 2,5-dimethyldithiofurophthene (Mammi, Bardi, Traverso & Bezzi, 1961):



The carbonyl bond is 1·27 Å, which is essentially a double bond, and the S–S bond has a fairly typical single bond value. However, the S···O approach is extremely short for a non-bonded distance. The sum of the van der Waals radii would be about 3·2 Å for these two atoms.

Johnson & Paul (1969*b*) have reported the structure of a nitroso-disulfide compound in which a still shorter S···O contact (2·034) is observed between the nitroso oxygen and one of the disulfide sulfurs. The disulfide single bond was lengthened (2·178 Å) to a value intermediate between the S–S bonds of the dithiafurothene and the thiathiaphthene mentioned above. Several examples of abnormally short (2·4 to 2·7 Å) approaches between formally nonbonded S and O atoms were discussed by Kapecki, Baldwin & Johnson (1968). All of these systems are characterized by a planar sulfur environment and the presence of conjugation in neighboring regions of the molecule, in common with the molecule reported in this investigation.

A best least-squares plane was fitted to the four rings of the molecule, omitting the methoxyl substituents.

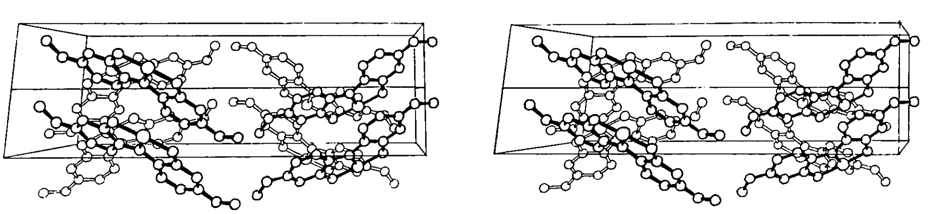


Fig. 4. A stereoview down the *c* axis of the unit cell. Two unit cells are displayed to illustrate the stacking along the a direction. Parallel planes containing the molecules are separated by 3·53 Å.

The deviations from this plane are illustrated in Fig. 3 and indicate a small torsion of the two benzene rings in opposite directions. The primary reason for this is probably the repulsion between the hydrogen atoms on C(5) and C(15). Even with the torsion, the two hydrogen atoms are separated by only 2·02(± 5) Å, Fig. 1. The usual intermolecular approach between hydrogen atoms is approximately 2·35 Å. Fused ring hydrocarbons often exhibit similar intramolecular crowding. A recent reinvestigation of the crystal structure of phenanthrene (Kay, Okaya & Cox, 1969) reports nonbonded hydrogen atoms only 2·04 Å from each other and a similar torsion of the fused-ring skeleton.

The methoxyl groups are coplanar with the ring skeleton (Fig. 3). This has been observed previously in several aromatic methoxy compounds (Yonemitsu, Nakai, Kanaoka, Karle & Witkop, 1969; Karle & Karle, 1968; Corbin, Karle & Karle, 1970; Karle&Karle, to be published). In each of these compounds, the methoxyl groups adopt a preferred orientation with respect to the neighboring phenyl or quinoidol ring. The methyl group turns toward the shorter bond in the neighboring ring and rotates to minimize methyl hydrogen interaction with the neighboring ring. The methyl hydrogen atoms of this compound were well defined in difference maps and are illustrated in Fig. 1. One hydrogen is coplanar with but directed away from the benzene ring, while the other two are staggered above and below the plane of the benzene ring. The C(8)···C(9) separation, as well as the C(18)···C(19) separation, are only 2·82 Å, and similar distances occur in molecules in the above references.

The packing of the molecules is illustrated in Fig. 4. The nearest intermolecular approaches are usual van der Waals distances involving molecules stacked along the short *a* axis (Fig. 4). The shortest of these contacts are S–C(3′), 3·61Å, C(10)–C(4′), 3·55 Å, and C(4)–C(6′), 3·59 Å (primed atoms are translated by +*a*).

References

Abrahams, S. C. (1956). *Quart. Rev.* **10**, 407.

Bezzi, S., Mammi, M. & Garbuglio, C. (1958). *Nature, Lond.* **182**, 247.

Corbin, J. L., Karle, I. L. & Karle, J. (1970). *Chem. Comm.* p. 186.

Giacometti, G. & Rigatti, G. (1959). *J. Chem Phys.* **30**, 1633.

Gleiter, R. & Hoffmann, R. (1968). *Tetrahedron* **24**, 5899.

Hordvik, A. (1968). *Acta Chem. Scand.* **22**, 2397.

Hosoya, S. (1966). *Acta Cryst.* **21**, 21.

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

Johnson, P. L. & Paul, I. C. (1969*a*). *Chem. Comm.* p. 1014.

Johnson, P. L. & Paul, I. C. (1969*b*). *J. Amer. Chem. Soc.* **91**, 781.

Johnson, S. M., Newton, M. G., Paul, I. C., Beer, R. J. S. & Cartwright, D. (1967). *Chem. Comm.* p. 1170.

Kapecki, J. A., Baldwin, J. E. & Paul, I. C. (1968). *J. Amer. Chem. Soc.* **90**, 5800.

Karle, I. L. & Karle, J. (1963). *Acta Cryst.* **16**, 969.

Karle, I. L. & Karle, J. (1968). *Acta Cryst.* B**24**, 81.

Karle, J. &. Karle, I. L. (1966). *Acta Cryst.* **21**, 849.

Kay, M. I., Okaya, Y. & Cox, D. T. (1969). *Acta Cryst.* A**25**, s147.

Kittleson, A. R. (1952). *Anal. Chem.* **24**, 1173.

Leung, F. & Nyburg, S. C. (1969). *Chem. Comm.* p. 137.

Maeda, K. (1960). *Bull. Chem. Soc. Japan*, **33**, 1466.

Maeda, K. (1961*a*). *Bull. Chem. Soc. Japan*, **34**, 785.

Maeda, K. (1961*b*). *Bull. Chem. Soc. Japan*, **34**, 1166.

Mammi, M., Bardi, R., Garbuglio, C. & Bezzi, S. (1960). *Acta Cryst.* **13**, 1048.

Mammi, M., Bardi, R., Traverso, G. & Bezzi, S. (1961). *Nature, Lond.* **192**, 1282.

Pomerantz, I., Miller, L., Lustig, E., Mastbrook, D., Hansen, E., Barron, R., Oates, N. & Chen, J. -Y. (1969). *Tetrahedron Letters*. 5307.

Salmond, W. G. (1968). *Quart. Rev.* **22**, 253 (see p. 272).

Yonemitsu, O., Nakai, H., Kanaoka, Y., Karle, I. L. & Witkop, B. (1969). *J. Amer. Chem. Soc.* **91**, 4591.

Åsbrink, S. & Werner, P. E. (1966). *Acta Cryst.* **20**, 407.