

X-Ray Diffraction and Melting-Point Studies on Some Long-Chain Sulfur-Containing Acids¹

LEE P. WITNAUER, DAVID LUTZ, N. H. KOENIG,² and DANIEL SWERN,
Eastern Regional Research Laboratory,³ Philadelphia, Pennsylvania

THIS PAPER reports the x-ray diffraction powder data and melting points of three series of crystalline long-chain sulfur-containing acids, namely, some terminally substituted undecanoic acids. These compounds are

- sulfones, 11-(*n*-alkylsulfonyl)undecanoic acids, $\text{RSO}_2(\text{CH}_2)_{10}\text{CO}_2\text{H}$;
- sulfoxides, 11-(*n*-alkylsulfinyl)undecanoic acids, $\text{RSO}(\text{CH}_2)_{10}\text{CO}_2\text{H}$; and
- sulfides, 11-(*n*-alkylthio)undecanoic acids, $\text{RS}(\text{CH}_2)_{10}\text{CO}_2\text{H}$;

where R is a selected radical from methyl through undecyl. Aside from 11-(carboxymethylthio)undecanoic acid (2) there seems to be no x-ray diffraction data available on the effect on the solid-state structure of interrupting long-chain aliphatic compounds with a sulfide, sulfoxide, or sulfone group.

Experimental

Preparation. The compounds studied had the general formulas given above. They were recrystallized solids of high purity unless otherwise indicated. In addition to the acids previously reported (2, 3, 6) the new compounds listed in Table I were also used; these were prepared by the published methods.

X-Ray Technique. All samples were run on a G. E. XRD-3 direct-recording diffraction unit, using nickel-filtered CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$), 1° beam slit, 0.1° detector slit, medium resolution Soller slit, 2° -per-min. scanning speed, 60 in./hr. chart speed, linear scale, and 2-sec. time constant. For the powder data reported in Tables II, III, and IV samples were carefully ground in an agate mortar to insure random orientation and packed into the recess of a plastic holder approximately 1.0 in. long, 0.5 in. wide, and 0.015 in. deep. The intensities of the diffraction lines reported were measured as counts/sec. at the peak height minus counts/sec. of the background, and then expressed on a relative scale ($I_{\text{rel.}}$) with the strongest line arbitrarily given a value of 1,000.

The long spacings reported in Table V were obtained from oriented samples. Unground samples were placed in a thin layer on a glass slide and firmly pressed to insure adherence. The exposed surface on the glass slides was about 0.5 in. wide by 0.5 in. long. In general, particularly sharp and intense peaks were obtained, and in a number of cases 20 or more orders of the long spacing were observed. At least five orders are included in each average reported in Table V. The first and sometimes the second orders were not included in the average because of the limited accuracy

with which they could be measured. Duplicate determinations showed a variation of less than $\pm 0.1 \text{ \AA}$.

All compounds studied were crystallized from acetone or petroleum ether except where indicated.

Results and Discussion

Sulfones. The relative intensities and interplanar spacings of the corresponding diffractions of seven sulfones in which the alkyl groups, R, vary from methyl to undecyl, identify each member of the series (Table II). The long spacing increases regularly with the increase in the number of carbon atoms in the alkyl group, R. As shown in Figure 1, the spacings of both the odd and even members, including the methyl derivative, fall on the same line. Thus the sulfone derivatives do not show the alternation in long spacing that is so characteristic of the normal long-chain aliphatic acids (1).

The increment in long spacing per carbon atom, obtained from the slope of the line of Figure 1, is about 2.19 \AA . This is much larger than the maximum calculated increment, 1.306 \AA , assuming that the angle between carbon atoms is 116° and C-C distance is 1.54 \AA . Therefore the sulfone derivatives, like the normal fatty acids, exist as dimers in the solid state. The sine of the angle of tilt is $2.19/2 \div 1.306 = 0.838$, or the inclination of the chain to the 001 planes is about 57° . This is similar to the value calculated for the C form of the even aliphatic acids and the B' and C' forms of the odd aliphatic acids (4).

The melting points of the even and odd members of the sulfone series, when plotted against the number of carbon atoms in the alkyl chain, R, fall on the same curve (Figure 1). The only apparent exception

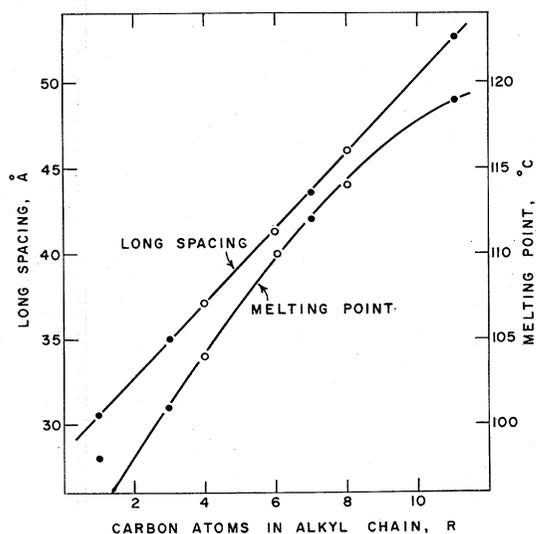


FIG. 1. Long spacings and melting points of sulfones, ● odd number of carbon atoms in alkyl chain, R, ○ even number of carbon atoms in alkyl chain, R.

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²Present address: Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany, Calif.

³Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I
Sulfides, Sulfoxides, and Sulfones^a

RS, RSO, or RSO ₂	Formula	M.P., °C. ^b	Neut. equiv.		Carbon, %		Hydrogen, %		Sulfur, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Amylthio.....	C ₁₀ H ₂₀ O ₂ S	45 ^c	288	288	—	—	—	—	11.1	11.3
Propylsulfanyl ^d	C ₁₄ H ₂₈ O ₂ S	60	276	277	60.8	60.4	10.2	10.4	11.6	11.4
Butylsulfanyl.....	C ₁₆ H ₃₀ O ₂ S	76	290	292	62.0	62.1	10.4	10.6	11.0	11.0
Hexylsulfanyl.....	C ₁₈ H ₃₄ O ₂ S	83	319	323	64.1	64.1	10.8	10.9	10.1	9.9
Heptylsulfanyl.....	C ₁₈ H ₃₆ O ₂ S	82	333	335	65.0	64.8	10.9	10.9	9.64	9.50
Undecylsulfanyl.....	C ₂₂ H ₄₄ O ₂ S	94	389	394	68.0	67.8	11.4	11.6	8.25	8.19
Butylsulfonyl.....	C ₁₆ H ₃₀ O ₄ S	104	306	307	58.8	59.2	9.9	10.3	10.5	10.4
Hexylsulfonyl.....	C ₁₈ H ₃₄ O ₄ S	110	335	333	61.0	60.7	10.2	10.5	9.59	9.46
Undecylsulfonyl.....	C ₂₂ H ₄₄ O ₄ S	119	402	412 ^d	65.3	64.7	11.0	10.4	7.92	7.74

^a The only compounds in this table are the 11-(*n*-alkylthio)-, 11-(*n*-alkylsulfanyl)-, and 11-(*n*-alkylsulfonyl)undecanoic acids not previously reported; for preparation and characteristics of other compounds studied see references (2, 3, 6).

^b Determined with a micro hot stage.

^c Melted to liquid at 45°, then formed fibrous crystals that melted at 48°.

^d Approximate value; insoluble material gave erratic results.

is the methyl derivative. This nonalternation in melting-point data is in agreement with the diffraction results. The melting points of the even and odd members of the normal long-chain fatty acids however do show alternation (1).

The reason for the nonalternation exhibited by the sulfone derivatives is not apparent. The alternation of properties in tilted long-chain compounds has been accounted for on the basis of structure—in particular, the packing of chain ends (1). The odd-numbered chains should show a looser end-packing and be expected to melt at lower temperatures than the even-numbered chains. That this was not confirmed experimentally for the sulfone derivatives indicates that the configuration of the aliphatic chains about the sulfone group has been altered in such a way that the terminal hydrocarbon group, R, is similarly oriented whether R is even or odd.

The methyl derivative exhibited polymorphism. A completely different diffraction pattern (Table II) was obtained when it was crystallized from ethyl acetate instead of acetone. The long spacing for this

form was about 28.2 Å, about 2.3 Å less than shown by the other form.

Sulfoxides. The diffraction data for six sulfoxides, in which the alkyl group, R, varies from propyl to undecyl, are listed in Table III. The methyl derivative is not included because it gave an essentially amorphous pattern. Each member can be readily distinguished and identified by the x-ray diffraction data. In Figure 2 the long spacings of the sulfoxides are plotted against the number of carbon atoms in the alkyl chain, R. Two nonparallel straight lines are obtained, one for the even-membered and one for the odd-membered series. Thus the sulfoxides, unlike the sulfones, show alternation in long spacings. The increment in long spacing per carbon atom is about 2.11 Å for the odd-membered series and about 2.19 Å for the even-membered series. The latter value is similar to that found for the sulfone derivatives. The sulfoxides, like the sulfones and normal fatty acids, crystallize in tilted bimolecular layers. The corresponding angles of tilt (calculated as previously de-

TABLE II
X-Ray Diffraction Powder Data on Sulfones

R = Methyl		R = <i>n</i> -Propyl		R = <i>n</i> -Butyl		R = <i>n</i> -Hexyl		R = <i>n</i> -Heptyl		R = <i>n</i> -Octyl		R = <i>n</i> -Undecyl		R = Methyl ^a	
d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}
29.82	72	17.45	36	37.09	13	40.49	87	43.27	180	45.30	208	53.8	476	28.11	106
15.17	979	11.72	1000	18.59	7.3	20.53	133	21.85	298	22.91	583	26.18	905	14.15	1000
10.16	330	8.77	262	12.37	1000	13.76	1000	14.52	1000	15.29	1000	17.45	324	9.40	176
7.62	100	7.02	214	9.28	120	8.26	43	10.91	138	11.47	90	13.08	1000	7.04	191
6.10	1000	5.86	6.0	7.43	27	6.89	82	8.72	64	9.17	60	10.44	171	5.64	765
5.09	604	5.00	24	6.19	73	5.90	80	7.26	14	7.66	23	8.72	290	4.70	691
4.36	438	4.87	16	5.30	21	5.18	102	6.96	5.0	6.55	229	7.47	33	4.47	18
4.02	708	4.70	119	4.82	6.0	4.74	20	6.23	149	5.75	13	6.54	248	4.35	176
3.82	229	4.53	13	4.69	47	4.68	93	5.45	39	5.12	27	5.81	29	4.03	382
3.72	108	4.37	30	4.48	8.0	4.61	32	4.36	20	4.69	13	5.23	133	3.90	16
3.42	31	4.27	29	4.41	7.3	4.45	37	4.04	22	4.39	17	4.72	110	3.63	32
3.18	31	4.21	51	4.22	13	4.42	33	3.63	16	4.17	27	4.36	81	3.52	265
3.07	17	4.03	226	4.19	24	4.15	39	3.48	6.0	4.02	75	4.17	67	3.22	12
2.89	19	3.91	35	4.13	20	4.02	278	3.35	5.0	3.81	25	4.03	476	3.11	12
2.78	25	3.75	31	4.02	140	3.74	39	2.21	7.0	3.42	6.2	3.74	52	2.82	29
2.34	10	3.54	26	3.93	14	3.57	17			3.15	8.3	3.67	38	2.74	7.3
2.20	10	3.50	38	3.81	9.3	3.53	20			2.93	6.2	3.46	24	2.56	47
2.09	13	3.34	14	3.76	11	3.44	15			2.88	6.2	3.36	14	2.40	7.3
		3.18	73	3.72	25	3.28	15			2.20	10	3.14	52	2.35	5.8
		3.07	14	3.53	6.0	3.15	44					3.07	9.5	2.26	7.3
		2.96	21	3.45	14	2.96	20					3.00	9.5	2.17	29
		2.86	17	3.26	5.3	2.80	9.3					2.88	24	1.88	22
		2.79	8.3	3.17	3.1	2.54	11					2.55	14		
		2.69	6.0	3.07	8.7	2.24	15					2.37	19		
		2.62	8.3	2.94	4.7	2.15	24					2.22	33		
		2.48	11	2.90	4.7	2.11	5.6					2.20	67		
		2.34	11	2.84	12	1.89	3.7					2.09	24		
		2.26	26	2.75	2.7							2.00	24		
		2.22	48	2.67	2.0							1.90	24		
		2.10	11	2.60	4.7										
		2.00	7.1	2.46	4.0										
		1.94	4.8	2.33	6.0										
		1.90	7.1	2.25	13										
				2.21	30										
				2.11	7.3										
				2.01	5.3										
				1.90	3.33										

^a Polymorphic form obtained from ethyl acetate.

TABLE III
X-Ray Diffraction Powder Data on Sulfoxides

R = <i>n</i> -Propyl		R = <i>n</i> -Butyl		R = <i>n</i> -Hexyl		R = <i>n</i> -Heptyl		R = <i>n</i> -Octyl		R = <i>n</i> -Undecyl		R = <i>n</i> -Propyl ^a	
d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}
34.21	295	35.03	148	39.06	387	42.44	517	44.13	840	51.92	150	19.88	155
11.53	1000	17.73	4.8	19.80	119	21.32	310	22.13	320	25.66	644	9.97	1000
8.63	105	11.87	1000	13.30	1000	14.36	1000	14.77	1000	17.11	526	7.56	25
6.92	70	8.89	45	9.97	77	10.75	217	11.07	540	12.84	696	6.63	93
5.76	28	7.11	17	7.98	19	7.16	35	8.84	46	10.28	1000	6.46	36
5.03	16	5.92	91	6.65	35	6.14	245	7.38	54	8.56	274	6.06	34
4.93	16	5.08	5.4	5.70	190	4.77	40	6.33	260	6.43	119	4.98	123
4.64	49	4.42	12	4.99	106	4.18	231	5.53	14	5.71	237	4.82	23
4.55	26	4.16	22	4.44	3.5	4.00	55	5.01	22	5.15	104	4.29	43
4.37	38	3.94	52	4.17	8.7	3.66	72	4.92	28	4.67	20	4.17	141
4.19	475	3.64	25	3.99	21	3.62	110	4.43	8.0	4.42	12	3.98	27
4.00	62	3.54	39	3.66	13	2.93	41	4.17	16	4.15	27	3.88	152
3.95	46	3.41	3.3	3.32	32	2.78	21	4.03	48	3.95	74	3.64	32
3.85	16	2.96	5.1	3.08	20	2.26	72	3.69	24	3.67	34	3.49	48
3.70	100	2.73	7.8	2.92	2.9			3.54	14	3.63	19	3.32	227
3.53	20	2.53	4.8	2.86	4.1			3.20	4.0	3.42	44	3.14	27
3.46	54	2.37	11	2.66	10			2.95	10	3.03	19	2.85	98
3.32	21	2.26	2.7	2.35	7.7			2.77	18	2.70	31	2.42	20
3.00	33	2.22	25	2.27	2.9			2.33	6.0	2.45	8.8	2.35	50
2.89	16	2.09	2.1	2.22	27			2.27	4.0	2.24	24	2.11	68
2.54	15	1.98	15	2.10	4.1			2.21	24	2.19	8.8		
2.28	30	1.89	0.9	2.00	22			2.11	6.0	2.14	37		
2.22	13	1.84	0.9					2.01	22	2.06	33		
2.17	21									1.98	15		
2.14	15												

^a Polymorphic form obtained from acetic acid.

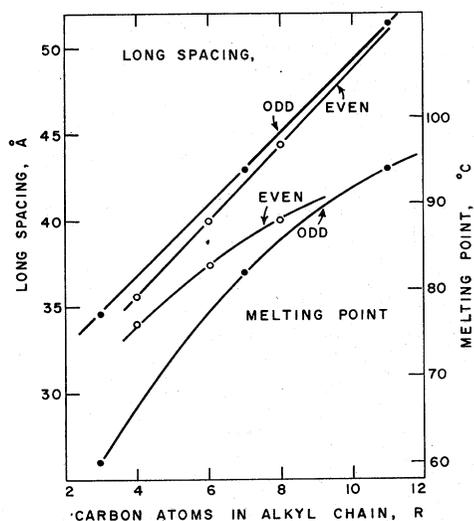


Fig. 2. Long spacing and melting-point alternation in sulfoxides, ● odd number of carbon atoms in alkyl chain, R, ○ even number of carbon atoms in alkyl chain, R.

scribed) for the odd- and even-membered sulfoxides are about 54° and 57°, respectively.

Although the angle of tilt of the even-membered sulfoxides is essentially the same as that of the sulfone derivatives, the long spacings of the sulfoxides are about 1.6 Å smaller. Apparently the end packing is different in the two series. Comparison of the long spacing of a given sulfoxide (Table V) with that reported for the C-form of the even-membered long chain fatty acids with the same number of atoms in the chain shows that the two are nearly identical. The covalent radius of a sulfur atom is 1.04 Å compared with 0.77 Å for a carbon atom (4), hence not identical though similar packing is indicated for the two series.

The odd members of the sulfoxide series give a different angle of tilt, 54°, from the A', B', or C' forms of the odd-numbered normal fatty acids. A comparison of the corresponding structures was not attempted.

The melting points of the sulfoxides (Figure 2) show alternation, unlike the sulfones (Figure 1).

The melting points of the even members fall on a curve that is above that of the odd members. The alternation in melting-point data is in agreement with the x-ray data. As a general rule, the even members of an aliphatic series possess more closely packed terminal planes and melt at a higher temperature than the odd. Examination of Figure 2 also indicates that the alternation in melting point and long spacing is becoming less pronounced as the chain length is increased. The curves appear to be converging at about an alkyl length, R, of 12 carbon atoms. The total number of chain atoms is about 24 at this point.

Another polymorphic form of the odd members was obtained through crystallization from acetic acid instead of acetone. The propyl derivative gave a completely new diffraction pattern (Table III) with a long spacing of about 19.9 Å. This abnormally short, long spacing indicates a single-chain-length structure.

Sulfides. The diffraction powder data for seven members of the sulfide series in which the alkyl group, R, varies from methyl to undecyl are listed in Table IV. In the even series the hexyl and octyl derivatives gave sharp and intense diffraction peaks; however the butyl derivative produced a relatively weak, essentially amorphous pattern. There was nothing in the preparation of the compound or its purity that afforded an explanation for this behavior. The only possible reason for the compound exhibiting such behavior was that it had undergone a transition of some type at a temperature below that of the x-ray study, 28°C. Therefore a pattern of the butyl derivative was recorded for a sample that had been crystallized from acetone at low temperature (-20°C.) and maintained at 20°C. until the diffraction pattern had been obtained. The pattern obtained was comparable to that of the other even members and yielded a long spacing that fell on the plot (Figure 3). When this sample was allowed to warm to 28°C. its crystalline pattern disappeared and the amorphous pattern first observed was obtained.

A similar behavior was observed in the odd series. Those derivatives containing more than 5 carbon atoms in the alkyl group, R, gave sharp and intense diffraction peaks while the propyl derivative produced

TABLE IV
X-Ray Diffraction Powder Data on Sulfides

R = <i>n</i> -Methyl		R = <i>n</i> -Butyl ^a		R = <i>n</i> -Amyl		R = <i>n</i> -Hexyl		R = <i>n</i> -Heptyl		R = <i>n</i> -Octyl		R = <i>n</i> -Undecyl	
d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}	d, Å	I _{rel.}
28.48	564	35.59	447	33.44	313	40.12	690	36.78	607	44.58	1000	44.58	941
14.34	1000	17.80	16	16.60	9.3	13.38	1000	18.47	75	22.18	25	21.18	110
9.56	600	11.90	1000	11.15	406	10.02	62	12.41	1000	14.82	950	14.82	500
5.73	473	7.13	89	8.35	26	8.01	33	5.30	57	11.07	230	11.10	172
4.78	182	5.95	55	6.68	13	6.67	20	4.63	43	8.86	90	8.87	155
4.15	118	4.46	32	5.56	6.8	6.40	9.0	4.41	18	7.38	15	7.38	114
4.09	218	4.31	26	4.78	38	5.73	100	4.21	11	6.33	180	6.33	76
3.77	62	4.09	97	4.69	14	5.01	36	3.80	786	4.02	65	5.55	14
3.57	142	3.96	71	4.18	25	4.11	113	3.41	21	3.69	45	5.01	12
3.46	85	3.67	553	3.80	1000	2.86	9.4	3.09	18	2.76	20	4.92	14
3.17	22	3.56	74	3.50	15	2.23	40	2.49	7.1	2.27	15	4.66	43
3.03	13	2.54	16	3.41	28	2.00	40	1.90	14	2.21	35	4.57	29
2.94	7.2	2.37	16	3.35	19					2.01	35	4.43	114
2.86	33	2.23	53	2.99	7.5							4.21	16
2.38	15	1.98	39	2.79	3.7							4.02	26
2.20	85			2.39	8.1							3.78	1000
2.04	11			2.09	5.0							3.67	50
1.91	33			1.90	18							3.56	45
												3.40	40
												3.15	53
												2.62	16
												2.45	43
												2.10	21
												2.01	21
												1.94	12
												1.90	31

^a Crystallized from acetone at -20°C., maintained below +20°C. until diffraction pattern recorded.

a relatively weak pattern at 28°C. However a sample of the propyl derivative that was recrystallized at -20°C. and maintained at 20°C. did not produce a sharp and intense diffraction pattern. It is probable that at 20°C. the sample had already undergone a transition.

The long spacings of the sulfides fall on two non-parallel lines. The even members have much larger long spacing values. The difference increases with increase in the number of carbon atoms in the alkyl chain. This is the exact opposite observed for the sulfoxide series (Fig. 2). The sulfide derivatives, like the sulfone and sulfoxides, crystallize in tilted bimolecular layers. The corresponding angles of tilt are about 55° and 44° for the even and odd members, respectively. The large difference in long spacings of the even and odd members of the sulfide series indicates that the mode of packing of the aliphatic chains is quite different.

The methyl derivative of the series gave sharp and intense diffraction peaks unlike the weak pattern of

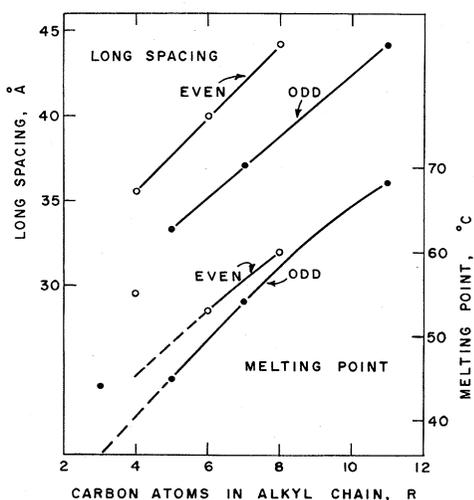


FIG. 3. Long spacing and melting-point alternation in sulfides, ● odd number of carbon atoms in alkyl chain, R, ○ even number of carbon atoms in alkyl chain, R.

TABLE V
Comparison of Sulfoxes, Sulfoxides, and Sulfides

R	No. of chain atoms	Melting point, °C. ^a			Long Spacing, Å		
		Sulfoxone	Sulfoxide	Sulfide	Sulfoxone	Sulfoxide	Sulfide
Methyl	13	98	87	46	30.50 ^b ^c	28.65
<i>n</i> -Propyl	15	101	60	44	35.10	34.55 ^d ^c
<i>n</i> -Butyl	16	104	76	55	37.15	35.55	35.65
<i>n</i> -Amyl	17 ^e ^e	45 ^e ^e	33.43
<i>n</i> -Hexyl	18	110	83	53	41.30	39.90	40.03
<i>n</i> -Heptyl	19	112	82	54	43.60	42.95	37.10
<i>n</i> -Octyl	20	114	88	60	45.90	44.30	44.25
<i>n</i> -Undecyl	23	119	94	68	52.35	51.40	44.30

^a Determined with a micro hot stage.

^b Polymorphic form from ethyl acetate, long spacing 28.2 Å.

^c Weak pattern, long spacing uncertain.

^d Polymorphic form from acetic acid, long spacing, 19.9 Å.

^e Not prepared.

the methyl sulfoxide derivative. Its long spacing however does not fall on the straight line produced by the other odd members of the series (Figure 3). The compound apparently crystallized in another manner which is also characteristic of methyl esters of long-chain aliphatic acids (1, 5).

The melting points of the sulfide derivatives are plotted in Figure 3. The melting points of the even and odd members show the expected alternation. It should be noted that the melting point of the butyl derivative in the even series and the melting point of the propyl derivative in the odd series are not in line with the other members of the series. Both exhibit melting points that appear to be much too high. This is in agreement with the x-ray data as discussed above. Attempts to observe visually a change in the appearance of the solid butyl derivative on slow heating were unsuccessful; only x-ray diffraction could detect that a change had taken place.

Acknowledgment

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Summary

X-ray diffraction powder data and melting points have been determined on three series of crystalline

long-chain sulfur compounds, namely 11-(*n*-alkylsulfonyl)-undecanoic acids; 11-(*n*-alkylsulfinyl)undecanoic acids; and 11-(*n*-alkylthio)undecanoic acids; where R is a selected alkyl group from methyl through undecyl. In the sulfone series the long spacings increase regularly with the increase in the number of carbon atoms in R. In contrast to unsubstituted long-chain fatty acids the odd and even members fall on the same line in the plot of long spacings against carbon atoms in R. As expected, a nonalternation in melting point is observed. In both the sulfoxide and sulfide series two nonparallel straight lines are obtained, one for the even-membered and one for the odd-membered compounds, in the plot of long spacings against carbon atoms in R. As expected, the melting points of the sulfoxides and sulfides show an

alternation. Polymorphism is more evident and complicates the interpretations most in the sulfide series and least in the sulfone series. All three series of compounds crystallized as tilted dimers.

REFERENCES

1. Holman, R. T., Lundberg, W. O., and Malkin, T., "Progress in the Chemistry of Fats and Other Lipids," vol. I, ch. I, Academic Press Inc., New York, N. Y. (1952).
2. Koenig, N. H., and Swern, Daniel, *J. Am. Chem. Soc.*, **79**, 362-365 (1957).
3. Koenig, N. H., and Swern, Daniel, *ibid.*, **79**, 4235-4237 (1957).
4. Pauling, L., "The Nature of the Chemical Bond," 2d ed., p. 164, Cornell University Press, Ithaca, N. Y. (1952).
5. Ralston, A. W., "Fatty Acids," ch. 5, John Wiley and Sons Inc., New York (1948).
6. Susi, H., Koenig, N. H., Parker, W. E., and Swern, Daniel, *Anal. Chem.*, **30**, 443-447 (1958).