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The Crystal and Molecular Structure of β-Thiophenic Acid

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The structure of β-thiophenic acid has been determined by X-ray diffraction, with three-dimensional data collected at -170 °C. The crystal is monoclinic; the unit-cell dimensions are:

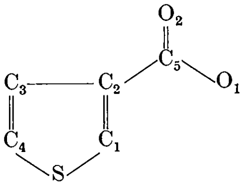
$$a=13\cdot601,\ b=5\cdot447,\ c=15\cdot054\pm0\cdot005\ \text{Å};\ \beta=99\cdot1^\circ\ .$$

The space group is $C2/c$, with $Z=8$. The structure was solved by Patterson methods with sulphur as a heavy atom and the parameters were refined by least-squares methods, with anisotropic temperature factors. The final R value was 0·128; the estimated standard deviations of coordinates are of the order of 0·002 Å for sulphur and 0·006 Å for the lighter atoms.

The thiophene ring is almost, though not perfectly flat: the carbon atoms are strictly planar while the sulphur atom stands out of this plane by 0·016 Å. The carboxylic acid group is twisted with respect to the thiophene ring by $4\frac{1}{2}^\circ$. The molecules form hydrogen-bonded centrosymmetric dimers. It is shown that van der Waals contacts between dimers are probably responsible for the twisted condition of the central hydrogen-bonded portion of the dimer.

Introduction

As part of a study of heterocyclic five-membered ring carboxylic acids, the crystal structure of thiophene-2-carboxylic acid, or β-thiophenic acid, has been



determined by X-ray analysis. This paper contributes to a series of structure determinations of similar molecules which have included the structure of α-thiophenic acid (Nardelli, Fava & Giraldi, 1962; Hudson & Robertson, 1962), α-selenophenic acid (Nardelli, Fava & Armellini, 1958; Nardelli, Fava & Giraldi, 1962) and α-furoic acid (Goodwin & Thomson, 1954; Hudson, 1962*a*).

Experimental

A preliminary investigation of the space group and cell dimensions of β-thiophenic acid was made by Care (1952) but his results have been shown to be in error (Hudson, 1962*b*).

Crystals of β-thiophenic acid were very kindly provided for us by Dr Gronowitz of the University of Uppsala. The product was in the form of colourless needles, m.p. 135–137·5 °C which showed parallel extinction between crossed polars. Crystal specimens suitable for X-ray work were obtained by recrystallization from water.

The specimen was enclosed in a thin-walled (0·01 mm) glass capillary tube of the type supplied by Pantak, Ltd. It was cooled to minimize the thermal motion of the atoms: all the X-ray diffraction photographs were taken with the crystal maintained continuously at a temperature of -170 °C ± 10 °C. Cooling equipment, similar to that previously described (Robertson, 1960) provided a stream of cold nitrogen gas which flowed axially over the thin-walled capillary containing the crystal. Accurate cell dimensions were obtained from high-order reflexions recorded on Weissenberg photographs on which aluminum powder lines were superimposed. The values obtained were:

$$a=13\cdot601,\ b=5\cdot447,\ c=15\cdot054\pm0\cdot005\ \text{Å};$$
$$\beta=99\cdot1^\circ,\ \text{at}\ -170\ ^\circ\text{C}\ .$$

The observed density at room temperature was 1·514 g.cm^{-3}, corresponding to $Z=8$. The volume of the cell is 1096·7 Å^3 and the calculated density 1·549 g.cm^{-3}. Systematic absences indicated that the space group was either C2/*c* (centrosymmetric) or *Cc* (non-centrosymmetric). In an attempt to differentiate between these two space groups, a test for piezoelectric properties was carried out, but with a negative, and therefore indecisive, result. The Wilson (1949) statistical test was conducted and gave the ratio of square of mean structure factor to mean intensity as 0·62. In relation to the theoretical values, 0·637 for centrosymmetric and 0·785 for non-centrosymmetric space groups, the test clearly indicated a centre of symmetry. The same conclusion was reached by

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* Dr Peter Hudson died, tragically, as a result of a traffic accident in Sydney on the 8th February 1963.

application of the Howells, Phillips & Rogers (1950) $N(z)$ test, which was conducted on the $h0l$ zone. A satisfactory structure has been found in this space group and no attempt was made to find a structure in the non-centrosymmetric group Cc. The centrosymmetric space group $C2/c$ was thus established.

Complete sets of data for crystal-mountings about the b and c axes were collected at −170 °C with a Weissenberg camera, non-zero layer-lines being recorded in the equi-inclination position. Copper K radiation was used, unfiltered, except for certain high layer-lines on the c axis where a nickel filter had to be employed to remove the β radiation of the next higher layer-line. Reflexion intensities were recorded on multiple film packs and estimated by visual comparison against a standard scale of carefully timed reflexions from the same crystal. Lorentz, polarization and Phillips' (1954) spot-shape corrections were applied. The linear absorption coefficient for β-thiophenic acid is 40 cm^{-1}. The diameter of the crystals used was approx. 0·015 cm, and cylindrical-specimen absorption corrections were applied. The data were placed on the absolute scale and an approximate temperature factor determined by Wilson's (1942) graphical method.

Structure determination and refinement

An attempt was made to solve the structure in the (010) projection by 'direct' methods. By means of Harker–Kasper inequalities (Harker & Kasper, 1948) and the Sayre (1952) probability relation, 80 of the 120 structure amplitudes observed in this zone could be given signs. A Fourier map based on these signs was not interpretable, however, and the method was discarded. When the structure was eventually determined it became evident that about 30% of these signs had been incorrect, and that these errors had stemmed from the wrong sign of one of the original sign-determinations by the Harker–Kasper inequalities.

A three-dimensional Patterson distribution was then computed from the $|F(hkl)|^2$ data, 'sharpened', to enhance resolution. From the Harker sections and lines it was possible to deduce three alternative positions for the sulphur atom. Structure factors were then calculated solely on the basis of the sulphur coordinates for these three possible locations of the S atom and (010) electron-density projections computed from the corresponding three sets of signs. Only one of the three electron-density projections showed a recognizable outline of a molecule and from that map it was possible, by introducing one atom at a time and recalculating the Fourier synthesis, to solve the structure in projection, *i.e.* in respect of the x and z coordinates. The final R value for this projection was 0·20. The y coordinate of the sulphur atom was then taken from the three-dimensional Patterson map and a trial set of y coordinates for the light atoms was obtained by geometrical construction from the x and z coordinates and a trial set of molecular dimensions. These trial coordinates all behaved satisfactorily when three-dimensional least-squares refinement was begun. After three cycles of refinement, anisotropic vibration parameters were introduced and the refinement continued for a further five cycles until the coordinate shifts were all less than half of the estimated standard deviations. The atomic scattering factors employed were those of Dawson (1960) for sulphur and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen and carbon. The contributions from hydrogen atoms were neglected in the structure factor calculations. After the refinement of the S, O and C atoms an attempt was made to locate the hydrogen atoms by means of a three-dimensional difference Fourier synthesis. This proved unsuccessful; presumably the original structure amplitude measurements were not of sufficiently high quality. The final R value for the three-dimensional data was 0·128; this figure included unobserved reflexions (within the sphere for copper radiation) with F_o set equal to half the minimum observable. The final set of observed and calculated structure factors is given in Table 1.

The resulting atomic parameters were subjected to a molecular vibration analysis (Cruickshank, 1961) to determine coordinate errors arising from molecular oscillations. The corrections found were all quite small, the largest being 0·004 Å.

The final set of atomic coordinates, vibration parameters and their estimated standard deviations, calculated by Cruickshank's method (1949), are given in Table 2. The atoms numbered are as shown in Fig. 1. Atomic coordinates X, Y, Z are also given, in Table 3, for the molecule referred to orthogonal axes defined by:

$$A = a + c\cos\beta\,,\quad B = b\,,\quad C = c\sin\beta\,.$$

In this table approximate coordinates of hydrogen atoms are also given. These atoms were placed in

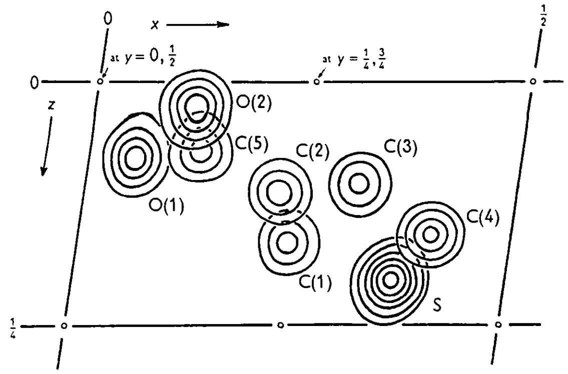

Fig. 1. Composite Fourier synthesis map. For C and O atoms the contours are drawn at 2, 4, 6, and 8 e.Å^{-3}; for S they are at 2, 4, 8, 12, 16 and 20 e.Å^{-3}.

Table 1. *Values of* F_o *and* F_c ($\times 10$)

	00L	
2	159	70
4	584	-489
6	94	-14
8	563	-566
10	257	358
12	66	-103
14	143	134
16	94	-108
18	51	30
	02L	
0	239	260
1	268	-402
2	388	-383
3	750	754
4	482	388
5	272	-194
6	338	300
7	644	-631
8	76	-65
9	101	85
10	329	291
11	359	-361
12	206	-217
13	54	75
14	38	-41
15	94	-93
17	86	-79
18	54	-43
	04L	
0	419	-327
1	530	-517
2	132	105
3	199	218
4	94	-105
5	167	172
6	245	-250
7	248	-253
8	76	48
	06L	
0	335	-280
1	38	34
2	38	16
3	76	77
4	148	-157
5	54	-79
7	76	-84
8	134	189
	11L	
-19	38	-36
-17	86	92
-16	86	76
-15	115	-96
-14	278	-229
-13	54	-48
-12	229	178
-11	318	-338
-10	417	-359
-9	286	-261
-8	206	188
-7	132	-49
-6	499	371
-5	803	640
-4	1917	-1772
-3	1552	1551
-2	228	-101
-1	1065	-1108
0	725	-916
1	509	-525
2	148	196
3	346	243
4	639	564
5	303	-208
6	535	-522
7	517	517
8	382	401
9	301	220
10	143	-140
11	175	188
12	278	262
14	54	47
15	38	42
16	202	-185
17	86	-90
18	236	142
	13L	
-15	184	-173
-14	108	-89
-13	86	60
-12	38	-31
-11	301	-306
-10	143	121
-8	223	125
-7	132	131
-6	239	-187
-5	443	-453
-4	76	52
-3	563	560
-2	449	351
-1	531	-605
1	436	379
2	76	-43
3	704	638
4	119	60
5	38	-21
6	236	-159
7	449	443
9	236	-200
10	66	53
11	210	195
12	66	-61
14	38	-33
17	94	77
	15L	
-8	38	-33
-7	158	161
-6	76	88
-5	54	-65
-4	405	372
-3	229	214
-2	223	-191
-1	115	-97
0	375	328
2	206	194
3	66	-66
4	195	-190
5	54	-54
7	175	184
8	158	-194
	20L	
-18	121	168
-16	54	-51
-14	365	372
-12	38	-37
-10	294	-321
-8	76	156
-6	109	-180
-2	38	28
0	431	-534
4	1263	-1327
8	710	-680
10	153	-117
12	164	211
14	54	53
16	121	120
18	394	-389
	22L	
-18	66	54
-16	38	-28
-15	184	196
-14	94	69
-13	121	-110
-12	254	-249
-11	259	240
-10	108	97
-9	66	99
-8	701	680
-7	1084	-1019
-6	101	-54
-5	478	459
-4	233	252
-3	132	-186
-2	476	-515
-1	359	-288
0	561	-442
2	296	328
3	626	-732
4	54	-26
5	74	-8
6	335	319
7	459	-402
8	276	-271
9	153	170
11	167	-163
12	143	-126
14	220	-237
15	392	384
16	101	79
17	38	-10
	24L	
-8	220	-225
-7	246	-266
-5	344	349
-4	335	-282
-3	444	-432
-2	112	58
0	239	195
1	108	118
2	66	-33
3	433	-368
4	199	150
5	311	309
6	54	-32
7	268	-281
8	38	12
	26L	
-8	149	-208
-6	184	195
-5	54	67
-4	187	-154
-3	38	46
-2	108	-112
-1	54	56
1	108	-105
2	101	-60
3	108	-112
4	206	199
5	121	141
7	54	57
8	115	169
	31L	
-19	86	-67
-18	239	-129
-17	138	114
-16	132	98
-15	121	-96
-14	108	-79
-13	299	-265
-12	66	-54
-11	171	134
-10	296	276
-9	202	120
-8	1082	-1010
-7	669	631
-6	262	236
-5	202	153
-4	344	206
-3	268	172
-2	365	-331
-1	167	244
0	690	822
1	615	-575
2	57	-133
3	318	236
4	898	872
5	171	-183
6	138	84
7	242	265
8	320	227
9	403	363
10	76	75
11	94	-99
12	417	-382
13	195	-166
14	431	391
15	301	-274
17	54	64
	33L	
-16	86	51
-15	153	-138
-14	127	149
-13	153	141
-12	101	-78
-11	385	462
-10	138	-136
-9	268	-259
-8	206	147
-7	384	379
-6	236	241
-5	262	-230
-4	138	-93
-2	94	-5
-1	626	671
0	171	-153
1	94	-110
2	390	-312
3	592	552
4	357	285
5	76	-117
6	115	82
7	187	166
8	294	-263
9	94	-77
10	76	68
11	327	-385
12	94	102
13	143	139
15	187	-177
16	38	-52
	35L	
-8	167	195
-7	143	179
-6	66	-64
-4	76	87
-3	86	86
-2	184	165
-1	191	152
0	304	-220
1	294	-270
2	86	-70
3	54	-20
4	344	-333
5	54	-66
6	38	22
7	171	204
	40L	
-18	153	189
-16	66	89
-14	284	-290
-12	401	388
-10	294	-323
-6	76	73
-4	107	-271
-2	365	506
0	1086	-1292
2	175	-196
4	1596	-1296
6	704	-509
8	919	747
10	153	-084
12	179	219
14	184	-184
16	66	-54
	42L	
-18	38	-57
-16	158	-147
-12	351	338
-11	581	-589
-10	132	-117
-9	223	190
-8	179	180
-7	108	-106
-6	114	-89
-5	514	-448
-4	473	-429
-3	423	419
-2	94	131
-1	451	-450
0	672	-669
1	54	98
2	138	-76
3	175	-235
4	66	90
5	187	144
6	301	270
7	38	53
8	162	157
9	54	-84
10	447	-466
11	590	675
12	54	30
13	66	-84
17	76	85
	44L	
-8	132	-143
-7	167	-204
-6	121	-124
-5	220	-253
-4	284	250
-3	175	175
-2	313	296
-1	143	-98
0	357	295
1	452	425
2	94	-65
3	403	-397
4	38	27
5	179	-145
7	340	328
8	76	-57
	46L	
-8	38	-34
-6	54	-60
-4	108	97
-2	179	-163
-1	101	-105
0	251	197
1	148	117
2	138	138
4	153	146
5	76	-71
6	38	-67
	51L	
-18	76	47
-17	127	-117
-16	158	-102
-15	248	187
-14	276	192
-13	121	-86
-12	296	-256
-11	54	74
-10	184	153
-9	342	283
-8	199	194
-7	54	44
-6	313	-319
-5	175	204
-4	879	881
-3	76	-105
-2	210	164
-1	54	-54
0	861	860
1	991	-882
2	132	94
3	76	-47
4	340	-203
5	658	526
6	245	246
7	370	-312
8	554	-503
10	377	360
11	162	-171
12	38	-40
13	153	-140
14	210	-192
15	38	41
16	179	128
17	38	20
	53L	
-16	143	-124
-15	342	287
-14	38	2
-13	121	-87
-12	86	86
-11	245	238
-10	162	134
-9	162	131
-8	54	14
-7	281	-280
-6	143	-153
-5	101	68
-4	233	-219
-3	449	-481
-2	69	-66
-1	457	485
0	403	284
1	191	115
2	167	-120
4	357	-283
5	108	-60
6	276	236
7	720	-835
9	132	119
10	66	-56
11	132	-120
14	76	-59
15	108	130
	55L	
-8	66	-91
-7	76	79
-6	94	109
-4	158	-140
-3	318	-335
-2	171	-123
-1	54	-28
0	379	-343
1	76	35
2	94	79
3	38	-32
4	115	117
5	54	44
6	153	-163
7	108	-102
8	121	179
	60L	
-18	138	-174
-16	191	223
-14	187	-198
-12	199	-188
-10	210	201
-8	517	-509
-6	161	-65
-4	446	-518
-2	405	396
0	531	-509
2	610	-656
6	543	-508
8	412	425
10	346	388
12	184	-202
14	148	151
16	54	-35
	62L	
-18	38	-33
-16	66	41
-15	184	-193
-14	132	-128
-13	76	-75
-12	38	41
-10	148	161
-7	459	489
-6	115	87
-5	284	-289
-4	833	-861
-3	251	301
-2	322	-280
-1	65	51
0	460	385
1	86	-90
2	273	244
3	497	524
4	412	409
5	108	-135
6	306	-336
7	572	549
9	38	39
11	54	-71
12	38	-51
13	121	111
14	138	118
15	223	-233
16	76	-87
	64L	
-8	121	93
-7	286	287
-6	220	233
-5	108	82
-4	251	266
-3	195	209
-2	54	42
-1	281	-284
0	127	102
1	54	-29
2	121	-95
3	556	573
4	438	-290
5	210	-228
6	76	74
7	167	176
	66L	
-8	66	87
-6	115	-132
-5	101	-97
-4	199	200
-2	38	43
0	66	-61
1	66	-57
2	86	71
3	38	26
4	138	-99
	61F	
-18	245	118
-16	38	-34
-16	38	34
-14	76	-66
-13	54	51
-12	54	27
-11	322	-266
-10	121	-117
-9	138	153

Table 1 (*cont.*)

-8	624	605
-7	242	170
-6	54	-59
-4	191	238
-3	606	-576
-2	66	83
-1	361	-425
0	813	-763
1	257	215
2	403	423
3	456	-393
4	584	-460
5	281	273
6	156	-152
6	94	79
9	251	-231
10	242	-221
11	167	173
12	223	219
14	191	-174
	73L	
-16	54	-22
-15	127	98
-14	121	86
-13	195	174
-12	94	73
-11	270	-251
-10	257	-209
-9	171	-125
-8	115	-68
-7	463	-503
-6	138	120
-5	171	185
-2	162	130
-2	226	-210
-1	216	-212
1	316	303
2	308	257
3	648	-697
4	86	84
7	54	-34
9	195	-236
10	143	-146
11	242	261
12	115	89
13	38	45
14	66	96
	75L	
-8	76	-83
-7	153	-172
-6	66	-92
-5	94	122
-4	143	-158
-3	66	64
-2	66	60
-1	294	-295
0	273	243
2	187	-161
3	38	-38
4	229	225
5	148	159
7	54	62
	80L	
-18	38	-52
-04	162	205
-12	487	-507
-10	101	-88
-6	327	330
-4	447	491
-2	325	-417
0	687	738
2	242	-253
4	358	303
6	535	531
8	421	-399
10	273	324
	82L	
-17	120	-151
-16	54	-48
-15	127	92
-14	127	123
-13	138	141
-12	38	56
-11	254	254
-10	132	111
-9	175	-180
-8	325	+360
-7	254	277
-6	101	-102
-5	162	200
-4	259	229
-3	355	-349
-2	206	-204
-1	533	583
0	446	455
1	257	-302
2	143	92
3	108	98
4	121	119
5	335	335
6	162	182
7	210	-203
8	223	-246
9	38	-50
11	245	-300
12	76	-79
14	162	177
	84L	
-8	86	97
-6	108	125
-5	54	24
-4	76	60
-3	54	-48
-1	373	412
0	478	-420
1	289	-253
2	138	-110
3	54	49
5	38	42
7	167	-171
8	132	167
	86L	
-4	184	-193
-2	121	121
0	216	-168
1	108	-79
2	38	40
	91L	
-17	121	-80
-16	54	17
-15	299	-241
-14	38	-8
-13	108	101
-12	276	229
-11	54	53
-10	191	-155
-9	20	-4
-8	115	-103
-7	66	55
-6	220	215
-5	273	-307
-4	649	-628
-3	38	57
-2	216	241
-1	236	-205
0	493	-470
1	38	25
2	529	-513
3	153	156
4	361	356
5	38	25
6	76	-95
7	467	418
8	226	194
9	66	-52
10	184	-179
11	76	-78
14	66	50
	93L	
-15	179	-130
-14	191	-038
-12	66	46
-11	239	-234
-10	86	72
-9	76	-58
-7	94	80
-6	76	-62
-5	289	-296
-4	138	107
-3	497	523
-2	127	103
-0	158	-118
1	94	-53
2	138	97
3	115	89
4	108	-98
5	308	-343
6	132	-139
7	294	318
8	148	172
9	132	147
10	54	1
11	216	239
12	115	-142
	95L	
-7	38	38
-6	54	-26
-5	184	-221
-4	239	280
-3	76	92
-2	38	-23
-1	54	-72
0	115	79
1	54	32
2	108	83
3	132	146
4	38	-53
5	66	-74
	10,0L	
-16	195	-258
-14	38	72
-10	76	-75
-8	490	532
-6	167	-202
-4	503	524
0	187	-211
2	66	-38
4	478	-510
6	417	439
10	86	-88
	10,2L	
-15	54	52
-14	66	68
-13	38	-26
-11	86	103
-9	162	169
-8	76	70
-7	379	-365
-6	276	-306
-5	213	200
-4	245	229
-3	245	-278
-2	162	164
-1	143	-121
1	444	435
2	340	310
3	367	-381
4	322	-294
5	167	-175
6	115	-110
7	223	-220
8	66	-81
10	54	47
12	86	70
13	66	-70
	10,4L	
-8	76	-76
-7	158	-200
-6	38	41
-4	115	135
-4	127	-127
-3	66	-65
-2	175	-175
-1	101	-90
1	94	69
2	115	-61
3	195	-173
4	132	114
5	108	122
6	54	68
7	299	-264
8	86	111
	11,1L	
-15	76	-63
-14	66	-46
-12	167	-118
-11	276	214
-10	294	229
-9	108	-86
-8	325	-296
-7	175	165
-5	66	45
-4	195	-188
-3	327	-338
-2	306	-201
0	580	550
1	254	226
2	54	-53
3	456	454
4	153	137
5	54	-25
6	54	-36
7	38	-32
10	268	215
11	191	-172
12	210	-128
	11,3L	
-13	138	-106
-12	66	-51
-11	202	124
-10	101	60
-9	199	-169
-8	38	-17
-7	291	301
-5	132	146
-4	108	103
-3	66	-68
-2	86	56
-1	254	237
0	101	-86
1	259	-205
2	108	-71
3	213	219
4	108	98
6	66	-64
7	108	103
8	115	-89
9	127	127
10	76	94
	11,5L	
-8	143	214
-7	94	116
-6	38	64
-5	101	-113
-4	101	-89
-3	76	-71
-2	115	88
-1	153	131
0	94	-50
	12,0L	
-14	148	-180
-12	175	224
-10	101	-125
-8	258	289
-6	451	507
-4	449	-454
-2	320	-301
0	429	-428
2	210	192
4	54	-64
6	132	-138
8	171	191
10	365	-336
	12,2L	
-14	38	-47
-13	76	89
-12	66	55
-11	162	-193
-10	65	-70
-9	76	-94
-7	66	-80
-6	38	-33
-5	66	-60
-4	108	-97
-3	248	245
-2	284	261
-1	348	-367
0	171	-123
3	54	-67
4	66	-90
6	202	-222
7	127	133
8	76	65
9	153	-125
10	54	-35
	12,4L	
-8	38	59
-7	86	99
-6	76	-105
-5	127	-159
-3	66	71
-1	132	-119
	13,1L	
-14	226	117
-12	143	-74
-11	236	191
-10	153	-128
-9	143	116
-8	66	47
-7	335	-314
-6	38	-32
-5	54	-35
-4	395	370
-3	66	59
-2	108'	-96
-1	191	168
0	148	146
1	38	53
2	153	153
3	38	39
4	76	-79
6	265	265
7	239	-256
8	296	-227
10	38	16
	13,3L	
-10	66	37
-9	121	88
-8	127	126
-7	94	-74
-6	54	-49
-5	242	237
-3	76	-58
-2	38	-27
-1	101	75
1	138	-129
3	127	-111
5	213	196
7	171	-212.
	14,0L	
-10	170	250
-8	251	-301
-6	66	-47
-4	245	-250
-2	143	-159
0	54	-53
2	158	-172
4	363	380
6	76	-86
8	127	113
	14,2L	
-11	38	57
-10	57	-83
-8	115	-132
-7	66	64
-6	94	111
-5	132	-152
-3	101	124
-2	66	64
1	115	-103
2	254	-236
3	304	292
4	153	137
5	158	-135
6	66	-51
7	162	148
	14,4L	
-6	38	54
-3	54	60
-1	38	51
	15,1L	
-12	143	96
-11	148	-107
-8	162	119
-7	127	-116
-6	54	-40
-4	132	118
-3	76	79
-2	184	175
-1	38	-37
0	262	-249
1	148	106
2	199	153
3	108	-97
4	281	-199
5	94	-76
6	86	-90
	15,3L	
-7	54	-55
-6	38	-29
-2	101	100
-1	175	-173
1	143	128
2	76	-108
	16,0L	
-8	96	-138
-6	153	-202
-4	121	124
-2	220	-189
0	333	287
2	175	180
4	38	30
	16,2L	
-4	66	65
-3	108	-101
-1	233	258
0	195	176
1	66	-77
2	94	-95
	17,1L	
-6	86	68
-5	167	-152
-4	299	-238
-3	127	107
-2	38	27
-1	94	88
0	66	-63

Table 2. *Atomic parameters*

Atomic coordinates (Å) and estimated standard deviations (Å × 10^{-3})

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
S	5·011	0·409	3·055	2	2	2
O(1)	0·712	1·323	1·105	4	5	5
O(2)	1·565	3·235	0·373	5	5	5
C(1)	3·321	0·557	2·450	6	7	7
C(2)	3·071	1·719	1·658	6	6	6
C(3)	4·289	2·452	1·565	6	7	7
C(4)	5·545	1·806	2·331	5	6	5
C(5)	1·721	2·165	0·996	6	7	6

Thermal vibration tensor components, U_{ij}, (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{33}
S	0·0353	0·0446	0·0459	0·0006	0·0132	−0·0024
O(1)	0·0238	0·0390	0·0430	−0·0059	0·0227	0·0010
O(2)	0·0243	0·0371	0·0470	−0·0057	0·0166	−0·0075
C(1)	0·0261	0·0295	0·0403	−0·0002	0·0038	−0·0092
C(2)	0·0310	0·0231	0·0269	−0·0047	0·0011	0·0055
C(3)	0·0261	0·0368	0·0318	−0·0048	0·0026	−0·0006
C(4)	0·0194	0·0225	0·0152	−0·0097	0·0024	0·0058
C(5)	0·0281	0·0321	0·0284	−0·0101	−0·0023	0·0014

Estimated standard deviations of U_{ij} (Å^2)

Atom	$\sigma(U_{11})$	$\sigma(U_{22})$	$\sigma(U_{33})$	$\sigma(U_{12})$	$\sigma(U_{23})$	$\sigma(U_{33})$
S	0·0009	0·0011	0·0010	0·0015	0·0017	0·0016
O(1)	0·0019	0·0026	0·0024	0·0038	0·0046	0·0037
O(2)	0·0021	0·0026	0·0026	0·0037	0·0046	0·0039
C(1)	0·0028	0·0032	0·0032	0·0047	0·0057	0·0051
C(2)	0·0028	0·0028	0·0025	0·0048	0·0052	0·0045
C(3)	0·0027	0·0033	0·0029	0·0049	0·0056	0·0048
C(4)	0·0022	0·0025	0·0020	0·0040	0·0043	0·0035
C(5)	0·0029	0·0033	0·0027	0·0048	0·0053	0·0047

Table 3. *Orthogonal coordinates* (Å)

Atom	X	Y	Z	Atom	X	Y	Z
S	4·528	0·409	3·016				
O(1)	0·537	1·323	1·091	H(1) [on C(1)]	2·23	−0·11	2·65
O(2)	1·506	3·235	0·368	H(2) [on C(3)]	4·16	3·31	1·04
C(1)	2·934	0·557	2·418	H(3) [on C(4)]	6·16	2·09	2·43
C(2)	2·809	1·719	1·636	H(4) [on O(1)]	−0·26	1·67	0·52
C(3)	4·041	2·452	1·545				
C(4)	5·177	1·806	2·300				
C(5)	1·564	2·165	0·983				

order to study the packing of the molecules (see below). The thiophene ring hydrogen atoms were assumed to be in the plane of the ring and a 1·00 Å from the carbon atoms; H(5) was placed at 1·05 Å from O(1) in the line joining O(1) to the carbonyl oxygen O(2) on the other side of the symmetry centre at 0, ½, 0.

A composite three-dimensional Fourier synthesis map is reproduced in Fig. 1. The molecular dimensions are shown in Fig. 2, together with the estimated standard deviations of the bonds and angles.

Discussion

The β-thiophenic acid molecule

Within the molecule, bond distances and angles appear to be normal. Among features of interest are the following: At the sulphur atom, the valency angle of 98° is intermediate between the tetrahedral angle and a right angle. This is expected of sulphur and is in line with the three α-compounds, furoic, thiophenic and selenic acids, where at O, S and Se the angles are 109°, 92° and 88° respectively. The two S–C distances, of average length 1·70 Å indicate considerable double-bond character for these bonds. The single-bond distance S(II)–C(sp^2) has been calculated (Truter, 1962) to be 1·77 Å. The double-bond distance must be about 1·71 Å, for in thioacetamide (Truter, 1960) 1·713 Å could be regarded as a pure double bond between sulphur and carbon in sp^2 hybridization. The two S–C distances found for β-thiophenic acid differ by less than two standard deviations of the bond yet even the greater of the two is less than the apparent double bond of thioacetamide. This is also the case in α-thiophenic acid. Data for other comparable bonds are S–C in thiourea, 1·71 Å (Kunchur & Truter, 1958), in ethylenethiourea, 1·71 Å (Wheat-

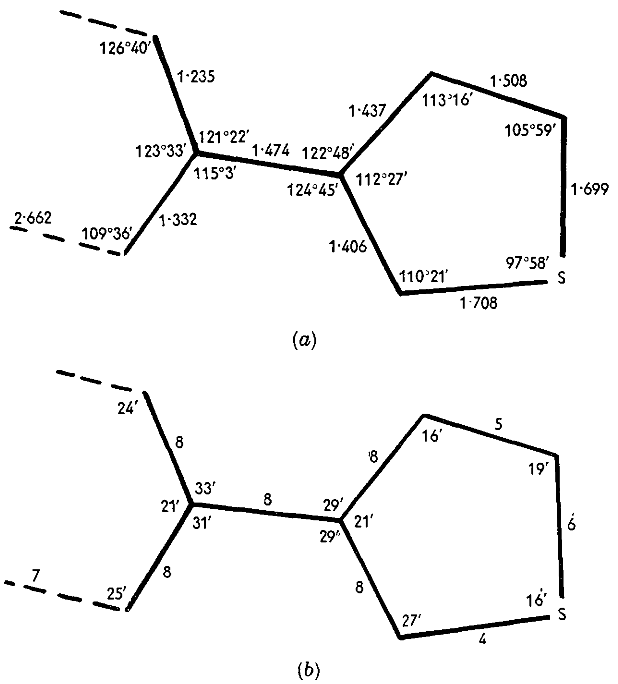

Fig. 2. (*a*) Molecular dimensions and (*b*) estimated standard deviations. Lengths are in Å, their e.s.d. in Å × 10^{-3}.

ley, 1953) and S–C in heterocyclic compounds, 1:4-thiophthen, 1·73 Å (Cox, Gillot & Jeffrey, 1949) and thiophene, 1·74 Å, by electron diffraction (Schomaker & Pauling, 1939). The carbon–carbon bonds are all shorter than single bonds and indicate considerable conjugation, including the exocyclic bond C(2)–C(5) (1·47 Å). For comparison, the lengths of the exocyclic bond in benzoic and salicyclic acids are 1·48 Å and 1·46 Å respectively.

The β-thiophenic acid molecule is not planar in the crystal. It deviates from planarity in two respects: (*a*) a minor one, common for five-membered rings, is that the thiophene ring is slightly buckled, with the hetero atom out of the plane; (*b*) a greater one, interesting because it is unexpected, is that the carboxylic acid group is twisted with respect to the ring.

With regard to (*a*), the sulphur is found to be about two standard deviations away from a plane drawn with minimum least-squares deviations through all five atoms of the ring. The situation is better represented, however, by consideration of the plane of the carbon atoms only. The equation of this plane, in orthogonal coordinates (Å) is,

$$-0{\cdot}160X+0{\cdot}338Y+0{\cdot}530Z=1{\cdot}000\;.$$

The carbon atoms are all less than 0·002 Å from this plane but the sulphur atom is displaced by 0·0185 Å — much more than the standard deviation of its coordinates. The inclination of this plane to the *b* axis is 31° 22′; the perpendicular separation of these planes, stacked in the *b* direction, is $2{\cdot}83_5$ Å.

With regard to (*b*), the displacements of the atoms of the carboxyl group from the plane of the ring as given above are

$$\begin{aligned}\mathrm{C}(5)&: +0{\cdot}003\ \text{Å}\,,\\ \mathrm{O}(1)&: -0{\cdot}063\ \text{Å}\,,\\ \mathrm{O}(2)&: +0{\cdot}073\ \text{Å}\,.\end{aligned}$$

These figures make it clear that the carboxyl group is rotated with respect to the plane of the thiophene ring, about the carbon–carbon bond. The rotation is such that O(2) is on the same side of the ring as the sulphur atom. The plane of the carboxyl group is

$$-0{\cdot}214X+0{\cdot}339Y+0{\cdot}611Z=1{\cdot}000$$

and between this and the ring plane (as defined above) the angle is calculated to be 4° 26′, *i.e.* about $4\frac{1}{2}$°. Although this is only a small rotation it is interesting to seek a reason for it; this is described in this discussion later.

As is usual for carboxylic acids, the molecules are linked in pairs by hydrogen bonding to form dimers. The O · · · O distance is 2·66 Å. Dimerization takes place around the point 0, $\frac{1}{2}$, 0 where the space group requires $\bar{1}$ symmetry. The dimers are centrosymmetric, therefore, but they are not planar because of the $4\frac{1}{2}$° twist of the carboxylic acid groups in the central region of the dimer molecule. On either side of the centre of symmetry the individual distorted molecules are equally and oppositely enantiomorphic. An additional contribution to non-planarity of the dimer is a displacement of the planes of the carboxylic acid groups (which are nevertheless strictly parallel to one another). The perpendicular separation of the two planes across the centre of symmetry at 0, $\frac{1}{2}$, 0 is 0·210 Å. This is similar to other carboxylic acid dimers (Jeffrey & Sax, 1963; Robertson, 1964). There is a displacement between the planes of the thiophene

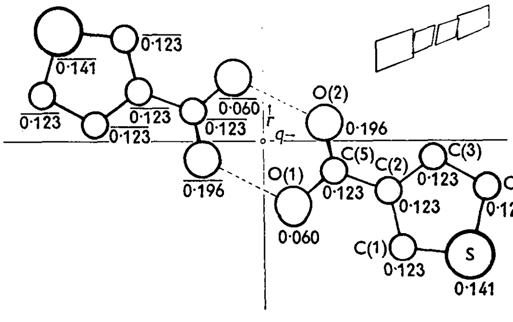

Fig. 3. The dimer viewed in its 'mean plane' (see text). Atomic positions are plotted in the coordinate system *p*, *q*, *r*, where *p* is the perpendicular distance from the mean plane; *q*, the 'horizontal' coordinate in the plane, is parallel to (010), *i.e.* perpendicular to the crystallographic *b* axis; and *r*, the 'vertical' coordinate in the plane, is perpendicular to *q*. The origin is taken at the symmetry centre. Values of *p*, the distances (Å) by which atoms are displaced from the plane, are given.

Inset: a schematic representation of the dimer showing the twist and displacement of planes.

rings too, on either side of the symmetry centre; this has the value 0·246 Å.

Since hydrogen bonding takes place only within the dimer, and the contacts between dimers are wholly van der Waals interactions, it is both convenient and proper to think of the dimer as the unit, from which the crystal structure is built up. In Fig. 3 the dimer is shown viewed in the optimum direction, perpendicular to the thiophene rings. It is drawn projected on what may be called its 'mean plane', *viz.* the plane

$$-0{\cdot}174X+0{\cdot}367Y+0{\cdot}576Z=1{\cdot}000\,,$$

which is parallel to both the thiophene ring planes and lies equidistant from them, passing through the centre of symmetry at 0, $\frac{1}{2}$, 0. This drawing clearly shows the two different angles formed by the hydrogen bonds with the covalent C–O bonds, *viz.* $126\frac{1}{2}°$ and $109\frac{1}{2}°$ at the oxygen bearing the lone pair and that bearing the hydrogen atom respectively.

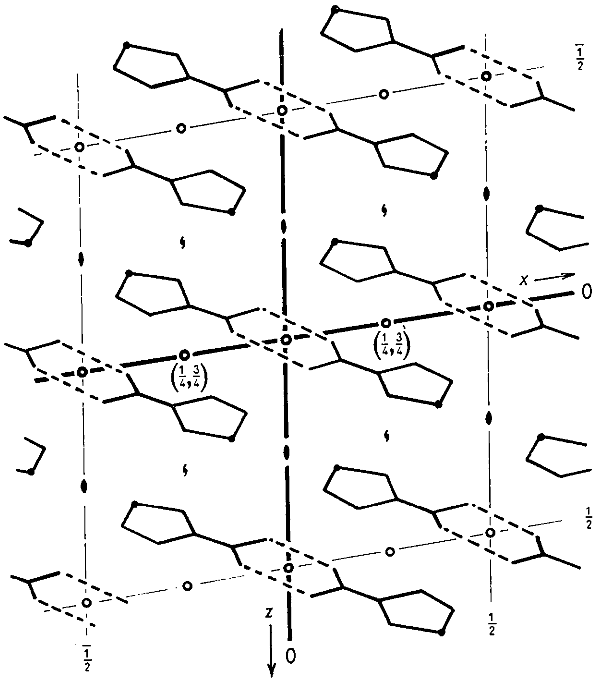

Fig. 4. Packing of β-thiophenic acid dimers. The origin is at the centre of the diagram.

The packing of the dimers, which for this purpose may be regarded as long flat plates, is shown in Fig. 4. They lie parallel to one another, steeply inclined to all three cell axes, so that a thick layer, built up of parallel dimers, is formed on the c face of the unit cell and extends throughout the crystal in the x and y directions. This layer, which comprises half the mass of the unit cell, contains the dimer at the cell origin and that which centres the c face of the cell, their mutual relationship controlled by the centres of symmetry in this face. The layer has the hydrogen-bonding in its interior and is bounded on both its surfaces by the ends of the thiophene rings, in particular by the sulphur atoms. An exactly similar layer lies across the centre of the unit cell. It is related to the first by the twofold axis parallel to **b**; therefore, in it, all the parallel dimers slope in the opposite way to those of the first layers. These thick layers of parallel stacked dimers lie in van der Waals contact with their thiophene rings and S atoms facing one another. The closest distance of approach between sulphur atoms of different layers is $3{\cdot}63_6$ Å, which compares well with the shortest non-bonded distance in elementary sulphur, $3{\cdot}69_2$ (Abrahams, 1955).

Why does the dimer twist?

We note first that over-all planarity is to be expected of the β-thiophenic acid molecule. The expectation is reasonable in view of the generally aromatic behaviour of the substance in chemical reactions, the analogy with such molecules as benzoic acid and the degree of conjugation indicated by the bond-lengths actually found in β-thiophenic acid. However, the central portion of the dimer, *i.e.* that comprising the two hydrogen bonded COOH groups, is here found to be rotated by $4\frac{1}{2}°$ out of the plane of the rest of the molecule. As with slight deformations of other flexible molecules, the twist is due to 'packing', of course. The forces producing such deformation must be quite small; nevertheless, it is of interest to enquire exactly how the twist in this particular case arises.

An explanation is put forward as follows: There are a number of close van der Waals contacts which exert two turning couples on the dimer: (i) a couple acting on the COOH groups, tending to rotate them (clockwise, as viewed from the symmetry centre towards the molecule, M, at the origin); this forces the $-CO_2\cdots O_2C-$ system to become more parallel to the b axis of the crystal; (ii) a couple acting on the thiophene rings, tending to rotate them (anticlockwise, viewed as above); this forces the two rings to be more inclined to the b axis. It is not proposed that there is anything abnormal about these contacts: only that the requirements of packing of the dimers into minimum volume so as to achieve minimum energy results in contacts which exert these turning moments, twisting the dimer as it is packed. These contacts occur, it should be noted, entirely within the 'thick layer' already described. Fig. 5, which shows these contacts, may be used in following the details now given.

Couple (i). — O(1) is close to C(4′) of a neighbouring molecule and closer still to the hydrogen atom H(3′) attached to it. The primes refer to the molecule M' which is related to M at the origin by the translations (in fractional coordinates)

$$x' = x-\tfrac{1}{2}\,,$$
$$y' = y-\tfrac{1}{2}\,,$$
$$z' = z\,.$$

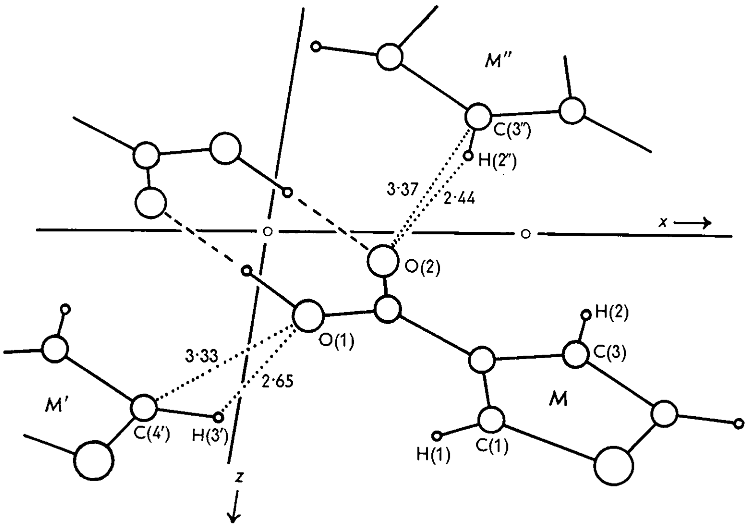

Fig. 5. Van der Waals contacts.

These atoms, although below O(1) in the y direction, are in front of the plane of the carboxyl group as it is viewed in Fig. 5, looking from positive y towards the origin. The separations are,

$$\mathrm{O(1)\text{–}C(4')} = 3{\cdot}33\ \text{Å}\,,$$
$$\mathrm{O(1)\text{–}H(3')} = 2{\cdot}65\ \text{Å}\,.$$

Similarly, O(2) is close to C(3″) of another neighbouring molecule and to the hydrogen atom H(2″) attached to it. The double primes refer to the molecule M'' related to that at the origin by the symmetry centre at $\frac{1}{4}, \frac{3}{4}, 0$, *i.e.* by

$$x'' = \tfrac{1}{2}-x\,,$$
$$y'' = \tfrac{3}{2}-y\,,$$
$$z'' = -z\,.$$

Again, although above O(2) in the y direction, these atoms are behind the plane of the carboxyl group as it is viewed in Fig. 5. The separations are

$$\mathrm{O(2)\text{–}C(3'')} = 3{\cdot}37\ \text{Å}\,,$$
$$\mathrm{O(2)\text{–}H(2'')} = 2{\cdot}44\ \text{Å}\,.$$

Corresponding contacts occur, of course, on the other side of the centre of symmetry $0, \frac{1}{2}, 0$, where they act in the same sense on the other member of the dimer.

Couple (ii). — This is simpler than couple (i). It arises from the packing of thiophene rings above one another. The carbon atom C(3) and its hydrogen atom H(2) are close to the carbon and hydrogen atoms C(1‴) and H(1‴) of the opposite side of the ring directly above. The triple primes refer to the molecule M''' related to that at the origin by the simple translation,

$$x''' = x\,,$$
$$y''' = 1+y\,,$$
$$z''' = z\,.$$

The separations are,

$$\mathrm{C(3)\text{–}C(1''')} = 3{\cdot}83\ \text{Å}\,,$$
$$\mathrm{C(3)\text{–}H(1''')} = 3{\cdot}58\ \text{Å}\,,$$
$$\mathrm{H(2)\text{–}C(1''')} = 3{\cdot}35\ \text{Å}\,.$$

These contacts occur below the ring also, by virtue of the unit-cell periodicity. They re-occur at the other end of the dimer according to the $\bar{1}$ symmetry.

Summarizing, we may say that the carboxyl group system is pushed into a more vertical orientation (with respect to the b axis) by pressure from the sides, while the thiophene rings at the ends of the dimer are pushed into a more inclined orientation by pressure from above and below.

It may be objected that since the forces acting on the carboxyl groups come from the thiophene rings of molecules at the sides, the argument might well be used in reverse: for the carboxyl groups must necessarily be acting equally on the thiophene rings which they contact, tending to orient them more vertically. Since action and reaction are equal and opposite, it is perhaps impossible to identify the prime mover of the process. This objection is met, however, by the observation that when the dimensions of the eight membered ring system formed by the carboxyl groups are compared with those of the thiophene ring, the former is clearly more narrow than the latter in the direction of tilt: it does not have hydrogen atoms that protrude outwards in the plane, as does the thiophene ring.

We conclude therefore that the thiophene rings are first pressed into greater inclination with the b axis by their packing above one another and that the carboxyl groups of the dimer are then forced to twist slightly, towards less inclination with the b axis, by pressures from molecules at the side. A balance is presumably achieved between these distorting *inter*-molecular forces and the *intra*-molecular forces which strive to maintain planarity.

It is of interest to note also that the displacement of the planes of the carboxylic acid groups, so as to be 0·2 Å apart, may be similarly accounted for. As the carboxyl groups are held firmly by nearly equal short distances on both sides, this displacement might be most simply relieved by a small increase in the y coordinates of the ring end of the molecule, lifting it slightly with respect to the carboxyl group, and so tilting the plane of the molecule to intersect the symmetry centre at 0, $\frac{1}{2}$, 0. However, raising the end of the molecule M would raise the ring end of M' and lower that of M'', both of which would decrease further the short contacts made already by these rings with the carboxyl group. The displacement distortion of the carboxylic acid dimer is thus a consequence of essentially the same packing forces that produce the twist.

Most aliphatic carboxylic acids form dimers whose acid groups are twisted in the crystal, *e.g.* lauric acid: about 16° (Lomer, 1963; Vand, Morley & Lomer, 1951; see also Abrahamsson, 1959). The better crystalline dibasic acids have given the most complete data: β succinic acid, 11½° (Broadley, Cruickshank, Morrison, Robertson & Shearer, 1959), glutaric acid, adipic acid and sebacic acid, ~30°, 6° and 3° respectively (Morrison & Robertson, 1949). However these molecules are without conjugated double bonds so that planarity is not to be expected. Benzoic acid, salicyclic acid, p-aminosalicyclic acid, tiglic acid and other aromatic or unsaturated acids are planar, except that in the case of benzoic acid (Sim, Robertson & Goodwin, 1955) the carboxyl group is apparently bent and the ring slightly buckled. (But this may be spurious, as the analysis was based on two projections only.) Exceptions are o-chloro- and o-bromobenzoic acids, whose carboxyl groups are twisted by 13·7° and 18·3° (Ferguson & Sim, 1961, 1962), but as these are overcrowded molecules the effect is *intra*-molecular. The heterocyclic α-furoic acids and α-thiophenic acids show distortions similar to that of β-thiophene but smaller: about 2° (Hudson, 1962*b*). Nicotinic acid (β-pyridinic acid) also shows a small but significant distortion of the carboxyl group (Wright & King, 1953) although not dimerized in the crystal. One is tempted to generalize that packing forces produce molecular distortions with heterocyclic acids more readily than with aromatic acids. Perhaps further experimental work will bear this out.

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