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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720

Structure Determination of 5-Methyl-2,2,4-Triacetyl-1,3-oxathiole[1]

BY HELENA RUBEN, DAVID KAPLAN, ALLAN ZALKIN, AND DAVID H. TEMPLETON

5-methyl-2,2,4-triacetyl-1,3-oxathiole, $(CH_3CO)_2COC(CH_3)C(COCH_3)S$, crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell of dimensions $\underline{a}$ = 9.817 ± 0.004, $\underline{b}$ = 9.089 ± 0.003, $\underline{c}$ = 13.776 ± 0.002 Å, and $\underline{\beta}$ = 114.35°. The calculated X-ray density is 1.35g/cc. 1119 reflections were measured on a manual diffractometer using MoKα radiation. The structure was solved using the Patterson function maps and was refined by full-matrix least-squares to a conventional R factor of 0.060. The bond lengths around the five membered oxathiole ring , starting with oxygen in position one, are: O--C = 1.425(6), C--S = 1.821(6), S--C = 1.775(6), C--C = 1.340(8), and C--O = 1.377(6) Å. The C--S--C angle is 87.6(4)°.

Introduction

Professor Edward C. Taylor and co-workers at Princeton University synthesized a material which they suggested contained a sulfur atom with two double bonds to it. We undertook the structure determination to check this possibility. The results of the determination showed the material to be 5-methyl-2,2,4-triacetyl-1,3-oxathiole which does not contain the postulated sulfur bonding, but rather is a cyclic compound with normal bond geometry.

Experimental

Crystals sent to us by Dr. Taylor were colorless, and poorly crystallized. They were recrystallized from hexane. X-ray powder diffraction patterns of the material before and after recrystallization were identical. Our initial irradiation of some of these crystals in air resulted in a degradation of the X-ray patterns with exposure to the X-rays. Encapsulation in glass capillaries stabilized the crystals for the X-ray experiments. Initially we studied two crystals with different orientations using the Weissenberg film technique. The resulting photographs indicated monoclinic symmetry with systematic absences characteristic of space group $P2_1/c$; $h0\ell$, $\ell \neq 2n$ and $0k0$, $k \neq 2n$.

A General Electric XRD-5 X-ray diffraction apparatus equipped with a molybdenum X-ray tube ($MoK\alpha_1$, λ 0.70926 Å), a scintillation counter, a pulse height discriminator, and a quarter-circle Eulerian-cradle type of goniostat was used. The X-ray tube was operated at 50 kV and 20 mA; a 0.003-in. Zr filter was used on the receiving slit. The crystal was oriented such that the b axis was parallel to the ϕ axis of the instrument. The cell dimensions were obtained from carefully measured 2θ values of the $0k0$, $h00$, and 00ℓ reflections whose α_1 and α_2 components were resolved. The β angle was measured directly from the angle between the $h00$ and 00ℓ sets of reflections.

A total of 1119 independent intensities were measured, of which 193 were recorded as having zero intensity. A stationary-crystal, stationary-counter technique with a 10-sec count for every reflection was used. The diffractometer was set at a 4° take-off angle to the tube. The maximum 2θ angle was 40° [$(\sin \theta/\lambda = 0.481$]. Background was plotted as a function of 2θ

and these values were used for most of the intensities; in the cases where background was seriously affected by streaking, individual backgrounds were measured. The absorption parameter is 2.77 cm^{-1}, from which we estimate the absorption factor to be negligible. Variations of the intensity of the 020 reflection when the ϕ setting was changed $90^{\circ}(\chi = 90^{\circ})$ were negligible. Lorentz and polarization corrections were made but no correction was made for either absorption or extinction.

Fourier, least-squares, and distance calculations were performed using our own unpublished programs. The full-matrix least-squares program, which is a modification of an early unpublished version of one given us by P. Gantzel, R. Sparks, and K. Trueblood, minimizes the function $\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^{\,2}$. F_o and F_c are the observed and calculated structure factors, respectively, and ω is the weighting factor. Atomic scattering factors for neutral S, O and C were taken from Cromer and Waber's compilation[3], and for neutral hydrogen from ref. 4. Both the real and imaginary parts of the anomalous dispersion for sulfur[5] were included in the least-squares calculations. For each reflection ω was set to $1.0/\sigma^2(F_o)$ with the exception that when I(net count) $\leqslant \sigma(I)$, then $\omega = 0$. The standard deviation of the observed structure factor was calculated as $\sigma(F_o) = F_o - [F_o^{\,2} - (s\sigma(I)/Lp)]^{1/2}$ where s is a scaling factor, $F_o = (sI/Lp)^{1/2}$, and Lp is the Lorentz-polarization correction. $\sigma(I) = (I + (\underline{p}I)^2 + 2B + \underline{q}^2)^{1/2}$, where $\underline{p}$ is a fractional uncertainty in I, B is the backgroun, and $\underline{q}$ represents an uncertainty in the background. Values of $\underline{p}$ and $\underline{q}$ were 0.05 and 10.

The primitive cell contains four formula units of $C_{10}H_{12}O_4S$. It is monoclinic with dimensions $\underline{a}$ = 9.817 ± 0.004, $\underline{b}$ = 9.089 ± 0.003, $\underline{c}$ = 13.776 ± 0.002 Å, and $\beta = 114.35^{\circ}$. The calculated density is 1.35 g/cc which corresponds to 1.3 ± 0.2 g/cc measured by flotation.

Determination of the Structure

From a three dimensional Patterson function positions were estimated for the sulfur atom and four carbon atoms. A least-squares refinement was run on these atoms followed by a three-dimensional Fourier calculation. Even though one of the original carbon atoms was found to be incorrect, this map showed all of the atoms except hydrogen. A least-squares refinement of the structure with isotropic temperature factors resulted in R = 0.126; where $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. Isotropic temperature factors have the form $\exp(-B\sin^2\theta/\lambda^2)$, where B is the isotropic thermal parameter in $Å^2$, θ is the Bragg angle, and λ is the X-ray wave length. With anisotropic temperature factors on all of the non-hydrogen atoms the R factor went to 0.096. Anisotropic temperature factors have the form $\exp(-\underline{h}^2\beta_{\underline{11}} - \underline{k}^2\beta_{\underline{22}} - \underline{\ell}^2\beta_{\underline{33}} - 2\underline{hk}\beta_{\underline{12}} - 2\underline{h\ell}\beta_{\underline{13}} - 2\underline{k\ell}\beta_{\underline{23}})$, where β is the anisotropic thermal parameter. When we list the results we report the parameters in terms of $B_{\underline{ij}}$, in units of $Å^2$, which is equal to $4\beta_{\underline{ij}}/\underline{a}_{\underline{i}}^*\underline{a}_{\underline{j}}^*$ where $\underline{a}_{\underline{i}}^*$ and $\underline{a}_{\underline{j}}^*$ are the $\underline{i}$th and $\underline{j}$th reciprocal cell lengths.

Hydrogen atoms were included in the least-squares refinement with isotropic thermal parameters. Since these thermal parameters refined poorly, the hydrogen thermal parameters of each methyl group were tied together. For H(1), H(2) and H(3) the isotropic thermal parameter is 7.7 ± 0.1, for H(4), H(5) and H(6) it is 11.7 ± 0.2, for H(7), H(8) and H(9) it is 6.6 ± 0.1 and for H(10), H(11) and H(12) it is 8.9 ± 0.2.

The final R value for 824 data with nonzero weights is 0.06. The R value for all 1119 data is 0.105. The weighted R value, $(\Sigma\omega(\Delta F)^2/\Sigma\omega F_o^2)^{1/2}$, is 0.047. The standard deviation of an observation of unit weight is 0.99. The

observed and calculated structure factors are given in Table I. The final values of the position parameters are listed in Table II. Table III lists the anisotropic temperature parameters.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS OF 5-METHYL-2,2,4-TRIACETYL-1,3-OXATHIOLE[a]

FCA(0,0,0) = 4560

L	FOB	FCA
H,K=	0,	0
-12	90	96
-10	273	276
-8	77	78
-6	470	467
-4	525	529
-2	599	606
2	616	606
4	531	529
6	481	467
8	70	78
10	280	276
12	107	96
H,K=	0,	-1
-12	0	48*
-11	217	210
-10	114	120
-9	203	207
-8	63	51
-7	29	9*
-6	180	180
-5	35	10*
-4	325	324
-3	236	230
-2	498	497
-1	476	480
1	472	480
2	493	497
3	238	230
4	322	324
5	43	10
6	172	180
7	0	9*
8	78	51
9	217	207
10	125	120
11	213	210
12	57	48
H,K=	0,	-2
-11	55	41
-10	187	193
-9	147	147
-8	73	58
-7	53	15
-6	343	342
-5	122	117
-4	203	204
-3	22	46*
-2	44	58
-1	140	129
0	300	298
1	129	129
2	60	58
3	38	46
4	199	204
5	120	117
6	337	342
7	43	15
8	86	58
9	134	147
10	191	193
11	55	41
H,K=	0,	-3
-11	97	104
-10	0	26*
-9	163	171
-8	307	316
-7	196	200
-6	30	24*
-5	122	116
-4	37	12
-3	192	189
-2	74	83
-1	553	565
1	553	565
2	87	83
3	189	189
4	26	12*
5	115	116
6	42	24
7	201	200
8	318	316
9	182	171
10	0	26*
11	97	104

H,K=	0,	-4
-10	68	20
-9	74	76
-8	61	52
-7	321	311
-6	101	93
-5	241	244
-4	95	85
-3	423	432
-2	174	180
-1	52	74
0	138	141
1	78	74
2	181	180
3	424	432
4	81	85
5	253	244
6	105	93
7	311	311
8	50	52
9	98	76
10	0	20*
H,K=	0,	-5
-9	135	161
-8	0	35*
-7	142	130
-6	220	213
-5	233	230
-4	166	171
-3	0	40*
-2	203	201
-1	116	108
1	109	108
2	201	201
3	0	40*
4	160	171
5	226	230
6	204	213
7	128	130
8	0	35*
9	150	161
H,K=	0,	-6
-8	39	11*
-7	100	98
-6	36	28*
-5	132	122
-4	48	53
-3	120	123
-2	166	156
-1	56	57
0	132	131
1	79	57
2	149	156
3	115	123
4	84	53
5	127	122
6	36	28*
7	92	98
8	0	11*
H,K=	0,	-7
-7	0	45*
-6	202	196
-5	53	72
-4	242	252
-3	36	64*
-2	0	22*
-1	0	18*
1	0	18*
2	0	22*
3	63	64
4	248	252
5	93	72
6	195	196
7	40	45*
H,K=	0,	-8
-4	89	97
-3	135	128
-2	134	133
-1	0	43*
0	54	67
1	0	43*
2	139	133
3	124	128
4	89	97
H,K=	1,	0
-12	0	14*

-10	167	172
-8	91	74
-6	485	491
-4	354	348
-2	616	619
0	136	135
2	91	92
4	937	972
6	99	105
8	47	22
10	37	34*
H,K=	1,	-1
-12	0	9*
-11	0	17*
-10	0	15*
-9	131	136
-8	75	60
-7	273	281
-6	58	73
-5	489	513
-4	820	856
-3	128	126
-2	606	601
-1	375	367
0	883	927
1	328	326
2	51	42
3	252	245
4	90	93
5	308	302
6	281	269
7	76	61
8	115	115
9	0	70*
10	38	18*
11	69	101
H,K=	1,	-2
-12	40	16*
-11	38	67*
-10	36	56*
-9	0	17*
-8	294	282
-7	224	229
-6	177	168
-5	349	333
-4	70	85
-3	288	281
-2	776	808
-1	168	164
0	296	298
1	0	5*
2	331	328
3	322	312
4	111	117
5	353	343
6	257	258
7	165	170
8	68	79
9	119	117
10	66	89
11	99	64
H,K=	1,	-3
-11	0	11*
-10	187	192
-9	60	69
-8	57	78
-7	216	218
-6	177	174
-5	314	311
-4	478	475
-3	59	64
-2	310	312
-1	141	143
0	128	134
1	380	389
2	585	602
3	401	397
4	172	167
5	350	352
6	31	53*
7	119	129
8	78	97
9	52	20
10	0	4*
H,K=	1,	-4
-11	155	158

-10	76	36
-9	276	273
-8	49	27
-7	143	135
-6	139	128
-5	30	48*
-4	325	323
-3	411	419
-2	315	319
-1	259	251
0	190	193
1	88	84
2	382	385
3	90	81
4	30	3*
5	232	233
6	155	152
7	134	149
8	63	66
9	210	210
10	57	52
H,K=	1,	-5
-10	56	56
-9	38	23*
-8	81	79
-7	35	23*
-6	67	79
-5	79	87
-4	54	60
-3	43	26
-2	436	431
-1	51	50
0	368	362
1	132	133
2	248	252
3	44	51
4	107	100
5	67	93
6	99	95
7	110	105
8	38	43*
9	0	2*
H,K=	1,	-6
-9	57	32
-8	139	146
-7	0	49*
-6	88	64
-5	0	15*
-4	0	8*
-3	57	87
-2	80	69
-1	287	300
0	72	78
1	156	168
2	33	8*
3	59	43
4	60	55
5	0	13*
6	0	12*
7	39	39*
8	0	25*
H,K=	1,	-7
-7	0	44*
-6	0	40*
-5	65	80
-4	0	48*
-3	36	97*
-2	178	177
-1	0	17*
0	106	100
1	87	100
2	0	15*
3	52	61
4	38	9*
5	39	17*
6	0	35*
H,K=	1,	-8
-5	40	38*
-4	118	144
-3	0	8*
-2	0	42*
-1	77	96
0	86	78
1	77	79
2	135	128
3	97	99

4	40	43*
H,K=	2,	0
-12	138	142
-10	102	108
-8	193	189
-6	81	94
-4	210	210
-2	767	798
0	76	69
2	322	314
4	79	87
6	53	28
8	344	343
10	55	83
H,K=	2,	-1
-12	39	53*
-11	159	149
-10	69	70
-9	79	31
-8	148	141
-7	28	115*
-6	144	155
-5	0	3*
-4	75	76
-3	773	799
-2	614	625
-1	414	399
0	577	575
1	21	42*
2	182	181
3	374	370
4	264	250
5	50	34
6	97	84
7	368	365
8	99	84
9	148	143
10	0	22*
H,K=	2,	-2
-12	136	141
-11	83	80
-10	227	217
-9	47	30
-8	0	38*
-7	184	185
-6	47	49
-5	136	139
-4	637	648
-3	906	913
-2	886	911
-1	30	51*
0	329	314
1	231	224
2	138	138
3	0	25*
4	55	34
5	0	47*
6	0	11*
7	199	188
8	155	152
9	0	72*
10	56	38
H,K=	2,	-3
-12	113	113
-11	38	22*
-10	72	74
-9	118	146
-8	0	3*
-7	183	164
-6	76	78
-5	47	38
-4	37	28*
-3	293	288
-2	134	130
-1	140	139
0	436	443
1	226	230
2	176	160
3	325	314
4	158	158
5	76	78
6	203	196
7	70	87
8	73	78
9	122	133
H,K=	2,	-4

-11	39	42*
-10	112	107
-9	196	189
-8	83	77
-7	152	148
-6	54	84
-5	268	273
-4	124	122
-3	28	40*
-2	105	107
-1	66	61
0	27	104*
1	195	190
2	86	85
3	85	108
4	99	108
5	218	225
6	162	172
7	136	131
8	38	27*
9	40	23*
H,K=	2,	-5
-10	68	43
-9	0	45*
-8	51	73
-7	120	114
-6	163	158
-5	45	16
-4	162	155
-3	136	135
-2	217	213
-1	112	110
0	52	33
1	87	93
2	181	177
3	0	2*
4	291	283
5	61	67
6	121	121
7	0	21*
8	105	118
H,K=	2,	-6
-9	112	116
-8	0	4*
-7	233	252
-6	0	35*
-5	155	163
-4	59	60
-3	0	34*
-2	119	119
-1	47	20
0	159	169
1	237	239
2	0	4*
3	168	169
4	0	8*
5	144	152
6	0	37*
7	0	61*
H,K=	2,	-7
-7	0	40*
-6	230	210
-5	53	60
-4	52	3
-3	89	75
-2	51	66
-1	134	128
0	88	96
1	51	18
2	157	158
3	141	140
4	150	154
5	199	195
H,K=	2,	-8
-5	0	13*
-4	97	93
-3	0	55*
-2	0	2*
-1	0	25*
0	87	103
1	0	37*
2	80	90
3	121	117
H,K=	3,	0
-12	137	135
-10	112	95

-8	243	244
-6	239	230
-4	144	142
-2	209	199
0	285	298
2	683	663
4	318	329
6	189	191
8	161	183
H,K=	3,	-1
-13	70	65
-12	0	9*
-11	96	103
-10	123	128
-9	188	189
-8	0	4*
-7	578	583
-6	0	7*
-5	86	101
-4	439	434
-3	807	834
-2	0	15*
-1	31	7*
0	149	145
1	188	191
2	103	114
3	478	471
4	157	157
5	76	64
6	0	53*
7	131	123
8	37	65*
9	0	35*
H,K=	3,	-2
-12	116	149
-11	110	97
-10	70	82
-9	74	72
-8	239	247
-7	124	133
-6	231	234
-5	181	193
-4	180	182
-3	226	219
-2	108	114
-1	169	158
0	247	243
1	153	160
2	512	503
3	386	384
4	131	131
5	101	94
6	117	129
7	101	96
8	0	4*
9	0	20*
H,K=	3,	-3
-12	97	103
-11	53	68
-10	108	172
-9	226	231
-8	86	75
-7	134	132
-6	381	386
-5	0	12*
-4	542	537
-3	217	228
-2	164	171
-1	26	55*
0	327	327
1	55	67
2	29	36*
3	0	28*
4	63	58
5	33	36*
6	0	79*
7	104	106
8	55	25
H,K=	3,	-4
-11	0	36*
-10	75	89
-9	0	62*
-8	76	34
-7	142	129
-6	31	1*
-5	249	248

-4	188	178
-3	0	37*
-2	103	106
-1	223	225
0	179	176
1	146	151
2	69	78
3	0	16*
4	100	89
5	125	136
6	0	16*
7	143	165
8	132	118
H,K=	3,	-5
-10	0	23*
-9	0	5*
-8	36	34*
-7	0	7*
-6	0	2*
-5	73	64
-4	143	147
-3	70	81
-2	207	209
-1	295	300
0	219	206
1	270	267
2	0	43*
3	68	73
4	35	46*
5	64	32
6	115	96
7	40	7*
H,K=	3,	-6
-9	88	93
-8	0	19*
-7	74	101
-6	36	64*
-5	127	121
-4	0	28*
-3	239	234
-2	0	15*
-1	248	237
0	0	5*
1	60	62
2	101	99
3	0	9*
4	146	158
5	123	114
6	57	71
H,K=	3,	-7
-7	143	142
-6	0	6*
-5	214	190
-4	217	202
-3	37	42*
-2	160	150
-1	52	83
0	74	132
1	84	102
2	0	26*
3	123	124
4	0	17*
H,K=	3,	-8
-4	40	7*
-3	105	104
-2	97	98
-1	40	79*
0	56	53
1	156	157
H,K=	4,	0
-12	0	22*
-10	34	24*
-8	61	65
-6	172	173
-4	343	348
-2	219	217
0	369	347
2	57	45
4	114	105
6	0	22*
8	104	116
H,K=	4,	-1
-13	57	66
-12	148	155
-11	36	16*
-10	97	100

-9	57	76
-8	54	23
-7	144	134
-6	193	187
-5	255	256
-4	26	17*
-3	363	369
-2	353	356
-1	0	25*
0	261	248
1	188	181
2	125	123
3	52	43
4	96	100
5	219	212
6	36	14*
7	140	127
8	39	50*
H,K=	4,	-2
-12	95	81
-11	90	92
-10	35	42*
-9	58	83
-8	0	11*
-7	358	366
7	76	57
-6	290	290
-5	452	447
-4	255	253
-3	26	44*
-2	149	148
-1	53	43
0	303	300
1	238	226
2	230	227
3	76	58
4	80	83
5	246	252
6	256	251
8	160	171
H,K=	4,	-3
-12	0	21*
-11	76	64
-10	114	91
-9	69	69
-8	162	146
-7	0	87*
-6	275	268
-5	386	407
-4	99	91
-3	102	89
-2	229	231
-1	189	182
0	130	136
1	99	97
2	289	299
3	80	85
4	247	245
5	112	128
6	200	202
7	0	19*
H,K=	4,	-4
-11	78	105
-10	53	74
-9	204	203
-8	0	49*
-7	106	87
-6	177	173
-5	218	214
-4	44	29*
-3	0	12*
-2	208	210
-1	75	41
0	93	99
1	45	12
2	109	102
3	48	46
4	151	141
5	74	78
6	0	37*
7	0	5*
H,K=	4,	-5
-10	111	105
-9	161	175
-8	121	109
-7	61	70

-6	60	59
-5	48	53
-4	0	29*
-3	0	32*
-2	143	136
-1	219	218
0	236	233
1	181	191
2	243	249
3	36	52*
4	129	137
5	67	71
6	90	89
H,K=	4,	-6
-9	144	138
-8	55	27
-7	65	89
-6	0	53*
-5	51	65
-4	50	21
-3	0	8*
-2	93	98
-1	198	195
0	0	41*
1	242	245
2	37	44*
3	191	200
4	0	50*
H,K=	4,	-7
-7	0	40*
-6	0	21*
-5	55	38
-4	0	11*
-3	0	72*
-2	0	37*
-1	54	119
0	38	46*
1	39	11*
2	97	76
H,K=	5,	0
-12	108	117
-10	126	130
-8	90	82
-6	72	72
-4	224	229
-2	479	478
0	709	719
2	109	106
4	77	81
6	66	71
H,K=	5,	-1
-13	0	53*
-12	0	34*
-11	173	167
-10	79	66
-9	217	217
-8	208	202
-7	144	150
-6	0	3*
-5	307	301
-4	40	48*
-3	0	18*
-2	49	56
-1	141	136
0	193	183
1	312	315
2	55	53
3	67	93
4	60	70
5	115	114
6	216	221
7	0	45*
H,K=	5,	-2
-12	39	72*
-11	0	25*
-10	182	183
-9	0	16*
-8	87	71
-7	145	151
-6	225	229
-5	73	59
-4	41	27
-3	331	326
-2	51	59
-1	350	330
0	219	241

1	83	92
2	226	221
3	48	65
4	331	331
5	83	99
6	134	136
H,K=	5,	-3
-12	40	52*
-11	127	123
-10	64	36
-9	71	66
-8	59	35
-7	171	173
-6	45	63
-5	0	13*
-4	31	38*
-3	118	115
-2	69	47
-1	204	204
0	177	182
1	33	48*
2	68	83
3	35	25*
4	52	59
5	66	55
6	143	139
H,K=	5,	-4
-11	0	13*
-10	0	34*
-9	138	122
-8	0	4*
-7	219	218
-6	75	62
-5	172	170
-4	46	8
-3	0	6*
-2	216	224
-1	81	80
0	0	37*
1	77	58
2	0	30*
3	52	74
4	0	36*
5	39	32*
H,K=	5,	-5
-10	0	34*
-9	154	157
-8	0	36*
-7	63	55
-6	205	211
-5	35	35*
-4	230	231
-3	35	28*
-2	252	246
-1	49	50
0	50	58
1	0	33*
2	0	7*
3	86	100
4	97	113
H,K=	5,	-6
-8	68	76
-7	0	15*
-6	38	71*
-5	135	113
-4	0	4*
-3	271	277
-2	74	72
-1	163	161
0	113	107
1	139	132
2	130	130
3	99	89
H,K=	5,	-7
-6	121	120
-5	0	2*
-4	112	120
-3	68	59
-2	39	48*
-1	40	35*
0	0	5*
H,K=	6,	0
-12	0	38*
-10	108	103
-8	157	160
-6	0	46*

-4	187	194
-2	124	130
0	56	78
2	0	15*
4	130	130
H,K=	6,	-1
-12	0	17*
-11	38	28*
-10	0	64*
-9	60	93
-8	75	42
-7	160	165
-6	45	61
-5	264	264
-4	170	176
-3	186	185
-2	153	150
-1	227	227
0	0	21*
1	0	10*
2	0	10*
3	51	59
4	106	95
5	124	106
H,K=	6,	-2
-12	138	122
-11	38	27*
-10	37	1*
-9	87	98
-8	34	45*
-7	125	128
-6	46	55
-5	64	76
-4	55	29
-3	78	90
-2	0	16*
-1	98	94
0	82	83
1	109	108
2	123	105
3	122	128
4	66	29
5	89	82
H,K=	6,	-3
-11	55	61
-10	76	103
-9	90	93
-8	94	95
-7	77	68
-6	0	35*
-5	0	2*
-4	196	207
-3	57	39
-2	94	90
-1	76	63
0	218	218
1	0	14*
2	216	206
3	38	48*
4	196	208
H,K=	6,	-4
-10	39	49*
-9	157	156
-8	161	169
-7	149	138
-6	112	89
-5	78	111
-4	222	230
-3	130	127
-2	178	181
-1	123	117
0	0	24*
1	37	48*
2	182	179
3	68	71
4	40	43*
H,K=	6,	-5
-9	56	43
-8	155	139
-7	38	39*
-6	37	24*
-5	0	27*
-4	0	40*
-3	137	137
-2	227	232
-1	53	25

0	156	159
1	55	78
2	158	152
H,K=	6,	-6
-7	69	39
-6	56	32
-5	95	98
-4	103	97
-3	55	40
-2	0	31*
-1	68	97
0	0	22*
H,K=	7,	0
-12	0	12*
-10	150	149
-8	71	80
-6	163	173
-4	34	27*
-2	221	215
0	151	154
2	210	219
4	0	23*
H,K=	7,	-1
-12	0	13*
-11	110	96
-10	53	51
-9	151	133
-8	71	98
-7	60	39
-6	0	5*
-5	34	50*
-4	162	165
-3	183	205
-2	175	183
-1	131	148
0	36	65*
1	104	103
2	107	110
3	0	4*
H,K=	7,	-2
-11	0	38*
-10	77	72
-9	118	91
-8	72	73
-7	71	64
-6	221	185
-5	138	124
-4	236	238
-3	134	131
-2	135	135
-1	36	37*
0	115	106
1	0	11*
2	77	76
3	0	2*
H,K=	7,	-3
-11	0	3*
-10	55	54
-9	66	92
-8	0	7*
-7	0	46*
-6	0	55*
-5	0	26*
-4	101	81
-3	0	4*
-2	81	59
-1	0	9*
0	0	44*
1	143	141
2	79	87
H,K=	7,	-4
-9	56	25
-8	144	145
-7	38	75*
-6	37	70*
-5	157	152
-4	0	16*
-3	170	167
-2	53	33
-1	142	138
0	77	50
1	68	10
H,K=	7,	-5
-8	70	77
-7	69	51
-6	103	106

-5	0	18*
-4	178	177
-3	55	35
-2	39	41*
-1	56	63
0	0	39*
H,K=	8,	0
-10	56	61
-8	38	70*
-6	121	128
-4	196	191
-2	52	67
0	39	63*
H,K=	8,	-1
-10	40	62*
-9	39	63*
-8	76	97
-7	174	163
-6	169	177
-5	127	133
-4	37	54*
-3	138	148
-2	91	107
-1	0	6*
0	134	143
1	0	3*
H,K=	8,	-2
-10	80	100
-9	0	8*
-8	138	134
-7	65	91
-6	112	103
-5	149	131
-4	37	19*
-3	92	79
-2	0	14*
-1	0	3*
0	56	25
1	0	2*
H,K=	8,	-3
-9	0	14*
-8	0	33*
-7	55	48
-6	167	189
-5	101	118
-4	101	110
-3	94	104
-2	0	13*
-1	0	5*
0	0	2*
H,K=	8,	-4
-7	57	53
-6	0	13*
-5	0	41*
-4	131	132
-3	0	46*
-2	0	33*
H,K=	9,	0
-6	39	12*
-4	39	87*
-2	170	167
H,K=	9,	-1
-8	57	80
-7	40	59*
-6	56	29
-5	56	60
-4	56	77
-3	80	82
-2	0	11*
H,K=	9,	-2
-7	80	68
-6	106	103
-5	98	96
-4	0	9*
-3	0	14*

[a] Asterisk indicates zero weighted datum.

TABLE II

POSITIONAL PARAMETERS[a]

ATOM	X	Y	Z
S	.2133(2)	.4534(2)	.4548(1)
C1	.2014(7)	.2717(7)	.3961(5)
C2	.1241(8)	.2750(9)	.2760(5)
C3	.1712(14)	.1609(15)	.2195(8)
C4	.1189(8)	.1722(8)	.4455(5)
C5	.9551(11)	.1979(11)	.4131(7)
C6	.3894(7)	.1003(7)	.0543(5)
C7	.4513(9)	.0035(8)	.1454(6)
C8	.5928(10)	.0406(10)	.2387(6)
C9	.4425(8)	.2210(7)	.0260(5)
C10	.5855(10)	.3056(10)	.0750(8)
O1	.3506(5)	.2194(5)	.4291(3)
O2	.0291(6)	.3634(7)	.2307(4)
O3	.1923(6)	.0857(5)	.5127(4)
O4	.3850(6)	.6091(5)	.6450(4)
H(1)	.2746(73)	.1789(75)	.2232(56)
H(2)	.1230(104)	.1568(107)	.1672(60)
H(3)	.1681(88)	.0723(78)	.2443(58)
H(4)	.0822(115)	.6794(114)	.1458(69)
H(5)	.0796(103)	.8049(95)	.0973(65)
H(6)	.0877(93)	.6588(95)	.0355(64)
H(7)	.3207(70)	.5461(77)	.2843(48)
H(8)	.4123(80)	.6211(74)	.2304(55)
H(9)	.3843(71)	.4679(68)	.2061(48)
H(10)	.3516(97)	.7920(101)	.3709(63)
H(11)	.3438(86)	.7447(88)	.4454(60)
H(12)	.4274(91)	.8909(81)	.4044(63)

[a]Standard deviation is in parentheses and refers to the least significant digit.

TABLE III

ANISOTROPIC THERMAL PARAMETERS[a,b]

ATOM	B11	B22	B33	B12	B13	B23
S	4.24(9)	3.68(9)	4.36(9)	.12(9)	1.36(7)	.06(8)
C1	3.40(36)	4.02(37)	4.11(38)	-.16(32)	1.82(31)	-.30(28)
C2	4.75(44)	6.06(47)	3.48(43)	-.46(38)	1.70(39)	-.42(38)
C3	9.13(81)	8.61(68)	5.31(54)	-.96(70)	3.25(63)	-.57(61)
C4	3.97(49)	4.56(42)	3.65(37)	-.98(33)	.74(35)	-.84(31)
C5	4.04(55)	7.78(56)	7.04(56)	-.87(42)	1.49(45)	.83(54)
C6	3.64(36)	3.25(36)	3.63(34)	.04(29)	1.38(30)	.30(29)
C7	5.44(48)	3.87(46)	4.36(39)	.75(35)	2.63(38)	.61(35)
C8	5.66(50)	6.40(53)	4.57(47)	1.23(54)	.46(45)	.40(39)
C9	4.04(39)	3.65(41)	3.27(36)	1.13(35)	1.59(32)	.13(32)
C10	3.60(49)	4.71(48)	8.31(58)	.20(44)	.53(42)	-1.41(50)
O1	4.16(26)	4.70(26)	4.37(24)	-.21(22)	1.58(21)	-.96(20)
O2	7.26(35)	9.37(38)	4.19(28)	2.11(31)	.75(26)	1.17(26)
O3	6.02(30)	6.45(32)	5.70(28)	-.81(25)	1.18(25)	2.23(24)
O4	7.63(35)	3.99(29)	6.06(28)	.35(25)	2.11(26)	-1.47(23)

[a]Standard deviation is in parentheses and refers to the least significant digit.

[b]Units of B are in $Å^2$.

Discussion

The 1,3 oxathiole ring is shown in Fig. 1. The C1--O1 and C1--S distances are typical of bond lengths found in paraffinic and saturated heterocyclic type compounds[6]. C6--C9 is a typical double bond at 1.34 Å. C9--O1 and C6--S are shorter by .05 and .04 Å respectively than the C1--O1 C1--S distances, probably because of their proximity to the double bond. The ring itself is puckered, with the sum of the internal angles being 533° opposed to a theoretical 540° for a planar model. This puckering is evident in the stereoscopic view of the molecule shown in Fig. 2. A stereoscopic view of the molecular packing is shown in Fig. 3.

Table IV lists all of the distances in the structure less than 3 Å, and Table V lists some of the angles.

References

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) Dr. Edward C. Taylor, private communication.

(3) D. T. Cromer and J. T. Waber, Acta Cryst., 18, 104 (1965).

(4) R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Phys. Chem., 42, 3175 (1965).

(5) D. T. Cromer, Acta Cryst., 18, 17 (1965).

(6) "Table of Interatomic Distances and Configurations in Molecules and Ions," Supplement 1956-1959, L. E. Sutton, Editor, published by the Chemical Society, Burlington House, London W1.

TABLE IV

INTERATOMIC DISTANCES (Å) IN 5 METHYL-2,2,4-TRIACETYL-1,3-OXATHIOLE[a,b]

Atom	Dist.	Atom	Dist.	Atom	Dist.
S -C(6)	1.775(6)	C(4) -O(3)	1.202(7)	C(1) -H(1)	2.88(7)
S -C(1)	1.821(6)	C(4) -C(5)	1.50(1)	C(2) -H(2)	1.84(9)
S -C(9)	2.592(7)	C(4) -O(1)	2.416(8)	C(2) -H(3)	1.98(7)
S -O(1)	2.620(5)	O(3) -C(5)	2.39(1)	C(2) -H(1)	2.09(7)
S -C(4)	2.704(7)	O(3) -O(1)	2.588(6)	C(2) -H(4)	2.8(1)
S -C(7)	2.729(8)	O(3) -C(9)	2.964(8)	O(2) -H(2)	2.4(1)
S -C(2)	2.772(7)	C(6) -C(9)	1.340(8)	O(2) -H(3)	2.83(7)
S -O(4)	2.840(5)	C(6) -C(7)	1.445(8)	O(2) -H(4)	2.9(1)
S -O(2)	2.978(5)	C(6) -O(4)	2.286(8)	O(2) -H(3)	2.95(7)
C(1) -O(1)	1.425(6)	C(6) -O(1)	2.295(8)	O(2) -H(1)	2.97(7)
C(1) -C(2)	1.509(8)	C(6) -C(8)	2.56(1)	C(3) -H(2)	0.68(7)
C(1) -C(4)	1.547(8)	C(6) -C(10)	2.61(1)	C(3) -H(3)	0.88(7)
C(1) -C(9)	2.306(9)	C(7) -O(4)	1.211(7)	C(3) -H(1)	1.01(6)
C(1) -O(2)	2.360(8)	C(7) -C(8)	1.49(1)	C(4) -H(4)	1.9(1)
C(1) -O(3)	2.360(7)	C(7) -C(9)	2.55(1)	C(4) -H(6)	2.15(9)
C(1) -C(6)	2.489(9)	O(4) -C(8)	2.35(1)	C(4) -H(5)	2.16(9)
C(1) -C(3)	2.53(1)	C(9) -O(1)	1.377(6)	O(3) -H(6)	2.52(9)
C(1) -C(5)	2.61(1)	C(9) C(10)	1.50(1)	O(3) -H(9)	2.60(6)
C(2) -O(2)	1.194(7)	C(10)-O(1)	2.36(1)	O(3) -H(6)	2.63(8)
C(2) -C(3)	1.48(1)	S -H(11)	2.97(8)	O(3) -H(4)	2.8(1)
C(2) -O(1)	2.405(9)	S -H(5)	2.98(9)	C(5) -H(4)	0.76(8)
C(2) -C(4)	2.54(1)	C(1) -H(3)	2.68(8)	C(5) -H(5)	1.02(9)
O(2) -C(3)	2.35(2)	C(1) -H(4)	2.7(1)	C(5) -H(6)	1.02(8)
C(3) -O(1)	2.74(1)	C(1) -H(5)	2.82(9)	C(6) -H(8)	2.80(7)

TABLE IV (continued)

Atom	Dist.	Atom	Dist.
C(6) -H(7)	2.84(6)	O(1) -H(12)	2.63(8)
C(6) -H(10)	2.90(9)	O(1) -H(1)	2.64(7)
C(6) -H(11)	2.93(7)	O(1) -H(3)	2.78(7)
C(7) -H(8)	1.99(7)	O(1) -H(11)	2.80(8)
C(7) -H(9)	2.04(6)	H(1) -H(2)	1.4(1)
C(7) -H(7)	2.08(6)	H(1) 9H(3)	1.5(1)
C(7) -H(1)	2.87(7)	H(1) -H(9)	2.89(9)
O(4) -H(9)	2.45(6)	H(1) -H(8)	2.9(1)
O(4) -H(8)	2.69(6)	H(2) -H(3)	1.2(1)
O(4) -H(11)	2.89(7)	H(4) -H(5)	1.3(1)
O(4) -H(5)	2.90(9)	H(4) -H(6)	1.6(1)
O(4) -H(8)	2.91(7)	H(4) -H(7)	2.6(1)
O(4) -H(7)	3.00(7)	H(5) -H(6)	1.6(1)
C(8) -H(8)	0.86(6)	H(7) -H(8)	1.5(1)
C(8) -H(9)	0.96(6)	H(7) -H(9)	1.62(9)
C(8) -H(7)	1.02(6)	H(7) -H(10)	2.5(1)
C(8) -H(10)	2.91(9)	H(7) -H(11)	2.8(1)
C(9) -H(11)	1.98(8)	H(8) -H(9)	1.43(8)
C(9) -H(12)	1.98(7)	H(8) -H(10)	2.7(1)
C(9) -H(10)	2.04(8)	H(9) -H(12)	2.9(1)
C(10)-H(10)	0.76(8)	H(10)-H(12)	1.1(1)
C(10)-H(12)	0.85(7)	H(10)-H(11)	1.1(1)
C(10)-H(11)	1.01(8)	H(11)-H(12)	1.8(1)
C(10)-H(7)	2.95(7)		

[a] Table contains all interatomic distances 3.00 Å or less.

[b] Estimated standard deviations are indicated in parentheses.

TABLE V

ANGLES IN 5 METHYL-2,2,4-TRIACETYL-2,3-OXATHIOLE

Atoms	Angle, deg[a]	Atoms	Angle, deg[a]
C(1)-S-C(6)	87.6(4)	C(1)-C(2)-O(2)	121.2(6)
S-C(1)-O(1)	107.0(3)	C(1)-C(2)-C(3)	116.0(7)
C(1)-O(1)-C(9)	110.8(6)	C(4)-C(1)-O(1)	108.7(6)
O(1)-C(9)-C(6)	115.3(5)	C(3)-C(2)-O(2)	122.9(7)
S-C(6)-C(9)	111.9(4)	C(5)-C(4)-O(3)	124.1(6)
S-C(1)-C(2)	112.4(4)	C(7)-C(6)-C(9)	132.5(7)
S-C(1)-C(4)	106.5(3)	O(4)-C(7)-C(8)	120.2(6)
S-C(6)-C(7)	115.5(4)	C(6)-C(7)-O(4)	118.5(6)
C(2)-C(1)-O(1)	108.7(6)	C(6)-C(7)-C(8)	121.3(7)
C(2)-C(1)-C(4)	112.1(5)	C(6)-C(9)-C(10)	134.0(6)
C(1)-C(4)-O(3)	117.7(6)	C(10)-C(9)-O(1)	110.7(7)
C(1)-C(4)-C(5)	118.1(6)		

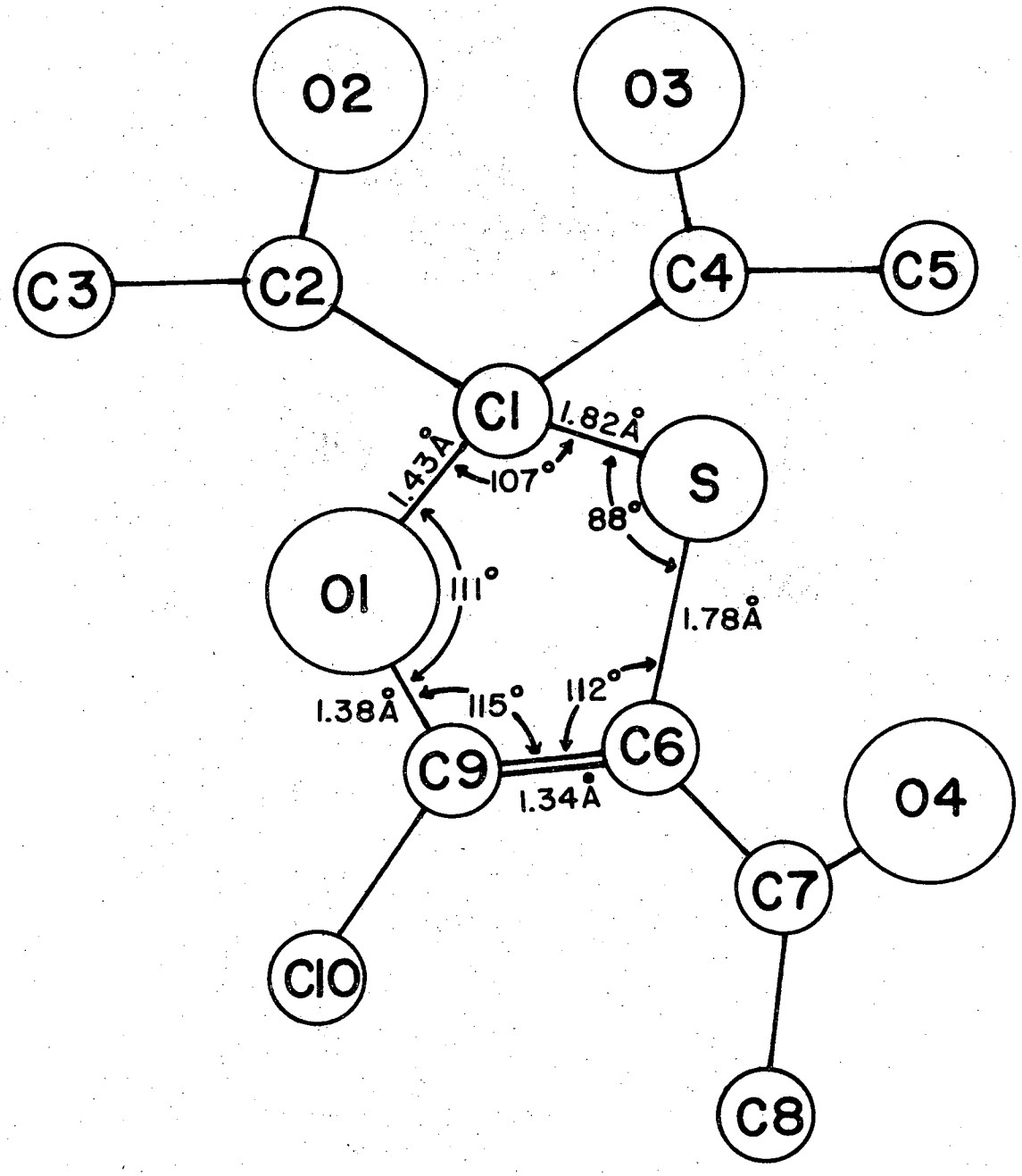
[a] Standard deviation is in parentheses and refers to the least significant digit.

Figure Captions

Fig. 1. Schematic drawing showing bonds and angles in the ring.

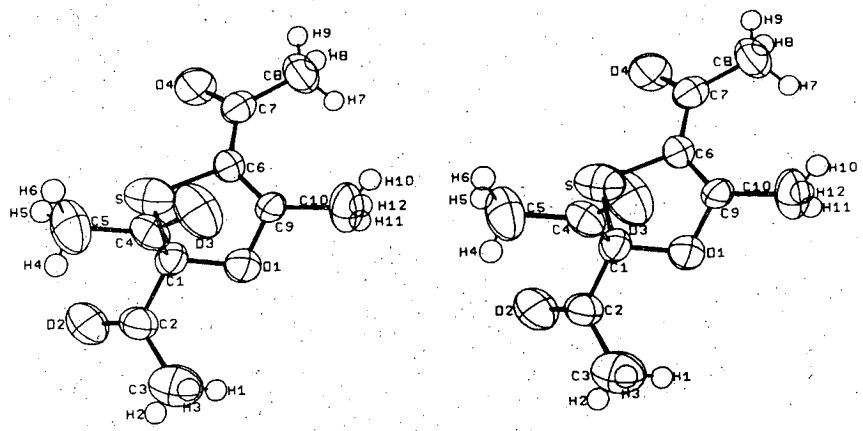
Fig. 2. Stereoscopic view of the 5-methyl-2,2,4-triacetyl-1,3-oxathiole molecule.

Fig. 3. Stereoscopic view of the packing of the oxathiole molecules in the unit cell.



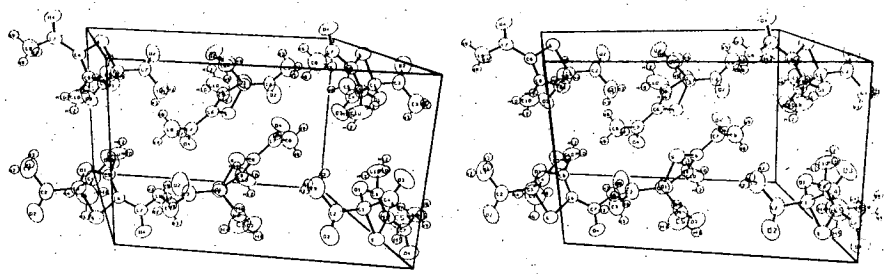
XBL 708-1791

Fig. 1



XBL 693-325

Fig. 2



XBL 695-504

Fig. 3

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