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The Crystal and Molecular Structures of α-Thiophene- and α-Selenophene-Carboxylic Acids

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α-Thiophene- and α-selenophene-carboxylic acids are isostructural. Their monoclinic ($P2_1/c$) unit cells ($Z=4$) have the dimensions: $a=5{\cdot}67$, $b=5{\cdot}03$, $c=19{\cdot}57$ Å, $\beta=98{\cdot}2°$ for SC_4H_3COOH and $a=5{\cdot}80$, $b=5{\cdot}05$, $c=20{\cdot}05$ Å, $\beta=97{\cdot}9°$ for SeC_4H_3COOH. The refinement of the structures has been carried out by means of three-dimensional differential syntheses using *hkl* ($k=0, \ldots, 4$) data. $R(hkl)$ is 11·0% for thiophene-acid and 8·5% for selenophene-acid.

The molecules are planar except that the sulphur and the selenium atoms are displaced by 0·03 (displacement perhaps significant) and 0·06 Å, respectively, from the molecular planes. Bond lengths and angles are given. The increase of the size of the hetero-atom does not seem to modify the C–C distances in the rings. The results are discussed in relation to the dimensions of thiophene and the theoretical calculations on thiophene and selenophene.

The molecules are linked by hydrogen-bonds forming centrosymmetrical dimers.

Introduction

The crystal structures of α-thiophene- and α-selenophene-carboxylic acids have been already determined by two-dimensional Fourier methods (Nardelli & Fava, 1958; Nardelli, Fava & Armellini, 1958), but these results were not refined sufficiently because of poor resolution in the (100) projections. In the present paper the results of three-dimensional refinements using *hkl* ($k=0, \ldots, 4$) data are reported.

Experimental

α-Thiophene- and α-selenophene-carboxylic acids are isostructural, with the following crystal data:

SC_4H_3COOH, $M=128{\cdot}14$;
$a = 5{\cdot}67 \pm 0{\cdot}01$, $b=5{\cdot}03 \pm 0{\cdot}01$, $c=19{\cdot}57 \pm 0{\cdot}01$ Å, $\beta=98{\cdot}2°$;
$U = 546{\cdot}6$ Å^3;
$D_x = 1{\cdot}557$ g.cm.$^{-3}$;
$\mu = 44{\cdot}2$ cm.$^{-1}$ (Cu $K\alpha$);
$F(000)=264$.

SeC_4H_3COOH, $M=175{\cdot}04$;
$a = 5{\cdot}80 \pm 0{\cdot}01$, $b=5{\cdot}05 \pm 0{\cdot}01$, $c=20{\cdot}05 \pm 0{\cdot}05$ Å, $\beta=97{\cdot}9°$;
$U = 581{\cdot}7$ Å^3;
$D_x = 1{\cdot}966$ g.cm.$^{-3}$;
$\mu = 81{\cdot}9$ cm.$^{-1}$ (Cu $K\alpha$);
$F(000)=336$.

Space group: $C_{2h}^5(P2_1/c)$; four molecules per unit cell.

Crystals of both compounds are prisms elongated along [010] with {001} and {10$\bar{2}$} predominating.

The intensities were determined photometrically on multiple-film integrated and non-integrated equi-inclination Weissenberg photographs (Cu $K\alpha$), taken by rotation around [010]. Discontinuous absorption effects were corrected graphically by Albrecht's (1939) method, the size of the samples being

	SC_4H_3COOH	SeC_4H_3COOH
along [100]	0·137 mm.	0·125 mm.
[201]	0·137	0·037

The numbers of observed and possible independent

Table 1. *Number of observed and possible independent reflections with final R and R′ indices*

	SC_4H_3COOH				SeC_4H_3COOH			
	Reflections				Reflections			
	Obs.	Poss.	R	R'	Obs.	Poss.	R	R'
*h*0*l*	75	144	12·05%	17·30%	116	147	7·73%	8·62%
*h*1*l*	181	277	11·71	14·58	206	293	9·14	10·57
*h*2*l*	161	250	10·55	13·13	178	268	7·80	10·86
*h*3*l*	128	222	8·27	10·02	127	233	7·81	9·39
*h*4*l*	97	172	11·04	13·78	84	179	11·83	17·48
Overall	642	1065	10·97	14·15	711	1120	8·54	10·67

Table 2. *Final atomic coordinates and their standard deviations*

	x/a	y/b	z/c	x' (Å)	y' (Å)	z' (Å)	$\sigma(x)$ (Å)	$\sigma(y)$ (Å) ($\times 10^3$)	$\sigma(z)$ (Å)
α-Thiophene-carboxylic acid									
S	0·6042	0·5693	0·1797	2·925	2·864	3·481	2	2	2
O_1	0·4332	0·1609	0·0764	2·243	0·809	1·480	6	6	6
O_2	0·7154	0·2203	0·0108	4·026	1·108	0·209	6	6	5
C_1	0·8130	0·8088	0·2016	4·048	4·068	3·905	10	9	9
C_2	0·9730	0·8210	0·1559	5·083	4·130	3·020	7	8	8
C_3	0·9223	0·6326	0·1022	4·945	3·182	1·980	8	9	7
C_4	0·7242	0·4865	0·1082	3·805	2·447	2·096	7	7	6
C_5	0·6222	0·2745	0·0604	3·360	3·381	1·170	7	7	6
α-Selenophene-carboxylic acid									
Se	0·5931	0·5731	0·1823	2·938	2·894	3·620	1	1	1
O_1	0·4361	0·1636	0·0741	2·325	0·826	1·472	8	9	6
O_2	0·7160	0·2179	0·0086	4·129	1·100	0·171	9	9	7
C_1	0·8227	0·8285	0·1986	4·224	4·184	3·944	11	12	9
C_2	0·9696	0·8269	0·1515	5·206	4·176	3·009	11	12	12
C_3	0·9136	0·6358	0·0998	5·024	3·211	1·982	10	15	9
C_4	0·7219	0·4872	0·1044	3·899	2·460	2·073	9	11	6
C_5	0·6248	0·2782	0·0604	3·457	1·405	1·200	9	12	8

Transformation matrix from monoclinic x, y, z to orthogonal x', y', z' coordinates:

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

reflections are given in Table 1. The intensities of the reflections in different layers were correlated by means of $0kl$ Weissenberg photographs. Only a few reflections with $k=5$ and 6 were present in these photographs; they were not used in the subsequent calculations. For non-equatorial layers the shape of the spots was taken into account following Phillips (1956).

Refinement

The refinement was carried out in the same way for both compounds. The starting coordinates assumed were those obtained from two-dimensional analyses with mean thermal parameters $B=4{\cdot}2$ and $3{\cdot}5$ Å^2 for the thiophene- and selenophene-compound respectively.

A first step was a three-dimensional Fourier synthesis which gave a new set of coordinates and isotropic thermal parameters for each atom, these last being deduced from the peak heights. Then two cycles of Booth's 'differential synthesis' with isotropic thermal parameters and three cycles with anisotropic thermal parameters were performed. The refinement was considered at an end when the coordinate shifts were less than one half of the corresponding standard deviations for the light atoms.

The atomic scattering factors used throughout the calculations were those of Thomas & Umeda (1957) for Se, of Dawson (1960) for S and of Berghuis *et al.* (1955) for O and C.

The final coordinates with their standard deviations (Cruickshank, 1949) are reported in Table 2; the largest difference with respect to the coordinates from two-dimensional analyses are observed for the y values, many peaks being incompletely resolved in (100) projections. The quoted $\sigma(y)$'s perhaps underestimate the errors in the y coordinates because reflections with $k=5$ and 6 have been omitted.

Table 3. *Thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
α-Thiophene-carboxylic acid						
S	3·87	5·74	4·38	−0·41	1·18	−0·18
O_1	4·06	5·93	4·48	−1·38	1·17	−0·31
O_2	5·77	5·69	3·95	−1·80	1·64	−0·79
C_1	4·10	4·99	4·82	0·35	0·80	−0·22
C_2	3·57	4·79	3·69	0·08	0·33	0·40
C_3	4·92	6·55	5·53	0·11	0·99	0·17
C_4	3·14	3·80	3·52	−0·53	0·57	0·15
C_5	3·04	4·01	2·90	−0·30	−0·06	0·35
α-Selenophene-carboxylic acid						
Se	4·16	3·56	3·79	−0·24	1·46	−0·15
O_1	4·12	2·79	3·74	−1·10	1·21	−0·66
O_2	6·24	3·78	4·07	−1·20	2·37	−0·93
C_1	5·49	2·16	3·60	0·62	1·16	−0·49
C_2	4·93	2·75	5·47	−0·83	1·36	−0·23
C_3	3·84	2·34	4·61	−1·07	0·92	0·12
C_4	3·96	0·38	3·06	−0·22	0·87	−0·21
C_5	3·70	1·98	3·31	0·27	0·57	0·12

In Table 3 are listed the anisotropic thermal parameters obtained at the end of the refinement with Cruickshank's (1956) method. Their numerical values are influenced by the omission of reflections with $k \geq 5$, so they must be considered only as additional parameters for improving the agreement between observed and calculated quantities.

The comparison between the observed and calculated structure factors is shown in Table 4 and the corresponding R (observed reflections only) and R' values (including $F_o = \frac{1}{2}F_{\min.}$ when $F_c > F_{\min.}$ for

Table 4. *Calculated and observed structure factors*

$F_o' = 10|F_o|$, $F_c' = 10F_c$. A minus sign after an F_o' must be interpreted as 'less than'

	SC_4H_3COOH		SeC_4H_3COOH			SC_4H_3COOH		SeC_4H_3COOH			SC_4H_3COOH		SeC_4H_3COOH			SC_4H_3COOH		SeC_4H_3COOH			SC_4H_3COOH		SeC_4H_3COOH	
l	F_o'	F_c'	F_o'	F_c'	l	F_o'	F_c'	F_o'	F_c'	l	F_o'	F_c'	F_o'	F_c'	l	F_o'	F_c'	F_o'	F_c'	l	F_o'	F_c'	F_o'	F_c'
			0 0 1		12	54-	30	324	-332	3	415	484	779	992	11	93	-76	148	-161				4 1 1	
2	156	98	286	-343	14	56-	-7	123	129	4	590	-798	902	-1066	12	112	116	182	194	0	143	136	263	252
4	404	-339	379	-389	16	219	206	313	331	5	47	-47	440	-481	13	110	108	301	297	1	104	119	368	375
6	280	263	678	717	18	56-	26	177	-184	6	125	-134	36-	0	14	36-	13	84	-82	2	33-	24	124	-113
8	459	-402	859	-970	20	51-	50	223	234	7	21-	-12	148	136	15	94	-99	267	-253	3	133	-133	301	-319
10	316	292	535	576	22	41-	21	69-	30	8	23-	24	71	67	16	36-	-21	71-	33	4	199	137	193	187
12	281	263	444	398	24	65	-82	134	-176	9	43	37	297	281	17	35-	27	84	68	5	107	109	100	107
14	94	-86	402	-366						10	70	-43	246	-197	18	33-	-34	67-	-19	6	35-	21	68-	54
16	109	126	416	407			4 0 1			11	255	-221	684	-622	19	57	61	117	107	7	86	97	208	215
18	58-	68	88-	-29	0	136	-129	374	-333	12	147	128	358	343	20	28-	-33	96	-95	8	53	-49	111	-129
20	54-	-19	86-	-76	2	184	151	123	103	13	229	207	503	437	21	54	-44	123	-115	9	107	-124	226	-249
22	47-	-2	134	151	4	241	210	531	463	14	51	-26	89	-86	22	44	51	80	72	10	45	39	102	101
24	34-	-46	120	-145	6	148	-132	395	-342	15	110	116	169	156	23			33-	47	11	35-	7	69-	85
					8	146	152	242	200	16	117	-102	165	-138						12	76	-75	89	-79
		1 0 1			10	58-	43	88-	90	17	156	-150	322	-285			$\bar{2}$ 1 1			13	33-	15	66-	5
0	465	-494	907	-1071	12	56-	-48	177	-180	18	83	-86	71-	-2	1	287	-301	789	-797	14	31-	-2	63-	-24
2	640	571	1044	1199	14	52-	95	227	189	19	35-	31	198	182	2	207	209	485	440	15	29-	-7	74	-69
4	436	-338	615	-599	16	64	-57	72-	-58	20	57	-52	134	-144	3	30	30	456	406	16	26-	36	73	81
6	210	191	93	-37	18	32-	-21	57-	-58	21	31-	-21	121	-113	4	33	24	106	-114	17	40	47	121	119
8	521	430	777	862						22	28-	-18	58-	9	5	110	-78	149	-86	18	18-	-28	43-	-38
10	44-	-56	431	-438			$\bar{4}$ 0 1			23	24-	-16	52-	-42	6	124	-104	280	-227	19			32-	-35
12	108	103	231	198	2	52-	29	410	368	24	19-	-12	44-	26	7	307	-308	763	-687					
14	54-	26	236	180	4	228	-233	563	-497	25			129	135	8	318	309	606	513			$\bar{4}$ 1 1		
16	201	-222	465	-447	6	53-	73	80	72						9	246	236	721	661	1	33-	17	129	-121
18	57-	54	156	151	8	350	323	627	596			1 1			10	113	84	55-	-33	2	32-	-16	62-	-32
20	109	142	129	119	10	56-	-47	394	-369	0	93	-74	230	-217	11	30-	24	199	-198	3	118	-114	194	-188
22	43-	7	71-	-36	12	57-	0	193	216	1	287	-291	354	-334	12	31-	-14	60-	19	4	33-	10	103	107
24	25-	44	114	127	14	58-	-4	88-	61	2	616	812	711	736	13	84	-78	145	-130	5	188	187	478	443
					16	130	-154	335	-366	3	561	-569	874	-952	14	171	172	301	261	6	33-	-41	224	-199
		$\bar{1}$ 0 1			18	52-	25	229	223	4	540	555	758	835	15	123	103	411	357	7	148	-123	444	-395
2	805	-850	716	-724	20	43-	17	71-	-56	5	489	491	857	940	16	40	-41	190	-169	8	112	77	236	205
4	168	163	486	502	22	78	-79	126	-135	6	124	72	154	-131	17	66	-74	360	-320	9	83	-92	67-	-13
6	253	-245	813	-841						7	96	87	160	-197	18	62	58	132	115	10	108	-93	68-	-63
8	453	389	808	873			5 0 1			8	126	128	171	201	19	35-	-17	68-	63	11	228	207	367	333
10	41-	-32	62-	37	0	152	166	355	321	9	42	-31	50-	-21	20	118	120	157	143	12	190	-171	314	-303
12	482	-450	799	-817	2	127	-116	208	-183	10	91	-81	54-	2	21	53	44	125	118	13	53	-54	253	-273
14	52-	75	412	420	4	57-	-44	137	-117	11	94	95	340	350	22	28-	-4	57-	-46	14	62	-61	71-	32
16	117	-129	328	-319	6	57-	14	187	161	12	82	-91	255	-241	23	51	-49	174	-175	15	35-	-6	174	176
18	58-	-76	137	-134	8	160	-147	248	-232	13	195	-183	496	-483	24	19-	8	75	82	16	34-	-42	130	-121
20	55-	62	259	272	10	51-	15	81-	25	14	110	96	219	191	25			100	97	17	33-	16	66-	-8
22	100	-119	262	-271	12	45-	58	73-	99	15	84	73	211	187						18	31-	-17	63-	-49
24	36-	-19	62-	13	14	36-	23	62-	-47	16	100	94	100	93			3 1 1			19	99	-86	222	-220
					16			43-	64	17	108	90	162	145	0	290	-294	523	-516	20	50	50	137	117
		2 0 1								18	35-	12	69-	-15	1	314	-293	626	-636	21	60	55	197	194
0	52	50	371	326			$\bar{5}$ 0 1			19	34	-62	192	-178	2	27-	-19	96	92	22	17-	1	40-	-50
2	262	-258	778	-761	2	127	-130	379	-320	20	49	64	121	115	3	118	99	213	224					
4	37-	-8	414	421	4	57-	-2	87-	83	21	29-	26	135	135	4	29-	-4	56-	13			5 1 1		
6	264	-231	295	-303	6	194	203	392	338	22	25-	22	54-	-2	5	30-	13	138	135	0	64	-60	86	-95
8	577	-408	681	-634	8	274	-270	579	-503	23	21-	-8	46-	-47	6	164	-172	265	-250	1	36-	-21	154	-147
10	49-	-20	286	290	10	118	-115	88-	43	24			35-	-31	7	117	-115	333	-346	2	36-	2	71-	58
12	54-	-2	234	-232	12	56-	11	87-	-34						8	48	37	170	168	3	36-	20	179	180
14	57-	55	86-	50	14	67	-86	245	-247			$\bar{1}$ 1 1			9	134	130	319	333	4	75	-81	136	-135
16	57-	78	256	238	16	105	98	300	306	1	343	393	825	841	10	119	-114	148	-165	5	135	-118	193	-207
18	89	-132	285	-265	18	40-	19	136	-86	2	42	-63	358	-325	11	35-	-21	68-	-67	6	59	55	69-	75
20	47-	-28	76-	14	20	88	-77	52-	-111	3	206	-192	796	-737	12	94	-109	128	-135	7	93	49	68-	10
22	34-	-4	59-	21						4	108	73	374	298	13	64	-24	101	-113	8	93	68	83	100
							6 0 1			5	259	258	600	561	14	73	78	114	117	9	82	88	154	177
		$\bar{3}$ 0 1			0	86	-96	250	-235	6	96	-65	101	-97	15	56	41	168	167	10	31-	33	63-	-15
2	32-	-12	148	141	2	52-	78	172	155	7	144	102	311	239	16	33-	-12	67-	-64	11	63	-59	108	-121
4	730	-593	1069	-1119	4	49-	-14	78-	-3	8	332	-324	536	-524	17	62	-72	141	-138	12	27-	23	56-	45
6	107	130	594	611	6	45-	57	73-	-17	9	357	-364	758	-778	18	28-	-6	58-	21	13	24-	10	52-	32
8	40-	22	156	-144	8	39-	52	129	127	10	26-	-1	177	194	19	25-	-6	54-	-14	14	21-	-1	46-	-15
10	413	-368	627	-646	10	51	-90	109	-115	11	138	117	496	458	20	20-	0	46-	13	15	16-	2	40-	12
12	277	277	600	636	12			38-	-52	12	166	-158	344	-312	21			64	73	16			29-	-19
14	55	-69	306	-321						13	47	36	60-	-69										
16	150	-183	152	-169			$\bar{6}$ 0 1			14	42	-30	101	-94			$\bar{3}$ 1 1					$\bar{5}$ 1 1		
18	146	135	295	287	2	54	-93	84-	5	15	172	-169	343	-290	1	124	121	464	455	1	36-	1	69-	8
20	54-	-57	265	-290	4	96	107	148	129	16	44	44	181	170	2	109	89	51-	-41	2	65	59	69-	89
22	46-	31	116	115	6	66	-76	239	-211	17	83	75	316	277	3	119	93	88	2	3	132	133	269	278
24	34-	81	84	111	8	51-	21	185	170	18	93	-92	236	-209	4	131	-119	153	-133	4	188	-197	289	-287
					10	49-	70	78-	2	19	35-	2	185	-160	5	76	-73	331	-291	5	112	-110	325	-323
		3 0 1			12	45-	-44	105	-112	20	34-	38	69	65	6	28-	-26	170	146	6	36-	-13	71-	59
0	272	253	265	247	14	86	82	236	237	21	32-	-19	64-	7	7	314	299	785	699	7	86	-68	71-	54
2	258	208	614	517	16	31-	-20	115	-129	22	29-	35	61	57	8	55	41	159	-141	8	36-	18	71-	-1
4	387	-328	738	-692						23	39	41	168	134	9	159	-159	464	-425	9	98	84	131	117
6	207	193	424	382			7 0 1			24	20-	-17	72	-79	10	41	32	147	142	10	90	-48	134	-126
8	108	123	195	156	0	32-	28	100	89	25			141	-137	11	161	-149	160	-148	11	67	-63	225	-227
10	213	-194	377	-349	2	28-	-35	97	-115						12	144	134	174	182	12	100	102	183	190
12	119	102	326	303	4			44-	37			2 1 1			13	194	177	383	390	13	33-	30	187	213
14	57-	-68	147	-140						0	124	-116	51	76	14	35-	18	90	-85	14	32-	38	64-	-22
16	54-	-67	112	-102			$\bar{7}$ 0 1			1	367	422	662	734	15	80	-66	341	-331	15	31-	10	62-	-58
18	47-	81	155	158	2	34-	55	58-	52	2	22-	-50	79	-121	16	44	-38	107	94	16	29-	-4	60-	0
20	36-	-16	95	-93	4	35-	-28	92	-87	3	22-	-38	43-	42	17	35-	31	176	180	17	72	-76	160	-153
					6	33-	34	140	141	4	127	-136	248	-250	18	34-	-19	68-	-28	18	24-	23	83	88
		$\bar{3}$ 0 1			8	30-	18	54-	-63	5	288	-307	593	-658	19	33-	65	131	112	19	58	61	170	187
2	60	-86	455	-467	10	23-	-43	48-	-62	6	26-	-42	132	145	20	58	-67	129	-113	20	15-	-6	61	-84
4	291	282	764	772						7	252	231	517	569	21	80	-74	215	-214					
6	133	109	136	-138			0 1 1			8	78	72	55-	-92	22	25-	-7	52-	54			6 1 1		
8	146	-143	209	-213	1	64-	-247	337	-481	9	125	-129	219	-277	23	36	29	147	148	0	45	-34	64-	-21
10	195	182	514	522	2	232	197	380	434	10	39	53	60-	47	24			38	-47	1	32-	12	63-	43

unobserved reflections) are reported in Table 1. The standard deviations of electron-density and of their first derivatives are:

for

SC_4H_3COOH $\sigma(\varrho) = 0{\cdot}19$ e.Å^{-3};
$\sigma(A_h) = 0{\cdot}44$, $\sigma(A_k) = 0{\cdot}33$, $\sigma(A_l) = 0{\cdot}40$ e.Å^{-4};

SeC_4H_3COOH $\sigma(\varrho) = 0{\cdot}26$ e.Å^{-3};
$\sigma(A_h) = 0{\cdot}67$, $\sigma(A_k) = 0{\cdot}65$, $\sigma(A_l) = 0{\cdot}64$ e.Å^{-4}.

Table 4 (*cont.*)

l	SC_4H_3COOH F_o'	F_c'	SeC_4H_3COOH F_o'	F_c'
		6 1	1	
2	36	45	63-	-8
3	35	-34	103	-114
4	30-	19	61-	58
5	28-	35	80	114
6	41	-53	56-	-72
7	49	-48	54-	-76
8	23-	-21	50-	-23
9	21-	5	46-	-22
10	17-	-19	41-	9
11			35-	82
		$\bar{6}$ 1	1	
1	41	61	111	123
2	52	-35	100	-92
3	108	-117	249	-245
4	32-	31	66-	98
5	32-	6	118	112
6	86	90	64-	65
7	61	77	63-	62
8	31-	4	62-	2
9	62	-48	187	-138
10	53	43	106	106
11	59	40	180	195
12	35	-17	94	-81
13	25-	-11	89	-101
14	23-	-16	49-	-9
15	86	-69	91	-100
16	40	32	90	79
17			131	148
		7 1	1	
0	18-	-16	41-	18
1	41	52	40-	69
2			38-	-11
3			35-	36
4			30-	-39
		$\bar{7}$ 1	1	
1	44	-56	99	-114
2	19-	6	44-	45
3	20-	20	69	94
4	39	-14	44-	-43
5	19-	39	44-	3
6	47	-15	43-	-10
7	18-	-55	71	-98
8	16-	22	39-	55
9			95	120
10			68	-69
		0 2	1	
1	252	-212	524	-608
2	354	-315	499	-574
3	240	-179	95	-69
4	260	-239	265	-275
5	29	-15	139	155
6	51	37	241	257
7	82	-72	432	-426
8	45	-40	287	-304
9	200	175	472	468
10	47	67	188	206
11	26-	9	64-	8
12	27-	-12	68-	41
13	166	-172	365	-363
14	222	-228	376	-407
15	61	60	271	247
16	31-	7	114	89
17	75	-60	169	-157
18	30-	3	77-	-39
19	44	-48	75	-86
20	47	-49	90	-80
21	57	69	157	159
22	41	44	104	112
23	27	-30	97	-104
24			60	-62
		1 2	1	
0	113	-116	408	-370
1	301	325	798	771
2	339	376	671	692
3	92	-62	373	-350
4	17-	19	111	-96
5	19-	2	50	-7
6	370	-344	445	-419
7	342	316	575	596
8	89	-15	168	171
9	126	-125	377	-399
10	113	-121	318	-320
11	27-	-14	138	149
12	42	49	102	114
13	30-	26	74-	48
14	90	92	185	195
15	50	-55	229	-224
16	81	-72	190	-179
17	86	82	242	251

l	SC_4H_3COOH F_o'	F_c'	SeC_4H_3COOH F_o'	F_c'
18	29-	14	75-	85
19	28-	-9	72-	-45
20	25-	-26	67-	-34
21	25	-24	61-	-61
22	27	-40	76	-79
23			74	82
		$\bar{1}$ 2	1	
1	193	234	457	512
2	141	166	266	221
3	15-	28	97	95
4	158	191	399	380
5	227	-231	597	-584
6	67	-72	361	-384
7	127	124	455	493
8	135	118	329	313
9	105	-105	245	-265
10	157	55	83	37
11	229	-215	393	-366
12	95	-100	258	-255
13	110	109	333	311
14	137-	119	313	295
15	35	46	133	-122
16	105	116	78-	39
17	31-	-9	78-	59
18	31-	-3	77-	0
19	49	58	152	147
20	46	52	141	130
21	59	-52	168	-174
22	22-	8	74	-83
23	18-	-27	52-	21
24			40-	31
		2 2	1	
0	19-	15	146	125
1	74	-69	380	-357
2	162	-151	423	-411
3	137	155	511	503
4	382	416	655	598
5	314	-313	564	-540
6	122	113	146	101
7	25-	-30	148	-140
8	26-	3	90	-84
9	233	218	449	449
10	163	139	310	296
11	89	-89	253	-260
12	97	-91	181	-194
13	50	53	91	118
14	31-	14	78-	16
15	31-	58	78-	101
16	53	61	121	131
17	49	-49	150	-151
18	27-	-29	97	-94
19	27	29	101	103
20	21-	25	58-	56
21	17-	12	93	-11
22			37-	36
		$\bar{2}$ 2	1	
1	151	-139	236	-186
2	202	203	373	315
3	276	-306	658	-609
4	27	-25	300	-252
5	244	270	712	672
6	166	175	475	451
7	130	122	85	-98
8	33	-35	83	-89
9	50	53	62-	46
10	59	-56	184	-177
11	83	80	350	345
12	155	138	347	360
13	107	-99	362	-374
14	30-	32	108	-101
15	31-	14	127	139
16	31-	8	78-	44
17	48	39	93	100
18	30-	4	115	102
19	43	-37	202	-193
20	59	-58	168	-165
21	34	39	144	154
22	21-	-3	63	59
23	17	27	49-	13
24			35-	34
		3 2	1	
0	25-	2	62-	30
1	50	-41	62-	55
2	83	-88	63-	58
3	104	-110	367	-326
4	154	-164	376	-358
5	88	95	314	309
6	109	93	210	189
7	29-	-29	123	-109
8	30-	1	74-	25
9	30-	26	76-	-54

l	SC_4H_3COOH F_o'	F_c'	SeC_4H_3COOH F_o'	F_c'
10	31-	5	77-	-92
11	31-	21	191	177
12	31-	36	124	125
13	95	-102	196	-209
14	30-	-34	76-	-92
15	28-	-14	74-	-25
16	27-	23	70-	-3
17	24-	21	65-	70
18	22-	23	59-	79
19	18-	-10	51-	-58
20			40-	-61
		$\bar{3}$ 2	1	
1	42	-28	202	-166
2	152	-171	356	-332
3	272	282	679	615
4	80	85	319	294
5	64	-77	344	-305
6	129	-130	297	-269
7	77	-65	67-	-41
8	119	-116	203	-203
9	58	68	261	248
10	167	165	356	356
11	181	-176	467	-473
12	142	-124	277	-267
13	126	109	264	268
14	105	-106	78-	-58
15	147	120	194	176
16	31-	-25	77-	17
17	92	-83	228	-224
18	105	-97	250	-246
19	26-	19	191	167
20	24-	22	65	100
21	21-	-10	85	-86
22	17-	32	50-	24
23			70	-72
		4 2	1	
0	46	-42	158	-122
1	142	155	199	197
2	30-	54	75-	21
3	30-	43	197	169
4	31-	-14	111	91
5	149	-158	339	-316
6	140	-156	286	-276
7	31-	-9	78-	70
8	31-	-32	78-	13
9	31-	12	78-	12
10	30-	18	77-	55
11	29-	-18	75-	-68
12	41	-36	73-	-80
13	51	53	125	142
14	25-	-3	66-	53
15	22-	-2	61-	-41
16	19-	1	55-	-28
17	15-	-29	46-	-40
18			33-	-25
		$\bar{4}$ 2	1	
1	57	68	287	238
2	116	119	333	282
3	76	-82	353	-295
4	32	-37	197	-175
5	30-	-15	78	78
6	148	-150	169	-150
7	152	158	273	244
8	104	100	224	207
9	142	-132	365	-337
10	85	-79	238	-234
11	31-	-17	165	144
12	61	-58	78-	13
13	57	46	78-	17
14	97	87	77-	88
15	108	-96	209	-205
16	28-	-2	112	-114
17	26-	30	172	174
18	72	66	189	184
19	22-	-2	123	-98
20	19-	22	53-	4
21	24	-24	43-	-38
		5 2	1	
0	31-	0	189	109
1	52	-52	155	-142
2	31-	-11	78-	-38
3	44	41	77-	30
4	71	77	77-	38
5	47	45	163	138
6	70	83	173	154
7	47	-42	165	-145
8	38	-35	99	-89
9	50	52	78	82
10	24-	19	65-	20
11	22-	7	61-	39
12	20-	20	56-	41

l	SC_4H_3COOH F_o'	F_c'	SeC_4H_3COOH F_o'	F_c'
13	17-	-43	50-	-86
14			74	-66
		$\bar{5}$ 2	1	
1	33	-28	78-	-175
2	45	-52	175	-173
3	31-	0	153	125
4	39	-16	78-	12
5	31-	14	78-	26
6	102	110	185	173
7	102	-85	251	-226
8	30-	30	95	-81
9	30-	15	169	163
10	30	26	154	148
11	29-	31	74-	-44
12	66	60	72-	55
13	27	-26	70-	-54
14	37	-23	67-	-96
15	63	52	184	185
16	47	38	141	141
17	33	-30	138	-135
18	17-	-1	48-	-42
19			39-	-32
		6 2	1	
0	46	-39	87	-101
1	69	69	159	157
2	24-	11	84	65
3	24-	-13	63-	-36
4	23-	-27	61-	-37
5	22-	-15	59-	-30
6	20-	-16	56-	-48
7	18-	17	52-	59
8	16-	23	48-	62
9			41-	-83
		$\bar{6}$ 2	1	
1	45	51	153	140
2	43	55	98	88
3	46	32	68-	27
4	57	63	92	92
5	38	-27	107	-93
6	56	-57	93	-128
7	52	61	185	173
8	24-	-12	64-	72
9	24-	-25	63-	-112
10	23-	1	61-	-34
11	42	-49	58-	-52
12	42	-39	55-	-85
13	62	52	51-	137
14	15-	18	45-	97
15			39-	-103
		$\bar{7}$ 2	1	
1			35-	-2
2			36-	21
3			37-	-71
4			65	-97
5			88	80
6			79	45
		0 3	1	
1	193	-202	337	-284
2	202	187	627	538
3	134	123	223	204
4	83	-79	527	-497
5	93	-73	173	-143
6	129	127	421	372
7	26-	5	49-	38
8	97	92	195	154
9	30-	5	57-	23
10	134	-126	427	-404
11	83	-82	131	-149
12	95	93	353	340
13	34-	-16	68-	14
14	35-	-5	105	-105
15	35-	-4	70-	-50
16	63	-55	142	-126
17	34-	12	67-	5
18	87	93	231	233
19	30-	2	60-	34
20	27-	2	99	-102
21	23-	11	48-	-15
22			39-	37
		1 3	1	
0	189	-204	429	-461
1	19-	-27	35-	-26
2	158	-179	287	-277
3	60	60	51	63
4	111	94	422	415
5	25-	-21	47-	23
6	231	-222	524	-566
7	126	-107	186	-182
8	40	-26	57-	74

l	SC_4H_3COOH F_o'	F_c'	SeC_4H_3COOH F_o'	F_c'
9	32-	31	60-	46
10	85	81	203	195
11	34-	-23	66-	1
12	96	-100	324	-318
13	59	-59	89	-86
14	59	50	226	207
15	35-	9	69-	17
16	34-	-24	68-	-48
17	33-	17	65-	21
18	76	-73	203	-163
19	33	-36	57-	-25
20	24-	17	94	107
21	18-	-18	42-	-24
		$\bar{1}$ 3	1	
1	178	169	244	274
2	84	-85	424	-481
3	30	-17	70	-70
4	201	189	485	520
5	149	-144	180	-167
6	25-	10	47-	-12
7	33	-39	51-	-53
8	146	-151	417	-411
9	46	37	57-	-26
10	132	136	522	480
11	175	180	290	293
12	34-	36	152	-121
13	34-	27	68-	54
14	35-	-6	69-	-12
15	35-	-22	70-	-48
16	94	101	267	286
17	34-	15	68-	55
18	45	-34	181	-206
19	30-	-33	91	-75
20	28-	-18	56-	47
21	24-	22	50-	30
22	26	22	41-	73
		2 3	1	
0	220	243	507	544
1	30	27	60	52
2	27-	-11	95	-81
3	28-	-1	53-	9
4	31	-37	197	-183
5	53	-51	59	-84
6	147	135	420	407
7	33-	-11	62-	1
8	168	-167	345	-358
9	111	124	118	124
10	34-	-21	68-	-11
11	68	73	131	118
12	74	72	210	204
13	35-	-10	70-	34
14	63	-59	204	-199
15	43	-38	89	-80
16	35	35	116	113
17	30-	-1	59-	-24
18	26-	17	54-	29
19	22-	15	47-	33
20			78	-92
		$\bar{2}$ 3	1	
1	50	44	49-	-2
2	118	103	415	443
3	57	59	99	88
4	78	-84	198	-209
5	82	89	104	113
6	165	-154	325	-329
7	33	25	57-	30
8	132	126	438	442
9	95	103	175	184
10	52	-57	310	-302
11	44	-34	66-	-41
12	34-	-29	68-	7
13	142	-148	204	-220
14	35-	20	173	171
15	44	44	70-	36
16	126	-129	343	-353
17	41	40	66-	36
18	32-	-27	97	76
19	29-	18	59-	60
20	26-	18	54-	37
21	22-	19	47-	51
22			92	-128
		3 3	1	
0	154	-164	426	-460
1	33-	23	62-	-8
2	140	149	361	340
3	147	154	266	211
4	64	53	89	88
5	78	74	113	124
6	34-	32	144	-135
7	130	-129	164	-193
8	98	122	283	308

Fairly good agreement has been found between observed and calculated peak heights and curvatures (Table 5).

The calculations were performed on an IBM 650 computer using the programmes of Brown, Lingafelter, Stewart & Jensen (1959) for structure factors and

Table 4 (*cont.*)

Fourier syntheses, and those of Shiono (1957, 1959) for differential synthesis and refinement of thermal parameters.

Discussion

Bond lengths and angles are reported in Table 6 and Fig. 1. The standard deviations are calculated from the formulae of Ahmed & Cruickshank (1953) for bond lengths and of Darlow (1960) for angles.

Using the significance test of Cruickshank & Robertson (1953) to compare bond lengths and angles, one can see that there is a mirror line of symmetry in the ring of both compounds. Thus in the thiophene-derivative S–C_1 and S–C_4 lengths are not significantly different ($\Delta/\sigma = (l_1 - l_2)/(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}} = 0{\cdot}67 < 1{\cdot}96$) and the same applies to C_1–C_2 and C_3–C_4 ($\Delta/\sigma = 0{\cdot}06$), S–$C_1$–$C_2$ and S–C_4–C_3 ($\Delta/\sigma = 0{\cdot}08$), C_1–C_2–C_3 and C_2–C_3–C_4 ($\Delta/\sigma = 0{\cdot}46$). Similar results are obtained for the selenophene-derivative: there is no significant difference between Se–C_1 and Se–C_4 ($\Delta/\sigma = 1{\cdot}53$), C_1–C_2 and C_3–C_4 ($\Delta/\sigma = 0{\cdot}05$), Se–$C_1$–$C_2$ and Se–C_4–C_3 ($\Delta/\sigma = 1{\cdot}48$), C_1–C_2–C_3 and C_2–C_3–C_4 ($\Delta/\sigma = 1{\cdot}14$).

Considering the results obtained by Goodwin & Thomson (1954) for α-furoic acid, the angle on the hetero-atom increases from Se (87° 6′) to O (107°) according to the general rule. With increasing size of the hetero-atom, the X–C distances increase also but the other dimensions in the ring are not sensibly affected, excepting the angles on C_2 and C_3 which increase from furane- (∼ 104°) to selenophene-derivative (∼ 115°).

The carboxyl groups in the two acids are not in the same distance from the rings, and there is a small but significant difference between the distances ($\Delta/\sigma = 2{\cdot}53$). It seems that in the selenophene-derivative the carboxyl group is more co

Table 5. *Atomic peak heights* (e.Å^{-3}) *and curvatures* (e.Å^{-5})

			ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{hk}	A_{hl}	A_{kl}
α-Thiophene-carboxylic acid									
	S	obs.	24·5	229	160	218	−1	56	−1
		calc.	24·2	228	160	218	−1	60	2
	O_1	obs.	9·8	78	58	72	−7	17	0
		calc.	9·7	77	58	72	−7	17	0
	O_2	obs.	9·5	71	57	81	−8	17	−1
		calc.	9·5	71	57	79	−8	18	0
	C_1	obs.	5·9	44	36	46	2	11	2
		calc.	6·3	47	38	49	2	12	2
	C_2	obs.	6·7	61	43	52	2	9	1
		calc.	7·1	63	46	54	2	11	1
	C_3	obs.	7·0	59	38	59	−1	11	1
		calc.	6·4	54	35	56	2	12	0
	C_4	obs.	7·4	69	45	62	−1	12	4
		calc.	7·7	70	47	65	−1	15	4
	C_5	obs.	7·1	60	45	66	−5	11	0
		calc.	7·8	65	50	71	−5	14	0
α-Selenophene-carboxylic acid									
	Se	obs.	65·5	595	467	640	−6	156	−2
		calc.	64·6	586	456	632	−4	154	−1
	O_1	obs.	11·1	86	70	103	−3	19	−2
		calc.	11·1	82	69	102	−3	15	−3
	O_2	obs.	10·8	77	75	98	−5	25	2
		calc.	10·6	76	74	96	−5	24	2
	C_1	obs.	7·8	59	56	69	3	10	3
		calc.	7·7	59	54	68	3	10	2
	C_2	obs.	7·6	62	53	56	−7	8	−2
		calc.	7·3	60	52	55	−6	8	−2
	C_3	obs.	7·9	68	44	71	−8	14	2
		calc.	7·7	67	43	70	−7	15	1
	C_4	obs.	8·8	75	60	102	1	28	0
		calc.	9·2	80	61	108	1	31	−1
	C_5	obs.	8·2	72	56	79	−6	10	4
		calc.	8·5	73	57	82	−6	12	4

Table 6. *Bond lengths and angles*

	SC_4H_3COOH	SeC_4H_3COOH
X–C_1	1·701 ± 0·010 Å	1·850 ± 0·012 Å
X–C_4	1·693 ± 0·007	1·872 ± 0·008
C_1–C_2	1·363 ± 0·012	1·355 ± 0·015
C_3–C_4	1·362 ± 0·010	1·356 ± 0·015
C_2–C_3	1·414 ± 0·011	1·421 ± 0·017
C_4–C_5	1·481 ± 0·010	1·438 ± 0·014
C_5–O_1	1·292 ± 0·009	1·301 ± 0·013
C_5–O_2	1·201 ± 0·008	1·266 ± 0·012
$O_1H\cdots O_2'$	2·625 ± 0·008	2·613 ± 0·011
C_1–X–C_4	92° 1′ ± 24′	87° 6′ ± 26′
X–C_1–C_2	111 46 ± 39	112 15 ± 49
X–C_4–C_3	111 50 ± 32	110 40 ± 41
C_1–C_2–C_3	111 56 ± 43	114 12 ± 61
C_2–C_3–C_4	112 22 ± 38	115 43 ± 52
X–C_4–C_5	122 10 ± 31	120 57 ± 40
C_3–C_4–C_5	125 55 ± 37	128 19 ± 49
C_4–C_5–O_1	115 21 ± 35	117 49 ± 47
C_4–C_5–O_2	119 47 ± 40	120 32 ± 54
O_1–C_5–O_2	124 49 ± 40	121 38 ± 56

with the ring than in the thiophene-derivative; this explains the increased values of C_5–O_1 and C_5–O_2 in the former compound. The whole carboxyl group appears to be attracted by the hetero-atom, the angle C_3–C_4–C_5 being larger than X–C_4–C_5; the effect is more pronounced in the selenophene-derivative. The O_1 atom is probably that belonging to the hydroxyl group as indicated by the value of the distance C_5–O_1 which is longer than C_5–O_2 and by the angle C_4–C_5–O_1 which is smaller than C_4–C_5–O_2. These rules can be easily deduced considering the carboxyl group dimensions reported in the literature; some results are listed in Table 7.

In both compounds the oxygen of the OH group is facing the hetero-atom; the inverse situation occurs in α-furoic acid. The distances O_1–S = 2·948 ± 0·006 Å and O_1–Se = 3·046 ± 0·008 Å are slightly shorter than the sums of the van der Waals radii $r_O + r_S = 3·00$ Å (r_S = 1·60 Å, Donohue, 1950), $r_O + r_{Se} = 3·14$ Å (r_{Se} = 1·74 Å, Marsh, Pauling & McCullough, 1953). Shorter contacts of this kind have been observed in thioindigo (2·82 Å, von Eller, 1955*a*) and selenoindigo (2·99 Å, von Eller, 1955*b*).

Table 7. *Comparison of bond lengths and angles concerning carboxyl groups*

Acid	C–C	C–O	C–OH	C–C–O	O–C–OH	C–C–OH	OH · · · O	Reference
Formic	—	1·23 Å	1·26 Å	—	123°	—	2·58 Å	Holtzberg, Post & Fankuchen, 1953
Acetic	1·54 Å	1·24	1·29	122°	122	116°	2·61	Jones & Templeton, 1958
β-Nitropropionic	1·56	1·22	1·34	126	119·5	114·5	2·66	Sutor, Calvert & Llewellyn, 1954
β-Ionylidene crotonic (*trans*)	1·463	1·244	1·325	122·5	122·3	115·2	2·673	Eichhorn & MacGillavry, 1959
Malonic	1·54	1·24	1·29	117	128	115	2·71	Goedkoop & MacGillavry, 1957
	1·52	1·22	1·31	119	128	113	2·68	
Succinic (β-form)	1·51	1·25	1·30	124	122	114	—	Morrison & Robertson, 1949*a*
Maleic	1·44	1·20	1·28	118·4	125·5	114·8	2·46	Shahat, 1952
	1·47	1·21	1·28	111·3	119·2	124·1		
Glutaric (β-form)	1·53	1·23	1·30	123	122	115	2·69	Morrison & Robertson, 1949*b*
Adipic	1·52	1·23	1·29	120	126	114	—	Morrison & Robertson, 1949*c*
Pimelic (α-form)	1·48	1·20	1·34	126·6	119·8	113·9	2·67	Kay & Katz, 1958
	1·50	1·24	1·26	121·2	121·0	117·8	2·68	
Sebacic	1·51	1·24	1·27	120	124	116	—	Morrison & Robertson, 1949*d*
Racemic tartaric hydrate	1·44	1·22	1·28	123	124	113	2·72	Parry, 1951
	1·52	1·20	1·33	120	120	116	—	
Citric (anhydrous)	1·494	1·236	1·324	127·5	120·9	111·2	2·659	Nordman, Weldon & Patterson, 1960
	1·533	1·210	1·331	123·4	124·0	112·7	2·730	
	1·511	1·239	1·305	122·4	123·1	114·6	2·633	
Benzoic	1·48	1·24	1·29	122	122	118	2·64	Sim, Robertson & Goodwin, 1955
Salicylic	1·458	1·241	1·333	122·7	120·2	117·0	2·627	Cochran, 1953
p-Amino-salicylic	1·41	1·21	1·35	125	121	114	2·70	Bertinotti, Giacomello & Liquori, 1954
1-Naphtoic	1·40	1·25	1·28	127	110	122	2·58	Trotter, 1960
2-Naphtoic	1·44	1·33	1·37	122	112	127	2·54	Trotter, 1961
Nicotinic	1·48	1·18	1·34	124	122	114	—	Wright & King, 1953
α-Furoic	1·47	1·16	1·26	117	124	119	2·53	Goodwin & Thomson, 1954
Allokainic	1·55	1·25	1·26	116	130	113	2·71	Cruickshank, 1959
	1·54	1·20	1·32	123	125	112		

The analyses for the planarity of the molecules in the two acids are summarized in Table 8. The best least-squares planes have been calculated following Schomaker, Waser, Marsh & Bergman (1959), using a diagonal weight matrix. The statistical analysis, χ^2 test (Weatherburn, 1947), of the significance of the distances from the planes, Δ, shows that they are significant for the mean planes calculated through all the atoms in both compounds, the deviation from planarity being larger in the case of selenophene-derivative. For non-significant Δ values it is sufficient to exclude the hetero-atom only from the calculations of the mean planes. The distance ($\Delta = -0{\cdot}065$ Å) of Se from the plane of the other atoms is nearly twice that ($\Delta = -0{\cdot}028$ Å) of S and both are on the same side of the plane. It is possible that, owing to systematical errors, this last displacement could have a lower significance than that given by the statistical analysis.

The dihedral angle formed by the planes SeC_1C_2 and and SeC_3C_4 is 176° 39′; the corresponding angle in the thiophene-derivative is 178° 0′. The lack of planarity in the selenophene-acid is in agreement with the study of the Raman and infrared-absorption spectra of liquid selenophene (Gerding, Milazzo & Rossmark, 1953) which indicates a C_s symmetry for this molecule. The same feature has not been observed for the thiophene molecule which is generally assumed to be planar (Schomaker & Pauling, 1939; Bak, Christensen, Rastrup-Andersen & Tannenbaum, 1956). The hetero-atom does not lie in the plane of the ring in thioindigo ($\Delta = 0{\cdot}08$ Å, von Eller, 1955*a*) and selenoindigo ($\Delta = 0{\cdot}11$ Å, von Eller, 1955*b*), while in

Table 8. *Analysis of the planarity of the molecules*

Equation of the plane referred to orthogonal axes: $m_1x'+m_2y'+m_3z'=d$

	α-Thiophene-carboxylic acid					α-Selenophene-carboxylic acid				
Best plane through		$SO_1O_2C_1C_2C_3C_4C_5$		$O_1O_2C_1C_2C_3C_4C_5$			$SeO_1O_2C_1C_2C_3C_4C_5$		$O_1O_2C_1C_2C_3C_4C_5$	
m_1		−0·5058		−0·4981			−0·5146		−0·4970	
m_2		0·6788		0·6780			0·6790		0·6770	
m_3		−0·5324		−0·5406			−0·5236		−0·5428	
d		−1·3867		−1·3688			−1·4415		−1·4010	
Atom	$\sigma_\perp$* (Å) (×10³)	Δ (Å) (×10³)	$\Delta/\sigma_\perp$	Δ (Å) (×10³)	$\Delta/\sigma_\perp$	$\sigma_\perp$* (Å) (×10³)	Δ (Å) (×10³)	$\Delta/\sigma_\perp$	Δ (Å) (×10³)	$\Delta/\sigma_\perp$
X	2	−2	−1·0	−28	(−14·0)	1	−1	−1·0	−65	(−65·0)
O_1	6	13	2·2	0	0	8	36	4·5	6	0·8
O_2	6	−9	−1·5	2	0·3	8	−26	−3·3	1	0·1
C_1	9	22	2·4	0	0	11	44	4·0	−7	−0·6
C_2	8	11	1·4	5	0·6	12	23	1·9	8	0·7
C_3	8	−8	−1·0	−7	−0·9	12	−1	−0·1	2	0·2
C_4	7	7	1·0	0	0	9	20	2·2	4	0·4
C_5	7	2	0·3	−1	−0·1	10	−12	−1·2	−17	−1·7
$\Sigma(\Delta/\sigma_\perp)^2$			17·9		1·3			58·0		4·6
$\chi^2_{95\%}$			11·1		9·5			11·1		9·5
$\chi^2_{99\%}$			15·1		13·3			15·1		13·3

* $\sigma_\perp=\{m_1^2\sigma^2(x')+m_2^2\sigma^2(y')+m_3^2\sigma^2(z')\}^{\frac{1}{2}}$.

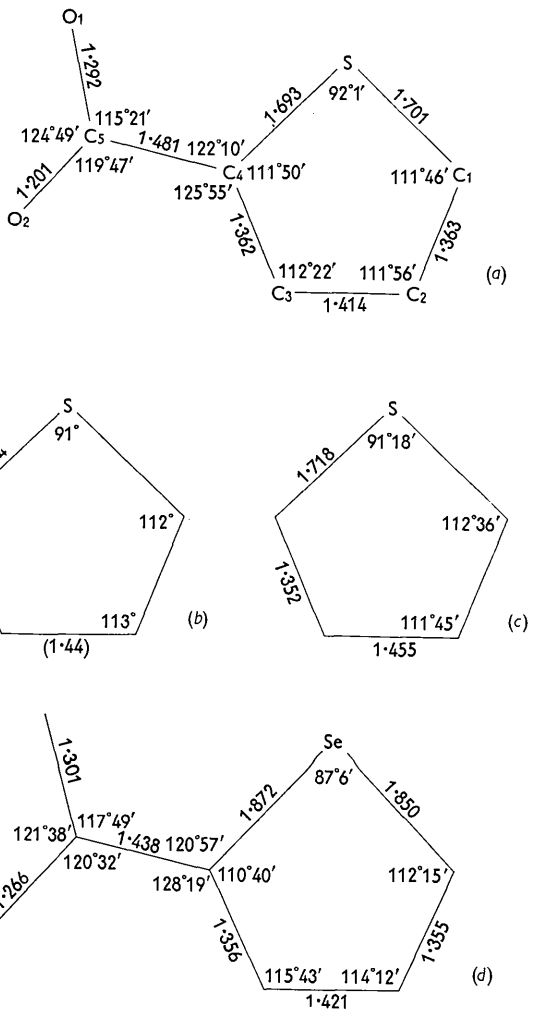

Fig. 1. Bond lengths and angles in: (*a*) α-thiophene-carboxylic acid, (*b*) thiophene by electron diffraction (Schomaker & Pauling, 1939), (*c*) thiophene by microwave spectra (Bak *et al.*, 1956), (*d*) α-selenophene-carboxylic acid.

thiophthene (Cox, Gillot & Jeffrey, 1949) the distance of the S atom from the plane through all the atoms* is −0·007 Å, and has negligible statistical significance.

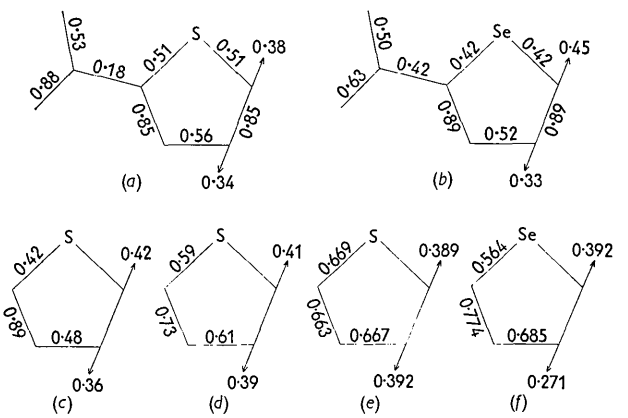

Fig. 2. M.o. bond orders and free valences in: (*a*) α-thiophene-carboxylic acid (from exp. lengths), (*b*) α-selenophene-carboxylic acid (from exp. lengths), (*c*) thiophene (from exp. lengths of Bak *et al.*, 1956), (*d*) thiophene (calc. by Longuet-Higgins, 1949), (*e*) thiophene (calc. by Milazzo & De Alti, 1959), (*f*) selenophene (calc. by Milazzo & De Alti, 1959).

From bond distances, 'experimental' π-bond orders were derived using for C–C a smooth curve drawn through the points (0, 1·50), (0·525, 1·421), (0·667, 1·39), (1·0, 1·34) (Goodwin & Vand, 1955). For the other

* This plane, calculated with unit weights from the coordinates indicated with *D*, has the equation:

$$-0{\cdot}6423x+0{\cdot}3294y-0{\cdot}6920z=-1{\cdot}6125\ .$$

The plane through $C_1C_2C_3$ calculated with the same coordinates is

$$-0{\cdot}6400x+0{\cdot}3205y-0{\cdot}6983z=-1{\cdot}6438$$

and the distances of $\bar{1}(\frac{1}{2},\frac{1}{2},0)$ and of S from this plane are: $p_1=-0{\cdot}001$, $p_2=-0{\cdot}029$ Å respectively.

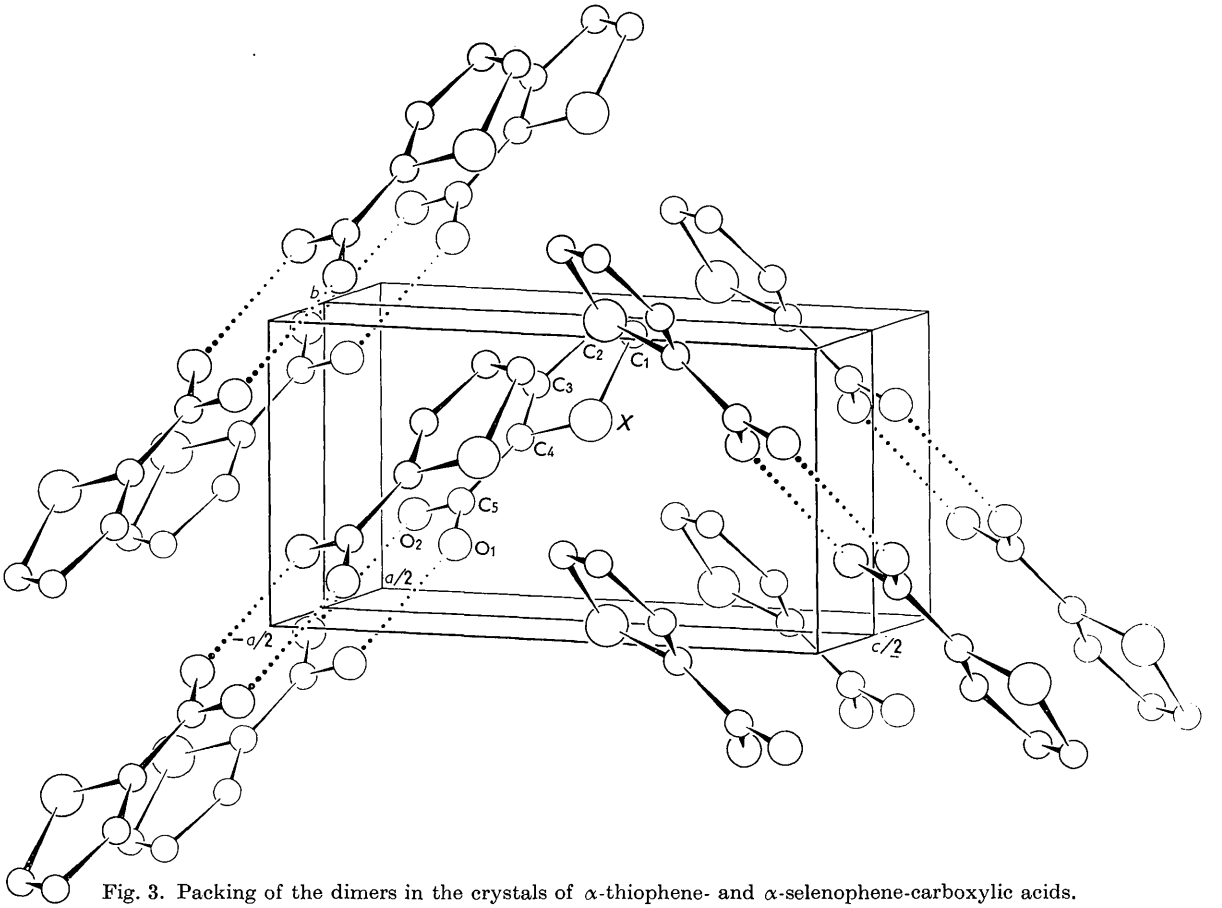

Fig. 3. Packing of the dimers in the crystals of α-thiophene- and α-selenophene-carboxylic acids.

bonds linear relationships were assumed between the points: (0, 1·43), (1·0, 1·17) for C–O, (0, 1·97), (1·0, 1·71) for C–Se (Abrahams, 1956) and (0, 1·81), (1·0, 1·59) for C–S (Wheatley, 1953). The bond orders obtained are reported in Fig. 2 with free-valence values (Coulson, 1953). These last agree with the generally greater reactivity of the α′ position in these compounds (Hartough, 1952; Chierici & Pappalardo, 1959). Longuet-Higgins (1949) has made molecular-orbital calculations on thiophene; it is interesting to observe that the results from his model are in a better agreement with the corresponding ones found in the ring of thiophene-acid than those deduced from experimental lengths for thiophene itself. The same cannot be said for the results of the m.o. calculations on thiophene given by Milazzo & De Alti (1959), although some qualitative agreement is observed between the bond orders and free valences calculated by these authors for selenophene and the corresponding values deduced from distances in selenophene-acid.

Bond orders for S–C and Se–C indicate a greater π-delocalization in the ring of thiophene-acid, but this is not supported by the dimensions of the remaining part of the ring which is practically unchanged in the two compounds. The difficulty of assigning the correct multiplicity to the C–S and C–Se bonds does not permit much weight to be put on bond orders derived from the corresponding bond lengths.

A comparison between thiophene-acid and thiophene itself shows that, as a result of conjugation between carboxyl group and ring, there is a shortening in the C–S and C_2–C_3 bonds, corresponding to an increased π-delocalization in the ring. This seems to indicate that in the model for thiophene, calculated by Longuet-Higgins and much more in the model of Milazzo & De Alti, the π-delocalization is overemphasized. The lack of knowledge on dimensions of selenophene does not permit a similar comparison.

The molecules form centrosymmetrical dimers, being linked together by hydrogen-bonds which are not significantly different in the two acids (mean value of OH · · · O distance: 2·62 ± 0·01 Å). The dimers are nearly coplanar; the dihedral angle between the planes

Table 9. *Intermolecular distances*

	SC_4H_3COOH	SeC_4H_3COOH
O_1–$C_3(x-1, y, z)$	3·923 ± 0·010 Å	3·943 ± 0·014 Å
O_1–$C_2(x-1, y-1, z)$	3·648 ± 0·009	3·711 ± 0·014
X–$C_2(x-1, y, z)$	3·762 ± 0·008	3·807 ± 0·011
X–$X(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$	4·028 ± 0·004	3·963 ± 0·003
C_1–$C_2(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·862 ± 0·012	3·978 ± 0·016
C_1–$C_1(2-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3·641 ± 0·018	3·700 ± 0·021
O_2–$C_3(2-x, 1-y, z)$	3·308 ± 0·009	3·339 ± 0·013

$O_1O_2\bar{I}$ and $O_1O_2C_1 \cdots C_5$ is equal in the two compounds: 178° 4′ for thiophene- and 178° 6′ for selenophene-acid.

The packing is shown in Fig. 3. The non-bonding distances are listed in Table 9.

Note added in proof.— A lack of planarity in the ring of α-thiophenic acid has been observed independently from a three-dimensional least squares low temperature (−170 °C) refinement by P. Hudson and J. H. Robertson (private communication) who find the sulphur atom lying 0.027 Å out of the best plane through the four carbon atoms of the ring.

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