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The Crystal Structure of 4,4'-Diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl (C₁₂H₁₂N₂S₂O₄)*

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The reaction product of α-mercapto acids with cyanogen undergoes unusual *N*-methylation in addition to esterification when treated with diazomethane and converts to the bicyclic symmetrical 4,4'-diketo-Δ^2-bithiazolinyl. The structure of the bicyclic compound has been a moot question for many years. Some investigations favored two six-membered rings with a shared edge; others, two five-membered rings bonded together. A crystal-structure determination of 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl proves that this compound consists of two five-membered rings joined by a C–C bond. The crystallographic data for the monoclinic crystals are $a = 13\cdot125 \pm 0\cdot005$, $b = 4\cdot830 \pm 0\cdot002$, $c = 10\cdot995 \pm 0\cdot004$ Å, $\beta = 94\cdot09 \pm 0\cdot01°$, $Z = 2$, space group $P2_1/c$. The intensities of 1367 independent reflections were measured with an automatic diffractometer. Least-squares refinement with anisotropic thermal parameters for the ten heavy atoms and isotropic thermal parameters for the hydrogen atoms gave an R value of 0·050.

In their studies of the reaction of α-mercapto acids with cyanogen, Mutha & Ketchum (1968) found that the reaction between mercaptoacetic acid and cyanogen (Fig. 1) gave a white crystalline product which proved to be monocyclic. Cyclization can result in the formation of a five-membered ring [Fig. 1(*a*)] or a six-membered ring [Fig. 1 (*b*)]. Their study of the ultraviolet (UV), infrared (IR), and nuclear magnetic resonance (n.m.r) spectra of this product and several derivatives did not furnish a clear distinction between the two structures.

To obtain additional information, Mutha & Ketchum synthesized a bicyclic compound whose structure after acetylation, was either that of Fig. 2(*a*) or 2(*b*). Their study of the UV, IR, and n.m.r. spectra and a dipole-moment determination again failed to provide an unequivocal assignment of structure. Attempts to grow crystals suitable for X-ray analysis, from the various derivatives of both the monocyclic and bicyclic

compounds, led to the selection of the diacetate derivative of the bicyclic compound for crystal-structure analysis. The compound turned out to be 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl, hereafter referred to as DDB.

Experimental

The material used in this investigation was provided by Professor R. Ketchum and Dr S. Mutha. Crystals suitable for X-ray analysis were grown from chloroform. The crystals are elongated prisms with **b** parallel to the long axis and (100) prominent. The crystals cleave easily, parallel to the **ab** plane, but cannot be cut perpendicular to **b** without introducing X-ray line broadening. Consequently, the intensity data were taken on an uncut specimen with dimensions of 0·07 × 0·20 × 0·14 mm.

Multiple-level Weissenberg photographs showed that the only systematic absences are 0*k*0 when *k* is odd, and *h*0*l* when *l* is odd. These extinctions indicate space group P2₁/*c* which was confirmed by the struc-

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ture determination. The density, measured by flotation restricts the number of molecules per unit cell to two; consequently, the asymmetric unit is half the molecule ($C_6H_6NSO_2$).

Unit-cell dimensions were obtained by taking 2θ scans with a 1° take-off angle for several reflections of the type $h00$, $0k0$, and $00l$. The cell dimension and other physical data are:

$C_{12}N_{12}N_2S_2O_4$ F.W. 312·36
Monoclinic   Space group $P2_1/c$
$a=13\cdot125\pm0\cdot005$ Å $Z=2$
$b=\ 4\cdot830\pm0\cdot004$ $F(000)=325\cdot25$
$c=10\cdot995\pm0\cdot002$ $D_m=1\cdot44$ g.cm^{-3}
$\beta=94\cdot09\pm0\cdot01°$ $D_c=1\cdot49$
λCu $K\alpha=1\cdot5418$ Å λ Cu $K\alpha_1=1\cdot5404$ Å
Number of independent reflections 1367

Intensity data were obtained with a card-oriented 4-circle automatic X-ray diffractometer. The diffracto-meter consists of a G.E. power supply and spectrometer, Electronic and Alloy's full-circle goniostat, Datex controller, and a Picker solid-state detector equipped with a single-channel pulse-height analyzer. Integrated intensities were determined by scanning over the peak at a rate of 1°/min and subtracting a background obtained by averaging two values, one taken $\frac{1}{2}$° before the beginning point and the other $\frac{1}{2}$° beyond the end of the 2θ scan. Each background was counted for 10 sec.

Intensities of 1752 reflections were measured, of which 1367 were independent. Of these, 25 had zero intensity and 57 had intensities which were less than 1σ, where σ was calculated by the expression $\sigma(I)=[C+(T_c/2T_b)^2\ (B_1+B_2)+(0\cdot05\ I)^2]^{1/2}$ where C is the total counts in scan time T_c. B_1 and B_2 are the background counts taken for $T_b=10$ sec. The factor 0·05 was arbitrarily chosen to account for nonrandom errors.

Lorentz and polarization corrections were made in the usual way. No corrections were made for absorption, but in the final stages of least-squares refinement a correction for secondary extinction was made as discussed below.

Determination of the structure

Normalized structure factors $|E|$ were calculated with Wilson's method by means of a computer program written by Maddox & Maddox (1965). A second program (Long, 1965) was used to calculate phases
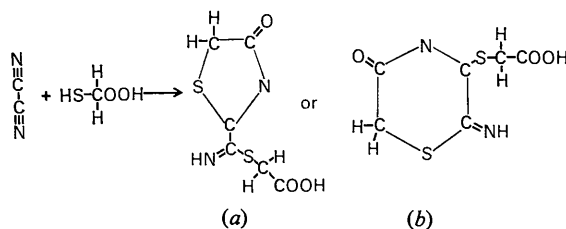

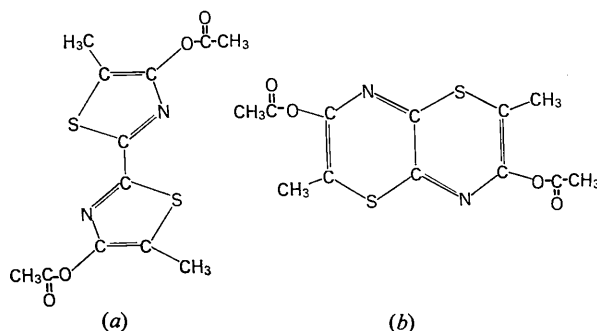Fig. 1. Reaction between mercaptoacetic acid and cyanogen to produce a monocyclic compound.

Fig. 2. Two possible structures for the methyl ester of the bicyclic product.

Table 1. Positional and anisotropic thermal parameters

The positional parameters are for a molecule centered at $(0,\frac{1}{2},0)$. Calculated standard deviations are in parentheses. Thermal parameters for the heavy atoms are in the form exp $(-\sum \beta_{ij}h_ih_jb_ib_j/4)$, where b_ib_j are reciprocal cell lengths.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	0·05298 (4)	0·2132 (1)	0·14485 (4)	2·93 (3)	3·35 (3)	2·52 (3)	0·17 (2)	0·67 (2)	0·31 (2)
O(1)	0·2619 (1)	0·0981 (4)	−0·0789 (2)	2·77 (6)	4·68 (9)	3·25 (7)	0·22 (6)	0·88 (5)	−1·05 (6)
O(2)	0·3703 (2)	0·3797 (7)	0·0254 (3)	3·67 (9)	9·6 (2)	8·3 (2)	−1·8 (1)	1·99 (9)	−4·9 (1)
N	0·1163 (1)	0·3709 (4)	−0·0601 (2)	2·54 (7)	3·42 (8)	2·29 (7)	−0·16 (6)	0·45 (5)	−0·08 (6)
C(2)	0·0423 (1)	0·4062 (5)	0·0132 (2)	2·51 (7)	3·05 (9)	2·25 (7)	−0·28 (6)	0·28 (5)	−0·22 (6)
C(4)	0·1823 (2)	0·1813 (5)	−0·0100 (2)	2·41 (8)	3·30 (9)	2·54 (8)	0·02 (7)	0·49 (6)	−0·54 (7)
C(5)	0·1645 (2)	0·0696 (5)	0·1004 (2)	2·80 (8)	2·94 (8)	2·67 (8)	0·07 (7)	0·25 (6)	−0·37 (7)
C(6)	0·2254 (2)	−0·1377 (6)	0·1748 (3)	3·9 (1)	3·5 (1)	3·6 (1)	0·73 (9)	−0·02 (8)	−0·01 (9)
C(7)	0·3538 (2)	0·2193 (6)	−0·0550 (3)	2·64 (9)	4·8 (1)	3·7 (1)	0·31 (8)	0·76 (8)	−0·36 (9)
C(8)	0·4285 (2)	0·116 (1)	−0·1413 (3)	3·4 (1)	7·7 (2)	4·7 (1)	1·0 (1)	1·7 (1)	−0·4 (1)
H(1)	0·444 (3)	−0·10 (1)	−0·133 (4)	5·9 (9)					
H(2)	0·408 (3)	0·136 (8)	−0·220 (4)	5·5 (9)					
H(3)	0·490 (4)	0·20 (1)	−0·136 (4)	7·7 (12)					
H(4)	0·192 (5)	−0·23 (1)	0·215 (6)	9·8 (16)					
H(5)	0·284 (3)	−0·07 (1)	0·213 (4)	7·7 (11)					
H(6)	0·252 (5)	−0·22 (1)	0·137 (6)	8·7 (16)					

by use of Sayre's equation and a method similar to the symbolic addition procedure of Karle & Karle (1966). Origin-determining signs were chosen for $9\,2\,\bar{5}$, $3\,1\,\overline{10}$, and $6\,1\,\bar{8}$ as all positive. The 32 possible combinations of signs of five additional reflections were used to calculate probable phases for the 102 reflections whose $|E|$ values were $\geq 1{\cdot}50$. One combination of signs was clearly superior to the rest. This solution had a consistency index of 0·99 compared with the next best value of 0·92, and took the least number of cycles to converge (5). The signs of the seven starting reflections did not change during the five cycles, and the final distribution of signs was 50 plus and 50 minus. The chosen reflections, their $|E|$ values, and their correct phases are:

$9\,2\,\bar{5}$	$+2{\cdot}74$	$9\,1\,\bar{2}$	$-2{\cdot}56$
$3\,1\,\overline{10}$	$+2{\cdot}68$	$1\,1\,2$	$-2{\cdot}57$
$6\,1\,\bar{8}$	$+2{\cdot}35$	$7\,1\,\bar{8}$	$-2{\cdot}57$
$3\,2\,3$	$+2{\cdot}70$	$5\,1\,\bar{4}$	$+2{\cdot}46$

An E Fourier synthesis clearly showed the positions

Table 2. *Observed and calculated structure factors* ($\times$ 10)

FCA(0,0,0) = 3253

L	FOB	FCA
H,K=	0,	0
2	743	816
4	343	322
6	250	247
8	91	81
10	172	155
12	58	59
H,K=	0,	1
1	203	212
2	20	23
3	609	573
4	283	263
5	290	253
6	309	307
7	9	5
8	178	171
9	12	4
10	138	132
11	12	13
12	72	67
13	20	22
H,K=	0,	2
0	363	389
1	94	92
2	76	64
3	5	5*
4	196	187
5	134	124
6	198	190
7	124	122
8	48	50
9	21	18
10	189	178
11	50	52
12	20	20
H,K=	0,	3
1	155	148
2	256	243
3	210	207
4	129	119
5	33	36
6	120	113
7	193	179
8	92	81
9	0	3*
10	56	57
11	18	17
H,K=	0,	4
0	96	89
1	88	91
2	111	100
3	26	27
4	91	84
5	127	115
6	45	43
7	11	9
8	48	46
9	81	80
10	58	62
H,K=	0,	5
1	116	109
2	102	96
3	12	10
4	30	30
5	51	50
6	31	31
7	107	111
H,K=	1,	0
-12	79	75
-10	33	32
-8	261	227
-6	22	29
-4	752	705
-2	120	126
0	397	588
2	20	17
4	288	266
6	398	364
8	52	43
10	154	147
12	8	11
H,K=	1,	1
-13	8	6
-12	126	122
-11	9	6
-10	130	122
-9	10	8
-8	155	148
-7	33	34
-6	263	242
-5	160	154
-4	258	239
-3	171	162
-2	58	51
-1	12	13
0	557	817
1	188	184
2	1068	1091
3	23	17
4	240	231
5	108	104
6	357	324
7	70	64
8	202	200
9	31	40
10	15	20
11	0	3*
12	102	95
13	0	4*
H,K=	1,	2
-12	58	58
-11	88	87
-10	149	138
-9	12	15
-8	164	156
-7	9	8
-6	131	125
-5	135	124
-4	333	321
-3	323	282
-2	68	64
-1	177	178
0	215	240
1	387	372
2	220	206
3	225	208
4	109	105
5	261	236
6	256	251
7	8	4*
8	59	62
9	137	125
10	109	99
11	52	50
12	53	55
H,K=	1,	3
-11	87	87
-10	50	50
-9	0	1*
-8	96	93
-7	172	158
-6	186	176
-5	78	77
-4	55	50
-3	176	154
-2	324	295
-1	106	107
0	103	107
1	0	4*
2	19	30
3	76	76
4	68	63
5	118	106
6	66	63
7	121	108
8	115	109
9	11	6
10	76	73
11	0	10*
H,K=	1,	4
-10	58	59
-9	77	76
-8	36	35
-7	62	56
-6	37	32
-5	176	164
-4	83	76
-3	22	22
-2	44	42
-1	75	74
0	42	48
1	136	124
2	136	128
3	95	88
4	154	141
5	15	13
6	109	104
7	127	118
8	65	65
9	99	97
H,K=	1,	5
-7	79	79
-6	15	13
-5	25	28
-4	53	50
-3	59	55
-2	108	100
-1	118	115
0	33	37
1	88	82
2	47	43
3	68	63
4	33	34
5	46	45
6	11	5
7	97	103
H,K=	2,	0
-12	128	124
-10	154	151
-8	307	299
-6	25	19
-4	519	505
-2	468	450
0	29	22
2	762	753
4	81	63
6	612	591
8	162	147
10	193	196
12	5	8*
H,K=	2,	1
-13	46	47
-12	99	94
-11	151	140
-10	62	61
-9	8	12*
-8	53	49
-7	109	114
-6	202	188
-5	7	4
-4	99	86
-3	176	167
-2	521	525
-1	5	6*
0	192	204
1	642	693
2	527	526
3	533	495
4	248	242
5	56	43
6	47	43
7	107	102
8	290	275
9	24	20
10	24	23
11	59	57
12	40	41
13	13	15
H,K=	2,	2
-12	107	106
-11	83	86
-10	124	113
-9	110	109
-8	151	151
-7	103	98
-6	38	27
-5	79	76
-4	398	378
-3	117	118
-2	48	51
-1	197	196
0	209	229
1	249	241
2	257	250
3	135	132
4	157	160
5	70	30
6	105	99
7	164	154
8	62	63
9	72	69
10	104	100
11	58	53
12	78	81
H,K=	2,	3
-11	141	144
-10	108	101
-9	40	33
-8	13	4
-7	151	138
-6	294	284
-5	89	89
-4	32	29
-3	15	10
-2	212	202
-1	133	141
0	28	35
1	170	165
2	7	8*
3	274	253
4	166	156
5	66	59
6	31	30
7	25	22
8	156	148
9	65	58
10	15	13
11	23	22
H,K=	2,	4
-10	36	35
-9	91	91
-8	38	40
-7	88	83
-6	54	48
-5	146	138
-4	63	60
-3	95	87
-2	35	31
-1	62	58
0	110	115
1	140	145
2	132	126
3	14	16
4	147	138
5	62	59
6	12	14
7	113	107
8	57	56
9	73	74
H,K=	2,	5
-7	52	56
-6	26	30
-5	81	82
-4	54	51
-3	71	70
-2	53	50
-1	120	121
0	18	24
1	54	56
2	27	27
3	71	70
4	52	51
5	34	33
6	9	11
7	35	36
H,K=	3,	0
-12	84	81
-10	67	64
-8	145	146
-6	0	11*
-4	169	156
-2	322	320
0	176	194
2	66	67
4	66	75
6	265	268
8	62	55
10	210	205
12	18	18
H,K=	3,	1
-13	35	38
-12	15	17
-11	147	146
-10	281	272
-9	182	177
-8	131	129
-7	176	172
-6	324	318
-5	11	9
-4	106	102
-3	74	78
-2	292	301
-1	283	293
0	628	817
1	223	223
2	219	215
3	353	319
4	344	339
5	205	198
6	217	205
7	33	23
8	244	230
9	49	48
10	119	113
11	15	16
12	59	56
H,K=	3,	2
-12	104	107
-11	49	50
-10	48	46
-9	85	82
-8	127	124
-7	193	181
-6	216	205
-5	253	255
-4	428	406
-3	249	251
-2	131	134
-1	213	208
0	160	169
1	226	206
2	237	244
3	595	580
4	88	83
5	202	189
6	110	115
7	159	154
8	128	125
9	21	21
10	136	132
11	68	71
12	42	42
H,K=	3,	3
-11	88	94
-10	91	86
-9	13	7
-8	8	18*
-7	49	53
-6	109	110
-5	171	165
-4	128	120
-3	19	10
-2	171	170
-1	92	85
0	74	87
1	30	32
2	50	48
3	192	178
4	232	239
5	48	48
6	145	146
7	27	28
8	15	10
9	82	80
10	60	63
11	23	24
H,K=	3,	4
-9	68	70
-8	54	51
-7	95	90
-6	38	40
-5	60	59
-4	164	161
-3	149	148
-2	91	92
-1	19	20
0	85	91
1	188	201
2	124	125
3	26	24
4	26	22
5	83	80
6	55	53
7	58	56
8	83	86
9	19	21
H,K=	3,	5
-7	60	63
-6	45	45
-5	113	117
-4	23	19
-3	48	48
-2	22	21
-1	113	117
0	0	6*
1	8	13
2	31	35
3	49	51
4	54	57
5	77	81
6	8	3
H,K=	4,	0
-12	48	50
-10	215	207
-8	370	376
-6	177	160
-4	537	544
-2	54	50
0	120	113
2	593	661
4	56	53
6	300	295
8	222	228
10	115	119
12	134	136
H,K=	4,	1
-13	37	39
-12	65	63
-11	46	46
-10	221	218
-9	7	3*
-8	63	61
-7	86	81
-6	116	131
-5	165	150
-4	305	310
-3	12	4
-2	92	93
-1	319	345
0	374	428
1	235	235
2	85	82
3	101	92
4	203	206
5	111	106
6	145	144
7	90	82
8	78	85
9	159	150
10	136	134
11	22	27
12	64	71
H,K=	4,	2
-12	71	72
-11	108	110
-10	62	58
-9	219	216
-8	216	209
-7	28	27
-6	104	99
-5	11	2
-4	200	200
-3	63	68
-2	174	174
-1	6	17*
0	13	15
1	243	235
2	359	378
3	365	365
4	16	6
5	147	135
6	232	232
7	9	7
8	38	33
9	0	2*
10	34	34
11	28	29
12	60	62
H,K=	4,	3
-11	24	25
-10	78	76
-9	71	69
-8	63	63
-7	23	24
-6	55	53
-5	158	156
-4	285	276
-3	27	24
-2	247	244
-1	215	234
0	145	156
1	3	8*
2	20	14
3	125	129
4	202	196
5	95	83
6	9	13
7	0	7*
8	35	34
9	129	124
10	98	101
11	10	5
H,K=	4,	4
-9	25	26
-8	49	46
-7	89	86
-6	47	49
-5	73	73
-4	52	47
-3	217	217
-2	117	117
-1	54	58
0	0	2*
1	150	156
2	77	79
3	54	57
4	53	55
5	28	31
6	45	44
7	72	70
8	28	27
9	9	3
H,K=	4,	5
-6	48	51
-5	59	62
-4	35	36
-3	25	28
-2	6	4*
-1	59	63
0	33	33
1	96	102
2	7	11
3	75	79
4	27	29
5	63	66
6	41	45
H,K=	5,	0
-12	105	107
-10	144	148
-8	425	442
-6	176	171
-4	106	126
-2	235	281
0	236	251
2	153	169
4	317	324
6	205	201
8	183	184
10	12	11
12	111	122
H,K=	5,	1
-13	30	30
-12	25	23
-11	20	14
-10	101	101
-9	56	56
-8	234	237
-7	82	86
-6	101	106
-5	147	143
-4	546	571
-3	330	312
-2	240	240
-1	13	14
0	157	168
1	138	136
2	182	191
3	133	114
4	127	132
5	89	89
6	205	194
7	79	79
8	105	101
9	63	81
10	116	119
11	17	17
12	6	10*
H,K=	5,	2
-12	98	100
-11	113	112
-10	27	27
-9	21	20
-8	103	102
-7	128	130
-6	132	128
-5	101	101
-4	63	55
-3	56	54
-2	396	423
-1	214	231
0	23	21
1	25	25
2	305	327
3	148	152
4	84	84
5	153	150
6	124	117
7	94	96
8	120	120
9	109	102
10	10	9
11	70	71
H,K=	5,	3
-11	0	3*
-10	73	72
-9	81	81
-8	64	62
-7	55	52
-6	141	141
-5	56	54
-4	73	74
-3	83	78
-2	54	54
-1	190	195
0	110	110
1	57	60
2	174	178
3	34	38
4	238	244
5	147	148
6	57	58
7	32	29
8	49	50
9	87	88
10	57	59
H,K=	5,	4
-9	11	11
-8	0	5*
-7	119	117
-6	133	134
-5	28	30
-4	6	3*
-3	96	95
-2	142	149
-1	93	99
0	17	17
1	34	33
2	78	78
3	150	154
4	10	8
5	50	49
6	6	3*
7	78	82
8	52	55
H,K=	5,	5
-6	59	65
-5	15	16
-4	19	22
-3	121	134
-2	10	8
-1	97	103
0	45	48
1	87	91
2	14	8
3	56	58
4	26	27
5	60	61
H,K=	6,	0
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-10	166	165
-8	269	270
-6	111	124
-4	276	265
-2	667	792
0	212	228
2	338	378
4	244	260
6	30	32
8	152	146
10	82	85
12	74	77
H,K=	6,	1
-12	51	54
-11	23	21
-10	50	48
-9	43	41
-8	292	295
-7	87	86
-6	215	222
-5	196	204
-4	96	100
-3	59	69
-2	93	93
-1	18	21
0	334	361
1	116	135
2	135	120
3	130	130
4	11	14
5	162	166
6	201	206
7	37	37
8	48	51
9	54	55
10	124	127
11	47	48
12	20	25
H,K=	6,	2
-12	84	87
-11	77	81
-10	47	46
-9	27	26
-8	47	46
-7	62	69
-6	209	212
-5	76	70
-4	20	23
-3	171	170
-2	272	295
-1	130	134
0	35	41
1	67	66
2	105	108
3	20	22
4	250	256
5	103	104
6	88	96
7	51	50
8	133	133
9	105	107
10	5	3*
11	68	73
H,K=	6,	3
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-9	60	59
-8	15	21
-7	69	71
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-5	146	159
-4	141	138
-3	123	131
-2	170	179
-1	109	113
0	178	187
1	100	106
2	259	268
3	153	152
4	228	231
5	229	235
6	23	23
7	11	8
8	41	46
9	22	24
10	77	80
H,K=	6,	4
-9	24	26
-8	19	23
-7	92	94
-6	133	136
-5	8	5
-4	89	90
-3	63	64
-2	20	15
-1	208	210
0	41	36
1	62	59
2	23	26
3	105	107
4	86	90
5	15	18
6	55	58
7	97	100
8	49	48
H,K=	6,	5
-5	36	40
-4	51	58
-3	68	76
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-1	68	70
0	71	71
1	50	48
2	26	23
3	5	7*
4	8	8
5	71	74
H,K=	7,	0
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-8	26	26
-6	356	380
-4	63	59
-2	350	346
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2	398	412
4	121	111
6	112	114
8	57	63
10	87	86
H,K=	7,	1
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-9	29	30
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-7	87	91
-6	119	119
-5	74	73
-4	156	167
-3	163	165
-2	150	153
-1	208	200
0	206	211
1	52	46
2	221	235
3	14	12
4	48	52
5	19	18
6	300	315
7	78	83
8	53	53
9	69	73
10	62	65
11	31	32
H,K=	7,	2
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-10	113	117
-9	0	5*
-8	74	75
-7	13	14
-6	158	158
-5	118	123
-4	20	17
-3	50	57
-2	76	81
-1	156	167
0	261	263
1	107	106
2	68	63
3	48	47
4	250	265
5	104	99
6	57	58
7	98	101
8	76	81
9	65	64
10	59	61
H,K=	7,	3
-10	83	89
-9	76	78
-8	15	15
-7	77	79
-6	93	97
-5	104	103
-4	209	210
-3	78	83
-2	60	57
-1	30	33
0	132	126
1	118	119
2	55	54
3	64	69
4	19	25
5	78	83
6	89	95
7	16	12
8	44	43
9	6	5*
H,K=	7,	4
-8	45	48
-7	55	58
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-2	16	12
-1	162	160
0	79	80
1	68	67
2	20	20
3	28	24
4	150	153
5	106	108
6	58	62
7	98	98
H,K=	7,	5
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0	39	42
1	114	112
2	0	5*
3	19	20
4	17	18
H,K=	8,	0
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-10	123	120
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-6	332	345
-4	287	299
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2	40	41
4	80	90
6	199	195
8	242	246
10	23	20
H,K=	8,	1
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-8	162	168
-7	158	160
-6	7	0
-5	57	61
-4	134	151
-3	0	4
-2	234	237
-1	152	147
0	203	203
1	90	93
2	321	327
3	16	12
4	91	87
5	20	29
6	183	187
7	7	5
8	0	5
9	0	2
10	22	21
11	24	21
H,K=	8,	2
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-9	35	32
-8	20	19
-7	34	32
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-5	121	130
-4	93	102
-3	64	65
-2	125	123
-1	212	211
0	186	185
1	46	42
2	53	56
3	164	169
4	102	101
5	0	4
6	88	94
7	16	18
8	113	116
9	30	29
10	52	56
H,K=	8,	3
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-1	134	135
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1	129	129
2	117	113
3	0	13
4	82	82
5	15	16
6	117	114
7	61	59
8	58	60
9	17	18
H,K=	8,	4
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-6	32	30
-5	41	41
-4	28	28
-3	16	15
-2	71	62
-1	64	64
0	102	99
1	49	46
2	51	51
3	45	39
4	89	87
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-3	71	74
-2	42	44
-1	19	18
0	15	13
1	94	95
2	18	19
H,K=	9,	0
-10	117	121
-8	83	81
-6	175	181
-4	17	19
-2	74	63
0	326	321
2	82	79
4	200	207
6	64	63
8	226	227
10	54	59
H,K=	9,	1
-11	7	4
-10	13	11
-9	33	35
-8	123	122
-7	45	46
-6	155	163
-5	35	34
-4	76	76
-3	25	21
-2	405	428
-1	81	75
0	147	138
1	99	95
2	214	219
3	69	68
4	46	47
5	172	178
6	28	29
7	53	53
8	164	159
9	9	7
10	38	40
H,K=	9,	2
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-9	23	21
-8	80	78
-7	120	129
-6	163	162
-5	317	330
-4	101	100
-3	114	106
-2	66	63
-1	23	23
0	133	127
1	162	158
2	43	48
3	44	41
4	115	116
5	80	83
6	90	88
7	30	29
8	63	62
9	40	44
H,K=	9,	3
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-8	48	49
-7	55	59
-6	69	68
-5	11	9
-4	129	125
-3	32	28
-2	9	12
-1	52	53
0	37	41
1	76	77
2	130	128
3	43	41
4	15	12
5	62	55
6	65	62
7	47	48
8	56	59
H,K=	9,	4
-7	52	53
-6	65	66
-5	70	71
-4	84	85
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-2	51	47
-1	77	73
0	79	77
1	61	57
2	52	49
3	34	31
4	69	67
5	73	74
6	21	23
H,K=	10,	0
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-8	117	119
-6	37	36
-4	168	176
-2	149	145
0	377	385
2	31	32
4	195	196
6	111	117
8	61	65
10	65	68
H,K=	10,	1
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-9	11	13
-8	120	125
-7	109	114
-6	174	171
-5	211	220
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-3	130	138
-2	120	116
-1	49	55
0	142	138
1	65	69
2	206	199
3	63	62
4	90	94
5	41	41
6	51	51
7	6	11*
8	108	111
9	50	51
H,K=	10,	2
-10	138	143
-9	58	61
-8	53	51
-7	15	13
-6	76	73
-5	116	119
-4	162	159
-3	53	55
-2	58	55
-1	82	79
0	126	120
1	141	140
2	66	67
3	27	23
4	115	111
5	119	116
6	61	60
7	53	56
8	0	2*
9	25	22
H,K=	10,	3
-8	35	34
-7	16	11
-6	136	135
-5	98	101
-4	95	94
-3	135	133
-2	83	78
-1	41	43
0	16	11
1	95	95
2	81	78
3	44	38
4	67	64
5	7	3
6	39	38
7	58	59
H,K=	10,	4
-6	11	6
-5	104	106
-4	91	91
-3	25	26
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-1	57	55
0	53	48
1	63	62
2	25	27
3	22	23
4	10	4
5	22	21
H,K=	11,	0
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-6	101	101
-4	218	218
-2	122	121
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2	215	212
4	116	112
6	162	180
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H,K=	11,	1
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-8	53	52
-7	30	30
-6	121	117
-5	13	18
-4	131	134
-3	129	128
-2	208	207
-1	56	56
0	122	119
1	25	23
2	100	101
3	55	57
4	111	105
5	42	45
6	21	21
7	46	49
8	97	100
9	43	42
H,K=	11,	2
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-8	95	93
-7	10	8
-6	0	3*
-5	68	71
-4	197	196
-3	97	101
-2	27	31
-1	128	126
0	88	84
1	189	189
2	110	107
3	50	52
4	77	75
5	44	39
6	70	68
7	23	23
8	14	15
H,K=	11,	3
-7	43	46
-6	107	106
-5	69	68
-4	65	63
-3	149	146
-2	109	99
-1	9	6
0	34	33
1	15	7
2	95	93
3	88	86
4	37	34
5	16	17
6	10	8
H,K=	11,	4
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-3	73	74
-2	16	17
-1	55	53
0	22	23
1	58	58
2	33	33
3	20	18
H,K=	12,	0
-8	137	137
-6	88	90
-4	47	46
-2	312	312
0	132	130
2	213	210
4	13	3
6	118	114
8	50	51
H,K=	12,	1
-9	4	6*
-8	22	22
-7	20	22
-6	125	121
-5	30	28
-4	82	78
-3	31	26
-2	228	222
-1	75	71
0	41	38
1	197	193
2	20	6
3	106	107
4	126	124
5	30	34
6	6	3*
7	13	9
8	109	113
H,K=	12,	2
-8	101	102
-7	21	22
-6	17	22
-5	22	17
-4	151	143
-3	58	58
-2	86	78
-1	4	71*
0	109	101
1	17	17
2	127	125
3	15	14
4	71	75
5	50	47
6	31	26
7	6	6
H,K=	12,	3
-6	91	86
-5	78	76
-4	56	55
-3	52	49
-2	79	74
-1	56	52
0	99	98
1	76	75
2	38	35
3	99	90
4	72	73
5	30	28
H,K=	12,	4
-1	40	40
0	5	5*
H,K=	13,	0
-8	131	129
-6	27	23
-4	75	67
-2	246	237
0	200	191
2	15	15
4	55	57
6	50	51
H,K=	13,	1
-8	11	9
-7	24	20
-6	146	146
-5	51	47
-4	10	17
-3	32	30
-2	0	9*
-1	0	11*
0	132	124
1	25	24
2	36	36
3	18	17
4	172	172
5	0	2*
6	8	7
7	0	3*
H,K=	13,	2
-7	16	13
-6	64	67
-5	6	9*
-4	100	97
-3	62	61
-2	108	103
-1	56	54
0	56	43
1	37	36
2	91	88
3	87	86
4	19	19
5	36	37
H,K=	13,	3
-5	63	64
-4	111	109
-3	15	15
-2	82	79
-1	84	85
0	90	88
1	13	13
2	32	29
3	18	20
H,K=	14,	0
-6	127	129
-4	94	96
-2	90	87
0	41	40
2	46	46
4	136	136
6	75	77
H,K=	14,	1
-7	6	11*
-6	84	84
-5	29	29
-4	82	79
-3	8	8
-2	39	37
-1	20	20
0	164	160
1	0	2
2	17	17
3	21	21
4	83	83
5	6	3*
H,K=	14,	2
-5	28	26
-4	35	35
-3	71	69
-2	106	101
-1	9	7
0	16	16
1	65	65
2	98	99
3	29	26
4	42	42
H,K=	14,	3
-1	33	34
H,K=	15,	0
-6	43	42
-2	130	124
0	54	51
2	34	35
4	67	69
H,K=	15,	1
-5	49	46
-4	100	99
-3	40	41
-2	40	40
-1	2	9*
0	147	146
1	37	37
2	0	5*
3	49	54
H,K=	15,	2
-3	73	73
-2	92	90
-1	8	6
0	29	32
1	15	14
H,K=	16,	0
-2	58	56
0	79	78
H,K=	16,	1
-1	30	31

of sulfur and five other atoms. A least-squares refine-ment of the parameters of these 6 atoms resulted in an R index of 0·39, where R is defined as $\sum||F_o|-|F||/\sum|F_o|$. The function minimized in the least-squares calculation was $\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2$, where w is the weighting factor equal to $1/[\sigma(F_o)]^2$. The value of $\sigma(F_o)$ $= F_o-[F_o^2-\sigma(F_o^2)]^{1/2}$ when $I>\sigma(I)$ and $\sigma(F_o)\equiv 0$ when $I\leq\sigma(I)$. Observed and calculated structure factors are F_o and F_c. Atomic scattering factors for all atoms except hydrogen were taken from tables published by Cromer & Waber (1965). A correction for anomalous dispersion was applied to the scattering factor for sulfur (Cromer, 1965). The atomic scattering factors for hydrogen were those published by Stewart, David-son & Simpson (1965).

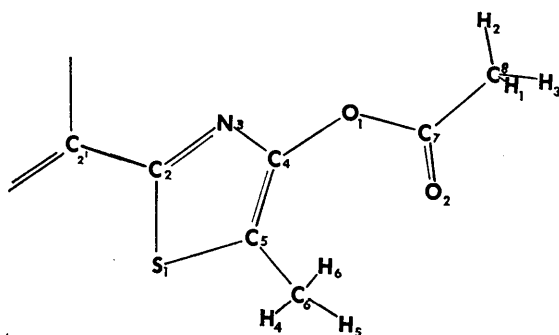A second Fourier synthesis led to the determination

Fig. 3. The asymmetric unit and numbering system used in this investigation.

of the atomic parameters for the remaining heavy atoms in the asymmetric unit. Least-squares refinement of these 10 atoms with isotropic thermal parameters gave an R index of 0·13. Anisotropic thermal parameters of the form exp $(-\sum\beta_{ij}\,h_i\,h_j\,b_i\,b_j/4)$ where b_ib_j are re-ciprocal cell lengths, reduced R to 0·071.

To find the hydrogen atoms, a Fourier difference synthesis was calculated. The six hydrogen peaks ranged in height between 0·73 and 0·37 Å^{-3}. When these were included in the least-squares refinement with isotropic thermal parameters the R index became 0·057.

A secondary extinction correction of the form $F_{corr}=$ $[1+(EF)I]\times F_{obs}$, where I is the net intensity, EF the extinction factor, and F_{obs} and F_{corr} the observed and corrected structure factors, respectively (Zachariasen, 1963) led to a final R value of 0·05 when $EF=1\times 10^{-7}$. This structure was used to calculate the positional and thermal parameters and their calculated standard deviations (Table 1). The observed and calculated structure factors are listed in Table 2.

Description of the structure

The crystal-structure determination of DDB proves that of the two postulated structures for this compound the correct one has two five-membered rings joined by a C–C bond. The other similar reaction products discus-sed by Mutha & Ketchum (1968) presumably also have five-membered rather than six-membered ring struc-tures. The correct structure of the asymmetric unit
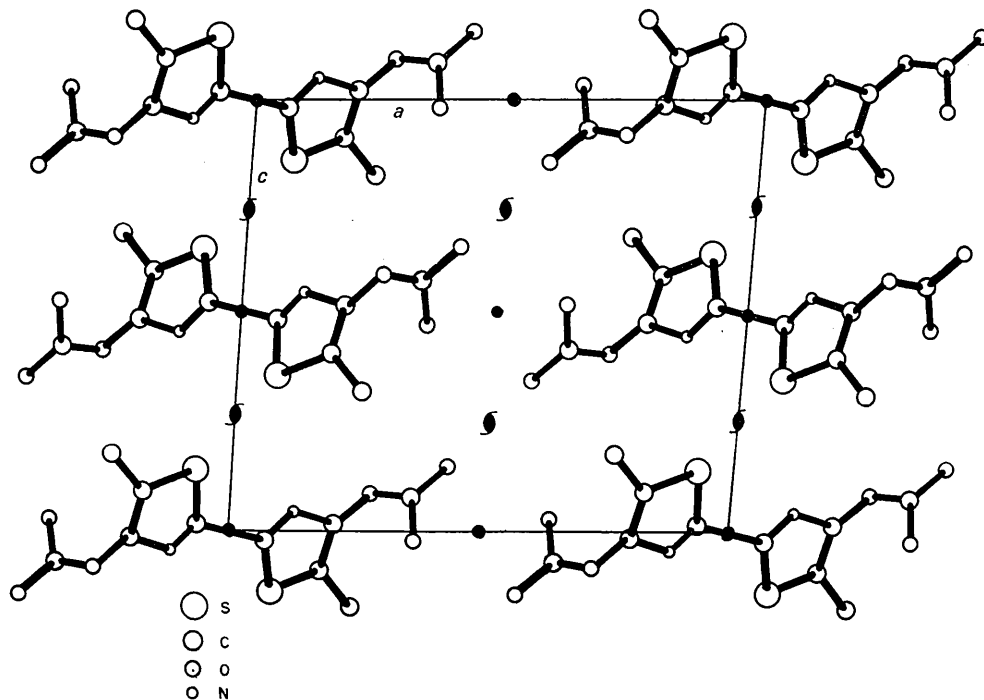

Fig. 4. Projection of structure on ac plane. The molecule through the origin is actually centered at $(0,\frac{1}{2},0)$.
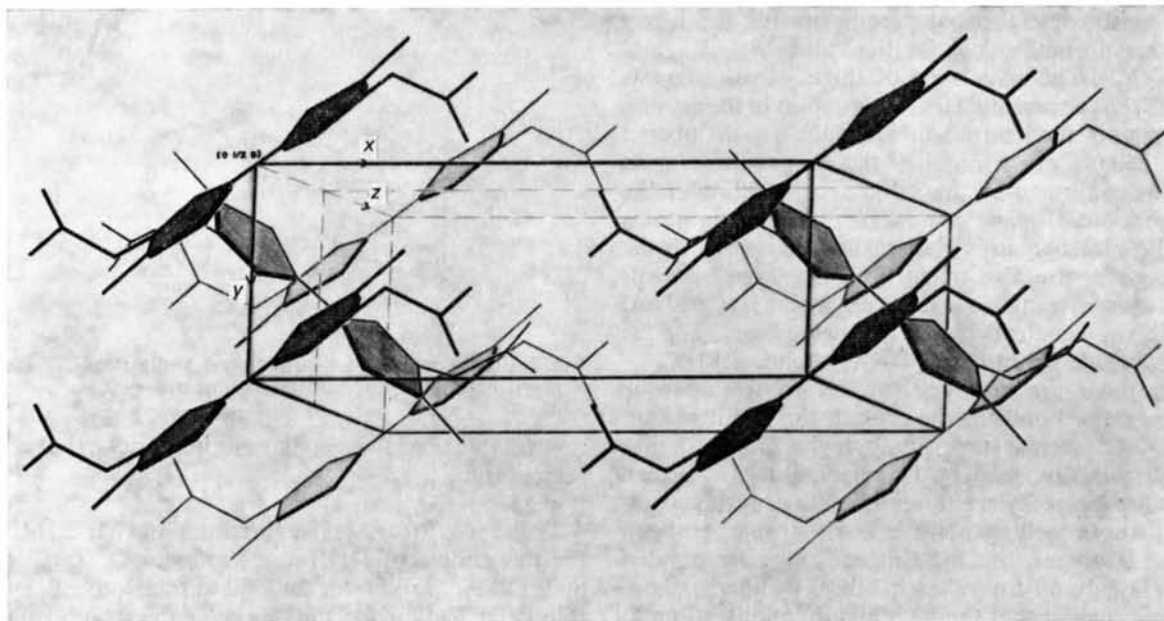
Fig. 5. Projection of structure parallel to **a** + **b** − 4**c**. This projection illustrates the angle between molecules related by a twofold axis and the packing of the molecules in the unit cell.

for DDB and the numbering system used in this investigation are shown in Fig. 3.

A projection of the structure on the **ac** plane is shown in Fig. 4. Identically oriented molecules form rows parallel to **a** and are related to molecules in adjacent rows by a twofold screw axis. Thus, molecules in adjacent rows have opposite inclination in both **ab** and **bc** planes and in addition have a relative translation of $\frac{1}{2}b$ with respect to each other. A view of the structure looking parallel to **a** + **b** − 4**c** is shown in Fig. 5. This view was chosen because it illustrates (schematically) the packing arrangement of molecules in the unit cell and the angle between two molecules related by a twofold

screw axis. The dihedral angle between the normals to the five-membered rings is 85·3°.

Interatomic distances and bond angles are shown in Figs. 6 and 7 respectively, except for those involving hydrogen; the latter are given in Table 3. Bond lengths of 1·447, 1·351, and 1·72 Å for the C(2)–C(2'), N–C(4) and S–C bonds, respectively, indicate that these bonds have considerable double-bond character. The ground state of this molecule must consist of contributions from the numerous ionic resonant structures which can be drawn with double bonds at C(2)–C(2)' and C–S. The bond distance of 1·35 Å for C(7)–O(1) agrees with literature values, but the C(7)–O(2) bond distance of 1·18 Å is somewhat shorter than the value of 1·23 Å usually observed for the carbonyl bond in carboxyl groups.
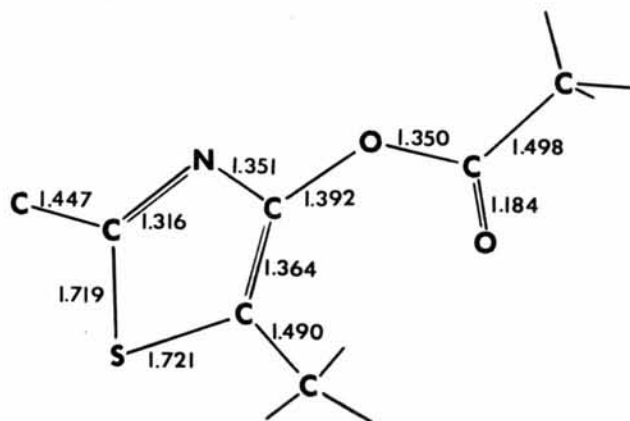

Fig. 6. Interatomic distances in 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl. Estimated standard deviations are ±0·003 Å.

Table 3. *Interatomic distances and bond angles involving hydrogen for 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithiazolyl*

Standard deviations × 10³ for distances; × 10 for angles.

C(8)–H(1)	1·07 (50) Å
C(8)–H(2)	0·89 (40)
C(8)–H(3)	0·91 (50)
C(6)–H(4)	0·78 (60)
C(6)–H(5)	0·92 (40)
C(6)–H(6)	0·69 (60)
H(1)–C(8)–H(2)	104· (50)°
H(1)–C(8)–H(3)	107· (50)
H(2)–C(8)–H(3)	102· (52)
H(4)–C(6)–H(5)	116· (77)
H(4)–C(6)–H(6)	110· (91)
H(5)–C(6)–H(6)	93· (71)

The anisotropic thermal parameters for the heavy atoms are normal except for the values B_{22}, B_{33}, and B_{23} for O(2). The magnitude of these values suggests that O(2) has appreciable thermal motion in the crystal.

The sum of the internal angles of the five-membered ring is 540·0°, which requires the ring to be planar. This was confirmed by the value of ±0·005 Å for the maximum out-of-plane distance of the five ring atoms from their least-squares plane. The four atoms of the acetate group are also planar and the largest out-of-plane distance from their least-squares plane is 0·0077 Å. The dihedral angle between the two planes, *i.e.* the torsional angle about the C(4)–O(1) bond, is 81·5°.

Since there are no opportunities to form strong intermolecular bonds in the crystal, the melting point of 242–243° seems surprisingly high, but a similar anomaly was discussed by Daubeny, Bunn & Brown (1954) for polyethylene terephthalate. In this compound, whose melting point is 264°, strong hydrogen bonding is absent, but the benzene rings are parallel and lie largely on top of each other. Daubeny, Bunn & Brown suggest that the high melting point is due to the stiffness of the chain resulting from resonance, whereas Rich (1959) believes that the high melting point of polyethylene terephthalate is due to the large van der Waals interaction that results from the highly polarizable π-electron system of the benzene rings. In any case, DDB possesses both resonance possibilities (hence, it is a stiff molecule) and closely packed, parallel five-membered rings (3·55 Å apart) with π-orbital overlap. Therefore the high melting point is in agreement with that observed for the aromatic polyester. Crystals of DDB cleave readily in a direction parallel to the **ab** plane. An inspection of Fig. 4 shows that this direction is parallel to the stacks of identical molecules and that there are only weak van der Waals forces between adjacent stacks. Attempts to cut crystals perpendicular to **b**, however, led to molecular disorder and a marked increase in the mosaic spread of X-ray reflections.

The relatively poor values for the C-H distances and the high temperature factors for the hydrogen atoms indicated that the methyl groups were undergoing
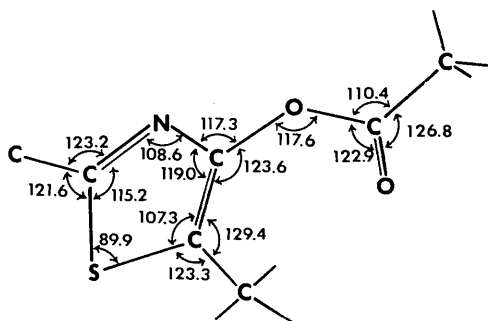

Fig. 7. Bond angles (°) 4,4'-diacetoxy-5,5'-dimethyl-2,2'-bithia-zolyl. Estimated standard deviations are ± 0.2°.

appreciable torsional oscillations in the crystal at room temperature.

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