

113. Physical Properties and Chemical Constitution. Part XXXII.* Thiophen Compounds.

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Pure samples of thiophen, 2-n-alkylthiophens (methyl to n-heptyl), n-alkyl 2-thenoates (methyl to n-heptyl), n-alkyl 2-thienyl ketones (methyl to n-hexyl), and a number of miscellaneous sulphur compounds have been prepared and their physical properties (refractive indices at 20° and densities and surface tensions over a range of temperature) determined: the ultra-violet and infrared spectra were measured in detail for a number of representative compounds. The parachors, molecular refractions, and molecular refraction coefficients for the 2-thienyl group have been evaluated from the new experimental data.

THE present investigation was undertaken to secure trustworthy data on the physical properties of pure n-alkylthiophens, n-alkyl 2-thenoates, n-alkyl 2-thienyl ketones, and 2-halogenothiophens, and to evaluate the refractions, molecular refraction coefficients, and parachors of the thienyl group and their dependence upon different substituents in the 2-position. The constants for the thienyl group in the various series were calculated in the usual manner (cf. Part XXVIII¹) and are summarised in Table I.

TABLE I. Mean constants for the 2-thienyl group.

Compounds	<i>P</i>	[<i>R</i>] _C	[<i>R</i>] _D	[<i>R</i>] _F	[<i>R</i>] _G	<i>Mn</i> _D ²⁰
Thiophen	169.1	22.56	22.69	23.27	23.58	124.4
2-n-Alkylthiophens	167.5	22.86	23.00	23.56	24.01	124.5
<i>s</i> †	0.35	0.02	0.02	0.11	0.03	0.27
n-Alkyl 2-thenoates	173.8	23.83	24.08	24.78	25.37	127.6
<i>s</i>	0.05	0.02	0.01	0.02	0.02	0.28
n-Alkyl 2-thienyl ketones	172.1	23.88	23.99	24.83	25.62	129.8
<i>s</i>	0.21	0.01	0.01	0.02	0.01	0.28
2-Chlorothiophen	165.6	22.62	22.80	23.37	23.67	126.7
2-Bromothiophen	165.8	22.53	22.71	23.20	23.51	134.1
2-Iodothiophen	167.1	22.42	22.63	23.15	23.27	144.7
2-Cyanothiophen	176.5	23.80	24.05	24.70	25.27	128.0

† *s* = Standard deviation.

The variation of the constants for the 2-thienyl group compared with the values deduced from thiophen is very marked, and it is hoped to discuss this in a future communication.

The mean values for the CH₂ increments in the three series of compounds are in good agreement with those previously found (cf. Part XXIII²).

EXPERIMENTAL

Physical Measurements.—Details of methods are given in Part XXVIII.¹ Unless otherwise stated, b. p.s are corrected. The compounds were refractionated immediately before the measurements were made; they were examined for impurities by vapour-phase chromatography (a Griffin and George apparatus, Mark II, was used), and by ultraviolet and infrared spectroscopy, but none was found.

Materials.—*Thiophen.* Commercially pure thiophen (1 l.) (Hopkin & Williams) was dried (MgSO₄) and slowly distilled in a Towers distillation unit filled with 1/16" Dixon gauze stainless-steel rings and fitted with a variable take-off head; the reflux ratio was 25:1. A middle fraction of constant b. p. and *n*_D²⁰ (1.5287) was separated and refractionated in the same apparatus.

n-Alkyl thienyl ketones. The 2-methyl to 2-n-butyl compounds were prepared from pure

* Part XXXI, *J.*, 1960, 4728.

¹ Part XXVIII, *J.*, 1960, 4454.

² Part XXIII, *J.*, 1948, 1842.

TABLE 2.

No.	Compound	B. p./mm.	d_4^{20}	d_4^{40}	d_4^{60}	d_4^{85}	γ^{20}	γ^{40}	γ^{60}	γ^{85}	P	Note
798	Thiophen	84°	1.0644	1.0405	1.0162	—	31.30	28.75	26.01	—	187.0	a
<i>Alkylthiophens</i>												
799	2-Methyl	112	1.0193	0.9978	0.9763	0.9460	30.95	28.17	25.51	22.67	226.8	b
800	2-Ethyl	134	0.9921	0.9726	0.9534	0.9277	30.05	27.71	25.37	23.45	264.8	c
801	2-n-Propyl	55.5°/20	0.9698	0.9531	0.9337	0.9079	29.67	27.65	25.62	23.12	303.7	
802	2-n-Butyl	64.5/7	0.9537	0.9389	0.9209	0.9886	29.74	27.94	26.14	23.89	343.3	
803	2-n-Pentyl	74.5/8	0.9430	0.9264	0.9097	0.8881	30.11	28.05	26.44	23.83	383.2	
804	2-n-Hexyl	76/0.9	0.9335	0.9182	0.9032	0.8820	29.95	28.25	26.57	23.89	422.6	f
805	2-n-Heptyl	81.5/0.3	0.9269	0.9118	0.8966	0.8774	30.40	28.53	26.68	24.35	462.1	
806	3-Methyl	115.5	1.0217	1.0007	0.9790	0.9552	32.37	29.88	27.44	24.51	229.0	g
807	2,5-Dimethyl	135	0.9848	0.9648	0.9441	0.9171	30.57	28.11	25.24	23.45	268.1	
<i>Alkyl 2-thenoates</i>												
808	Methyl	75.5/7	1.2289	1.2081	1.1873	1.1575	39.66	36.58	34.16	31.78	290.6	i
809	Ethyl	97/14	1.1625	1.1423	1.1224	1.0974	36.77	34.93	32.21	29.31	331.4	i
810	n-Propyl	88.5/9	1.1215	1.1013	1.0851	1.0618	34.20	31.23	30.02	28.30	368.2	i
811	n-Butyl	83/1	1.0872	1.0691	1.0512	1.0282	33.11	30.91	28.73	—	407.4	i
812	n-Pentyl	101.5/4	1.0700	1.0546	1.0375	1.0173	32.60	30.71	28.39	27.01	445.6	i
813	n-Hexyl	125.5/6	1.0505	1.0286	1.0079	0.9824	32.58	30.03	27.63	—	483.8	
814	n-Heptyl	133/3	1.0315	1.0153	0.9990	0.9810	31.71	30.08	28.18	26.11	522.0	
<i>Alkyl 2-thienyl ketones</i>												
815	Methyl	107/23	1.1707	1.1517	1.1325	1.1098	42.72	38.85	36.63	32.93	273.9	j
816	Ethyl	108/18	1.1312	1.1130	1.0948	1.0733	39.96	36.69	34.44	31.99	310.6	k
817	n-Propyl	108/11	1.0955	1.0761	1.0593	1.0383	37.29	34.69	33.04	32.00	348.9	k
818	Isopropyl	79/1	1.0880	1.0719	1.0530	1.0309	37.01	35.29	33.41	31.13	351.5	k
819	n-Butyl	131.5/20	1.0682	1.0490	1.0311	1.0108	35.66	33.90	32.17	30.03	387.0	k
820	n-Pentyl	107/3	1.0458	1.0292	1.0130	0.9945	34.70	33.24	31.36	29.09	424.9	k
821	n-Hexyl	110.5/4	1.0313	1.0151	1.0094	0.9891	34.17	32.84	31.24	28.81	463.0	
<i>Halogenothiophens</i>												
822	2-Chloro-	121	1.2862	1.2618	1.2347	1.2064	34.03	31.72	29.37	27.01	223.0	l
823	2-Bromo-	152	1.7071	1.6781	1.6632	1.6121	37.37	35.36	33.24	30.49	236.2	n
824	2-Iodo-	60/4	2.0645	2.0334	2.0006	1.9600	42.59	40.46	38.36	35.48	260.0	m
825	2,5-Dichloro-	65.5/23	1.4422	1.4154	1.3886	1.3541	37.77	35.75	34.28	29.89	263.2	o
826	2,5-Dibromo-	68/2	2.1439	2.1110	2.0741	2.0246	43.50	42.23	39.21	36.46	290.9	
<i>2-Thienylcarbinols</i>												
827	Methyl	82.5/4	1.1495	1.1301	1.1140	1.0907	40.40	37.74	33.81	32.43	280.9	
828	Ethyl	75/1.5	1.1079	1.0915	1.0752	1.0503	36.75	34.95	32.91	30.70	317.0	
829	n-Propyl	97.5/5	1.0764	1.0599	1.0429	1.0216	36.23	34.21	31.93	29.34	356.2	
<i>Miscellaneous sulphur compounds</i>												
830	2-Benzylthio-phen	95.5/1	1.0999	1.0845	1.0690	—	42.23	39.86	—	—	403.9	
831	2-Cyanothio-phen	73/10	1.1778	1.1586	1.1380	1.1129	46.42	43.74	41.02	37.55	242.2	
832	2-Methoxythio-phen	51/15	1.1335	1.1120	1.0919	1.0689	36.52	34.38	31.46	28.91	248.0	r
833	2-Ethoxythio-phen	62/11	1.0805	1.0603	1.0398	1.0147	33.82	31.54	29.69	27.10	287.1	r
834	Thiophen-2-aldehyde	73.5/11	1.2264	1.2080	1.1888	1.1657	49.25	46.23	44.01	—	242.3	s
835	Tetrahydrothio-phen	120	0.9989	0.9801	0.9615	0.9398	35.68	33.21	30.86	26.98	216.4	t
836	Tetrahydrothio-phen oxide	90/0.8	1.1725	1.1569	1.1392	1.1177	49.77	46.61	43.84	41.54	235.7	
837	Tetrahydrothio-phen dioxide	117/1	—	1.2549	1.2358	1.2161	—	49.46	43.11	35.65	252.6	u
838	Thiacyclohexane	93/82	0.9861	0.9681	0.9488	0.9255	36.06	33.74	31.17	—	254.4	v
839	Thiacyclobutane	94	1.0228	1.0017	0.9817	0.9566	34.60	—	—	—	177.0	w
840	1,4-Thioxan	147	1.1171	1.0990	1.0812	1.0587	42.39	40.54	37.49	34.23	238.4	x

For footnotes see under Table 3.

dry thiophen and the redistilled acid anhydride in the presence of orthophosphoric acid as catalyst.³ n-Pentyl, n-hexyl, and isopropyl 2-thienyl ketone were obtained from pure dry thiophen and the appropriate redistilled acid chloride in the presence of orthophosphoric acid as catalyst.⁴

TABLE 3.

No.	n_D^{20}	n_D^{20}	n_F^{20}	n_G^{20}	$[R]_C$	$[R]_D$	$[R]_F$	$[R]_G$	Mn_D^{20}	Note
798	1.52385	1.52866	1.54109	1.55196	24.23	24.37	24.96	25.28	128.31	a
<i>Alkylthiophens</i>										
799	1.51553	1.52013	1.53196	1.53841	29.07	29.29	29.85	30.15	149.26	b
800	1.50805	1.51223	1.52335	1.53240	33.71	33.94	34.56	35.06	169.61	c
801	1.50168	1.50575	1.51606	1.52487	38.38	38.65	39.31	39.85	190.01	d
802	1.49635	1.50021	1.51041	1.51915	43.03	43.32	44.06	44.66	210.43	e
803	1.49484	1.49851	1.50798	1.51638	47.67	47.97	48.74	49.42	231.10	
804	1.49198	1.49556	1.50466	1.51302	52.29	52.63	53.43	54.18	251.80	
805	1.49035	1.49384	1.50265	1.51097	56.90	57.26	58.11	58.93	270.24	
806	1.51581	1.52035	1.53201	1.54213	29.01	29.23	29.77	30.24	149.24	g
807	1.50789	1.51240	1.52377	1.53279	33.97	34.22	34.86	35.36	169.66	h
<i>Alkyl 2-thenoates</i>										
808	1.53671	1.54229	1.55711	1.56872	36.11	36.42	37.25	37.89	219.31	i
809	1.52001	1.52510	1.53859	1.55096	40.85	41.19	42.07	42.87	238.21	i
810	1.51245	1.51724	1.52990	1.53959	45.57	45.93	46.87	47.58	258.20	i
811	1.50436	1.50881	1.52056	1.53004	50.21	50.58	51.58	52.34	278.01	i
812	1.50330	1.50772	1.51896	1.52834	54.82	55.22	57.10	56.25	289.96	i
813	1.49980	1.50395	1.51488	1.52403	59.43	59.85	60.93	61.84	319.21	
814	1.49587	1.49983	1.51022	1.51914	64.08	64.51	65.61	66.61	338.89	
<i>Alkyl 2-thienyl ketones</i>										
815	1.56012	1.56681	1.58506	1.59719	34.85	35.19	36.03	36.72	197.68	j
816	1.54829	1.55436	1.57082	1.58629	39.41	39.75	40.64	41.62	217.93	k
817	1.53788	1.54356	1.55884	1.57317	44.05	44.41	45.43	46.46	238.05	k
818	1.53570	1.54134	1.55672	1.57109	44.18	44.56	45.61	46.58	237.70	k
819	1.53016	1.53545	1.54981	—	48.68	49.09	50.14	—	258.33	k
820	1.52943	1.52953	1.54302	1.55561	53.33	53.77	54.88	56.03	278.79	k
821	1.52135	1.52617	1.53929	1.54869	57.97	58.44	59.60	60.83	299.58	
<i>Halogenothiophens</i>										
822	1.54386	1.54888	1.56172	1.57145	29.10	29.32	29.95	30.31	183.66	l
823	1.58142	1.58705	1.60163	1.61181	31.84	32.10	32.74	33.19	258.75	m
824	1.64550	1.65290	1.67225	1.68149	36.89	37.24	38.11	38.55	347.16	
825	1.55778	1.56286	1.57657	1.58861	34.20	34.46	35.15	35.74	239.20	o
826	1.62222	1.62863	1.64547	1.66049	39.76	40.08	40.94	41.69	394.05	p
<i>2-Thienylcarbinols</i>										
827	1.54327	1.54803	1.56032	1.56976	35.16	35.42	36.08	36.57	198.42	q
828	1.53417	1.53856	1.55017	1.55953	39.89	40.22	40.92	41.50	218.80	q
829	1.52764	1.53228	1.54439	1.55390	44.70	45.00	45.86	46.42	239.41	q
<i>Miscellaneous sulphur compounds</i>										
830	1.58638	1.59125	1.60722	1.62030	53.20	53.55	54.72	55.67	277.31	
831	1.55870	1.56486	1.58114	1.59593	29.89	30.17	30.87	31.51	170.76	
832	1.52273	1.52738	1.53932	1.54882	30.75	31.00	31.56	32.03	174.47	
833	1.50988	1.51418	1.52518	1.53424	35.47	35.73	36.36	36.88	194.10	t
834	1.58278	1.59085	1.61313	1.63481	30.55	30.89	31.83	32.73	178.41	s
835	1.50108	1.50430	1.51243	1.52193	26.01	26.16	26.51	26.94	132.61	t
836	1.51896	1.52221	1.53028	1.53668	26.96	27.10	27.49	27.73	158.56	
837	1.48302	1.48538	1.49117	1.49584	27.00	27.11	27.39	27.61	178.50	u
838	1.50354	1.50698	1.51484	1.52272	30.66	30.83	31.24	31.64	153.97	v
839	1.50530	1.50887	1.51794	1.52613	21.51	21.64	21.96	22.25	111.86	w
840	1.50432	1.50748	1.51558	1.52221	27.62	27.77	28.14	28.44	157.02	x

n-Alkylthiophens. 2-Methylthiophen was prepared from sodium levulate and phosphorus trisulphide.⁵ 2-Ethyl- and 2-n-propyl-thiophen were obtained from 2-acetyl- and 2-propionyl-thiophen by Huang-Minlon's modification of the Wolff-Kishner reduction.⁶ n-Butyl-

³ See Kosak and Hartough, *Org. Synth.*, Coll. Vol. III, p. 14.

⁴ Hartough and Kosak, *J. Amer. Chem. Soc.*, 1947, **69**, 3093.

⁵ Hartough, "Thiophene and its Derivatives," p. 495, Interscience Publ. Inc., New York, 1952.

⁶ Buu-Hoi, *J. Org. Chem.*, 1950, **15**, 957; King and Nord, *ibid.*, 1949, **14**, 638.

n-pentyl-, n-hexyl-, and n-heptyl-thiophen were prepared by interaction of pure thiophen and the appropriate alkyl bromide in liquid ammonia solution in the presence of sodamide (cf. preparation of n-alkylpyridines, Part XXVIII¹); the products were isolated by fractionation under reduced pressure. 3-Methylthiophen was obtained from redistilled sodium methyl succinate and phosphorus pentasulphide in the presence of a mineral oil;⁷ 2,5-dimethylthiophen was prepared from acetylacetone and phosphorus trisulphide.⁸

n-Alkyl 2-thenoates. 2-Thenoic acid was prepared by oxidation of pure 2-acetylthiophen with potassium hypochlorite by an adaptation of the method for conversion of 2-acetylnaphthalene into naphthoic acid,⁹ and was recrystallised from hot water; it had m. p. 130°. The acid was converted into 2-thenoyl chloride with excess of pure thionyl chloride; the excess of the latter was removed by distillation on a water-bath, and the residue treated with the calculated quantity of the pure alcohol (methyl to n-butyl, n-hexyl, and n-heptyl thenoate). n-Pentyl thenoate was obtained by refluxing a mixture of the acid, pure n-pentyl alcohol, and benzene in the presence of Zeo-Karb 225H and was isolated in the usual manner.¹⁰

2-Chlorothiophen. This was prepared from pure thiophen (1 mol.) and redistilled sulphuryl chloride (1 mol.) and isolated by fractionation.¹¹

2-Bromothiophen. This was obtained by treatment of thiophen (1 mol.) in carbon tetrachloride with bromine (0.95 mol.) in carbon tetrachloride at 0–10° and was isolated by fractionation.¹²

2-Iodothiophen. Interaction of thiophen with iodine in the presence of mercuric oxide¹³ yielded, after fractional distillation at low pressure, the pure colourless 2-iodothiophen.

2,5-Dichlorothiophen. This was prepared from thiophen and sulphuryl chloride in the presence of iodine as catalyst.¹²

2,5-Dibromothiophen. A commercial sample (Fluka) was carefully fractionated under reduced pressure through a 4" column filled with Fenske helices.

Thiophen-2-aldehyde. Interaction of thiophen with N-methylformanilide and phosphorus oxychloride¹⁴ gave a light red oil, b. p. 66–67°/4 mm. This was steam-distilled in the presence of aqueous sodium hydrogen carbonate, a Dean and Stark apparatus being used as receiver for the aldehyde-water mixture: the colourless aldehyde was isolated by ether-extraction,

Footnotes to Table 3.

(a) Fawcett and Rasmussen (*J. Amer. Chem. Soc.*, 1945, **67**, 1705) give d_4^{20} 1.0644, n_D^{20} 1.5287, P 187.4. (b) Fawcett (*ibid.*, 1946, **68**, 1420) gives d_4^{20} 1.0194, n_D^{20} 1.5203; Haines (*J. Phys. Chem.*, 1956, **60**, 551) gives d_4^{20} 1.01965, n_D^{20} 1.5203. (c) von Auwers and Kohlhaas (*J. prakt. Chem.*, 1924, **108**, 322) give d_4^{20} 0.9908. (d) Scheibler and Schmidt (*Ber.*, 1921, **54**, 149) give n_D^{20} 1.5048. (e) Pines *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 5173) give n_D^{20} 1.5004. (f) Campaigne and Diedrich (*ibid.*, 1948, **70**, 391) give d_4^{20} 0.946, n_D^{20} 1.4970. (g) Fawcett (*loc. cit.*) gives d_4^{20} 1.0216, n_D^{20} 1.5204; Haines (*loc. cit.*) gives d_4^{20} 1.02183, n_D^{20} 1.5204, P 228.2. (h) Hartough (*J. Amer. Chem. Soc.*, 1951, **73**, 4035) gives n_D^{20} 1.5128. (i) Weinstein (*ibid.*, 1955, **77**, 6709) gives methyl, d_4^{20} 1.2290, n_D^{20} 1.5420; ethyl, d_4^{20} 1.1620, n_D^{20} 1.5248; n-propyl, d_4^{20} 1.1123, n_D^{20} 1.5170; n-butyl, d_4^{20} 1.0859, n_D^{20} 1.5122; n-pentyl, d_4^{20} 1.0573, n_D^{20} 1.5071. (j) Johnson (*ibid.*, 1947, **69**, 150) gives d_4^{20} 1.1709, n_D^{20} 1.5667, γ^{30} 44.5. (k) Spurlock (*ibid.*, 1953, **75**, 1115) gives ethyl, d^{20} 1.1390, n_D^{20} 1.5538; n-propyl, d^{20} 1.0941, n_D^{20} 1.5434; isopropyl, d^{20} 1.0894, n_D^{20} 1.5405; n-butyl, d^{20} 1.0664, n_D^{20} 1.5357; n-pentyl, d^{20} 1.0473, n_D^{20} 1.5301. (l) Coonradt, Hartough, and Johnson (*ibid.*, 1948, **70**, 2564) give d_4^{20} 1.2863, n_D^{20} 1.5487. (m) Keswani and Freiser (*ibid.*, 1949, **71**, 218) give d_4^{20} 1.6929, n_D^{20} 1.5815. (n) Keswani and Freiser (*loc. cit.*) give d_4^{20} 2.0493. (o) Coonradt *et al.* (*loc. cit.*) give d_4^{20} 1.4422, n_D^{20} 1.5626. (p) Steinkopf (*Annalen*, 1937, **532**, 250) gives n_D^{20} 1.6275. (q) Van Zyl *et al.*¹⁷ give ethanol, n_D^{25} 1.5430; propanol, n_D^{25} 1.5318; butanol, n_D^{25} 1.5220. (r) Sicé¹⁶ gives methoxy, d_4^{25} 1.1200, n_D^{25} 1.5261; ethoxy, d_4^{27} 1.075, n_D^{27} 1.5116. (s) Keswani and Freiser (*loc. cit.*) give d_4^{20} 1.2143, n_D^{20} 1.5838. (t) Haines (*loc. cit.*) gives d_4^{20} 0.9986, n_D^{20} 1.5048. (u) Solid, m. p. 24.8°; values at 20° (extrapolated), n_D^{30} 1.48188; n_D^{35} 1.48013. (v) Haines (*loc. cit.*) gives d_4^{20} 0.9856, n_D^{20} 1.50682. (w) Haines (*loc. cit.*) gives d_4^{20} 1.0200, n_D^{20} 1.5102. (x) Clark (*J.*, 1912, **101**, 1788) gives d_4^{20} 1.1178, n_C^{20} 1.50429, n_G^{20} 1.52223.

⁷ Feldkamp and Tullar, *Org. Synth.*, 1954, **34**, 73.

⁸ Buu-Hoi and Nguyen-Hoan, *Rec. Trav. chim.*, 1948, **67**, 309; cf. ref. 5.

⁹ A Newman and Holmes, *Org. Synth.*, Coll. Vol. II, p. 428, John Wiley & Sons, New York, 1943;

(b) Hartough and Conley, *J. Amer. Chem. Soc.*, 1947, **69**, 3096.

¹⁰ Sussman, *Ind. Eng. Chem.*, 1946, **38**, 1228; Vogel, "Practical Organic Chemistry," 3rd edn., p. 387, Longmans, Green & Co., London.

¹¹ Campaigne and Le Suer, *J. Amer. Chem. Soc.*, 1948, **70**, 415.

¹² Cf. Hartough, ref. 5, p. 498.

¹³ Minnis, ref. 9a, p. 44.

¹⁴ King and Nord, *J. Org. Chem.*, 1948, **13**, 635; Weston and Michaels, *J. Amer. Chem. Soc.*, 1950, **72**, 1422.

and the ethereal extract dried, and, after removal of the ether, distilled in nitrogen under reduced pressure through a 6" Fenske column.

2-Cyanothiophen. Pure thiophen-2-aldehyde was converted by hydroxylammonium chloride into the oxime, m. p. 128°, and the latter warmed gently with a mixture of acetic anhydride and anhydrous sodium acetate.¹⁵ The nitrile, isolated as usual, was distilled first at normal pressure (b. p. 192—193°) and then under reduced pressure.

2-Methoxythiophen. This was prepared by refluxing 2-iodothiophen and methanolic sodium methoxide for 30 hr. in the presence of powdered cupric oxide; it boiled¹⁶ constantly at 75—76°/50 mm.

2-Ethoxythiophen. This was prepared similarly to methoxythiophen.

2-Thienyl-carbinols. 2-Thienyl-ethanol, -propan-1-ol, and -butan-1-ol were prepared by the interaction of 2-thienylmagnesium bromide and the appropriate aldehyde.¹⁷ All were isolated by fractionation at 2—3 mm.

2-Benzylthiophen. Anhydrous zinc chloride (50 g.) was added during 1 hr. to a boiling mixture of thiophen (50 g.) and benzyl alcohol (50 g.); the 2-benzylthiophen, b. p. 115—116°/10 mm. (24 g.), was isolated by steam-distillation and ether-extraction.¹⁸

Tetrahydrothiophen. This was obtained from redistilled 1,4-dichlorobutane and sodium sulphide in dimethylformamide.¹⁹

Tetrahydrothiophen oxide and dioxide. Commercial samples (Robinson Bros., West Bromwich) were dried and fractionated under reduced pressure through a 6" Fenske column.

Thiacyclohexane. This was prepared by adding 1,5-dibromopentane to a boiling sodium sulphide solution, and refluxing the whole for 4 hr., with final steam-distillation.²⁰

Thiacyclobutane. This was obtained from alcoholic sodium sulphide and trimethylene dibromide.²¹

1,4-Thioxan. A commercial sample (Robinson Bros., West Bromwich), dried and redistilled, had b. p. 146.0°/759 mm.

Tables 2 and 3 summarise the physical properties of all the pure compounds investigated; the numbering of compounds in Clarendon type follows from Part XXXI.²² Table 2 contains the b. p. (at 760 mm., unless otherwise stated), rounded values of the density and surface tension at various temperatures, and the mean parachor, whilst Table 3 gives the refractive indices, molar refractivities, and the molar refraction coefficients.

Ultraviolet Spectra.—Measurements were made in matched 1 cm. silica cells on a Unicam spectrophotometer S.P. 500. n-Hexane "free from aromatic hydrocarbons" was purified by percolation through a 40" column of silica gel (14—20 mesh). Burroughs's absolute ethyl alcohol was used directly. Solutions were prepared by dissolving 10—20 mg. of the sample, accurately weighed, in 10.0 ml. of the purified solvent: 1.00 ml. of this solution was then diluted to 10 or 25 ml. in a graduated flask.

TABLE 4. *Ultraviolet absorption data.*

2-n-Alkylthiophens (in n-hexane)							Halogenothiophens (in alcohol)				
Compound	10°C	$\lambda_{\max.}$	$E_{\max.}$				Compound	10°C	$\lambda_{\max.}$	$E_{\max.}$	
(Thiophen)	109	231	8000				2-Chloro-	80	236	7900	
2-Ethyl ...	118	234	8000				2-Bromo-	82	236	8350	
2-n-Pentyl	118	234	8000				2,5-Dichloro-	77	252	10,050	
2-n-Hexyl	57	234	8000				2,5-Dibromo-	100	252	10,150	
3-Methyl ...	102	235	6050								
2-n-Alkyl thenoates (in n-hexane)							Miscellaneous sulphur compounds (in alcohol)				
Compound	10°C	$\lambda_{\max.}$	$E_{\max.}$	$\lambda_{\max.}$	$E_{\max.}$	$\lambda_{\max.}$	$E_{\max.}$	Compound	10°C	$\lambda_{\max.}$	$E_{\max.}$
Ethyl	59	244	15,100	250	15,100	262	12,150	2-Benzylthiophen ...	87	235	10,000
n-Propyl ...	91	244	15,100	250	15,100	262	12,150	2-Cyanothiophen	90	242	18,900
n-Heptyl ...	99	245	15,100	250	15,150	262	12,150	Thiophen-2-aldehyde	85	261	14,000
								Tetrahydrothiophen	83	210	1000
								Thiacyclohexane	82	210	1000

¹⁵ Putoknin and Egorova, *J. Gen. Chem. (U.S.S.R.)*, 1948, **18**, 1866; *Chem. Abs.*, 1949, **43**, 3816.

¹⁶ Sicé, *J. Amer. Chem. Soc.*, 1953, **75**, 3697.

¹⁷ Van Žyl, Langenberg, Tan, and Schut, *J. Amer. Chem. Soc.*, 1956, **78**, 1955.

¹⁸ Steinkopf, *Annalen*, 1939, **541**, 257.

¹⁹ Lawson, Easlay, and Wagner, *Org. Synth.*, 1956, **36**, 89.

²⁰ Haines, *J. Phys. Chem.*, 1956, **60**, 549.

²¹ Bennett and Hock, *J.*, 1927, 2496.

²² Part XXXI, *J.*, 1960, 4728.

Some typical results are collected in Table 4. Concentrations C are expressed in moles per l.; λ_{\max} is given in $m\mu$. Data for a few thiophen compounds in iso-octane have been published²³ and are in excellent agreement with ours.

Infrared Spectra.—The infrared absorption spectra (capillary film) were kindly measured by Mr. R. F. Branch, B.Sc., of the Ministry of Supply, Woolwich, using a Perkin-Elmer double-beam instrument with a rock-salt prism. Typical spectra, including those for which the ultraviolet spectra are recorded above, are contained in ref. 24. The infrared spectra published for some alkyl- and halogeno-thiophens²⁵ agreed well with our own.

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²³ Ref. 5, p. 101.

²⁴ R. S. Parker, Ph.D. Thesis, University of London, 1958.

²⁵ Ref. 5, pp. 109—127.
