704. *Infrared Absorption of Heteroaromatic, Five-membered, Monocyclic Nuclei. Part II.*[1] *2-Monosubstituted Thiophens.*

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The positions and intensities of nine characteristic bands are recorded and discussed for thirteen 2-monosubstituted thiophens.

2-MONOSUBSTITUTED furans show characteristic absorption bands which could be assigned to specific normal vibrations of the furan nucleus.[1] We have now extended this work to the corresponding thiophens. In the region of the spectrum investigated, 2000—800 cm.$^{-1}$, absorption corresponding to the modes (I—XI) might be found. As before,[1] the positions of the ring stretching modes (I—IV) and the ring breathing mode (VIII) should be similar to those in thiophen itself, and the positions of the CH-in-plane (IV—VII) and the CH-out-of-plane deformation modes (IX—XI) to those of vicinal trisubstituted benzenes.

Ring Stretching Frequencies at 1600—1300 *cm.*$^{-1}$.—Thiophen shows bands at 1591 cm.$^{-1}$ (8), 1409 cm.$^{-1}$ (32), and 1255 cm.$^{-1}$ (43) * in the infrared and an additional band at 1358 cm.$^{-1}$ in the Raman spectrum,[2] which were assigned to vibrations (I)—(IV) respectively. The bands shown by the substituted thiophens at 1537—1509 [1523 ± 9],† 1444—1402 [1422 ± 12], 1365—1339 [1354 ± 7], and 1258—1220 cm.$^{-1}$ (30—155) [1231 ± 10 cm.$^{-1}$ (80 ± 30)] (Table, cols. 1—4) are therefore assigned to modes (I)—(IV), respectively. The intensities of the first three bands are less when the ring is attached to weakly electron-accepting substituents {for Nos. 1—8 the intensities are respectively (3—30) [(15 ± 5)], (20—115) [(75 ± 35)], and (15—60) [(25 ± 20)]} than when the ring is attached to strong electron acceptors {for Nos. 9—13, intensities are (50—110) [(85 ± 30)], (120—280) [(190 ± 60)], and (45—150) [(95 ± 35)]}. This pattern of intensity variation is expected, for the thiophen ring is a strong electron donor and large interactions between ring and substituent are known to intensify ring stretching bands.[1,3]

Hydrogen In-plane Deformations at 1250—1000 *cm.*$^{-1}$.—The bands at 1086—1077 cm.$^{-1}$ (5—20) [1081 ± 3 cm.$^{-1}$ (10 ± 5)], and 1053—1031 cm.$^{-1}$ (5—110) [1043 ± 7 cm.$^{-1}$ (55 ± 40)] (Table, cols. 5—6) probably correspond to the modes (VI) and (VII). In vicinal trisubstituted benzenes[4] the corresponding modes absorb near 1160 and 1073 cm.$^{-1}$, and in 2-substituted furans[1] near 1158 and 1076 cm.$^{-1}$. The mode (V) probably occurs near 1200 cm.$^{-1}$ (cf. vicinal benzenes) and is possibly obscured by mode (IV).

Hydrogen Out-of-plane Deformations below 1000 *cm.*$^{-1}$.—The bands at 938—905 cm.$^{-1}$ (5—20) [925 ± 8 cm.$^{-1}$ (10 ± 5)] and 863—841 cm.$^{-1}$ (45—110) [853 ± 7 cm.$^{-1}$ (75 ± 25)] probably correspond to modes (IX) and (X); mode (XI) is probably obscured by solvent absorption below 800 cm.$^{-1}$. The corresponding bands for vicinal trisubstituted benzenes[4] absorb near 958, 893, and 770 cm.$^{-1}$ and for 2-substituted furans[1] near 925, 884, and below 800 cm.$^{-1}$.

Ring Breathing Frequency.—The band at 831 cm.$^{-1}$ (95) for thiophen has been assigned to mode (VIII).[2] The 2-substituted derivatives all show a band at 839—790 cm.$^{-1}$ (25—85) [823 ± 20 cm.$^{-1}$ (50 ± 20)] (Table, col. 9) which is accordingly assigned to this mode.

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* Measured in $CHCl_3$ solution at 0·700M.

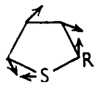
† Apparent extinction coefficients are in parentheses and arithmetic means and standard deviations in brackets. The intensities of shoulders and superimposed bands and the positions of shoulders are not treated statistically.

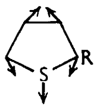
[1] Part I, Katritzky and Lagowski, *J.*, 1959, 657.

[2] (*a*) Thompson and Temple, *Trans. Faraday Soc.*, 1945, **41**, 27; (*b*) Waddington *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 797; (*c*) Lecomte, *Bull. Soc. Chim. France*, 1946, 415; (*d*) Hidalgo, *J. Phys. Radium*, 1955, **16**, 366.

[3] Katritzky, *J.*, 1958, 4162.

[4] Randle and Whiffen, Paper No. 12, Report of the Conference of Molecular Spectroscopy, 1954. Institute of Petroleum.


(I)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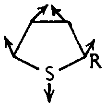
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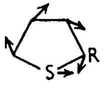
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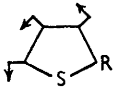
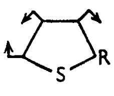
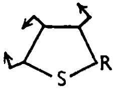
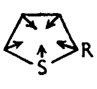
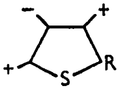
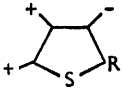

(V)

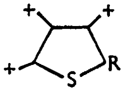

(VI)


(VII)


(VIII)


(IX)


(X)


(XI)

		1		2		3		4		5		6		7		8		9		10	11	12
		B_1 { νC–C νC–S		A_1 { νC–C νC–S		A_1 { νC–C νC–S		B_1 { νC–C νC–S		B_1 βCH		A_1 βCH		B_2 γCH		A_2 γCH		A_1 ring breath				
No.	Subst.	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	B. p.	mm.	Ref.
1	Me*	1537	3	1444	45	—		1239	40	1078	15	1043	12	938	5	846	50	817	45	112—113°	760	[a]
2	Ph*	1533	15	1433	20	1353	5	1258	30	1081	15	1047	5	905	10	849	75	826	30	37—39°	[b]	[a]
3	Cl	1518	30	1415	115	1347	10	1220	95	1085	10	1052	80	923	5	842	85	819	60			[c]
4	Br	1509	20	1405	95	1339	10	1220	80	1080	5	1044	25	926	5	841	85	819	55	56°	26	[d]
5	CH:CH·CO_2Me	1518	15	1428	110	1365	60	1230	100	1078	5	1043	90	923	20	855	110	827	85	47—48°	[b]	[e]
6	CH:CH·CO_2Et	1517	15	1428	60	(—)		1230	115	(—)		1042 ‡	160	926	5	855	110	828	90	109—111°	1·3	[f]
7	CMe:NOH	1532	15	1433	55	1352	25	($CHCl_3$)		1086	20	1036 †	20	(—)		850	65	828	50	117·5—118°	[b]	[g]
8	CH:NOH	1514	15	1424	90	1352	30	1230	55	1077	5	1053	55	(—)		856	45	825	30	132·5—134°	[b]	[h, i]
9	CO_2Me	1527	110	1418	120	1362	150	1225	60	(—)		1040	20	929	20	857	90	786	50	89—90°	17	[j]
10	CO_2Et	1528	110	1422	220	1357	75	1225	75	(—)		1042	40	923	5	859	55	810	25	101—102°	17	[j]
11	CHO	1517	50	1422	190	1358	45	1230	155	1082	10	1047	110	925	10	863	45	839	40	84°	17	[k]
12	COMe	1514	70	1415	280	1356	110	1230	80	1082	20	1032	35	932 ¶	50	858	95	839	35	57—58°	0·7	[l]
13	NO_2	1532	220 ‡	1402	130	1365 ‡	200	($CHCl_3$)		1083	5	1031	110	924	10	857	75	834	35	43°	[b]	[m]

* Measured in 0·700M solution. † Shoulder. ‡ Intensity of peak materially raised by overlap with another band. — Absence of absorption. (—) Band masked by stronger absorption. ¶ Peak considered to be the result of the superimposition of two bands.

The approximate symmetry type is given beneath the column number, those in cols. 1—3 and 9 by analogy with unsubstituted thiophen, and those in cols 5—8 by analogy with vicinal trisubstituted benzenes; see text.

Compounds were prepared by the methods indicated in the references (except for Nos. 3, 4, 11, 12, and 13 which were commercial products and Nos. 5 and 6 which were prepared as indicated in footnote *e*). The physical constants quoted (cols. 10—11) were in agreement with literature values as also were refractive indices of the liquid compounds.

[a] Kues and Paal, *Ber.*, 1886, **19**, 556, 3142. [b] M. p. [c] Weitz, *Ber.*, 1884, **17**, 794. [d] Krause and Renwanz, *Ber.*, 1929, **62**, 1710. [e] 3-(2-Thienyl-)-acrylic acid (1·0 g.) was refluxed for 6 hr. with methanol (25 c.c.) and sulphuric acid (2·5 c.c.). The cooled mixture was poured into water (150 c.c.) and extracted with ether. Drying ($MgSO_4$), evaporation of solvents, and distillation gave the *methyl ester* (b. p. *ca.* 100°/0·1 mm.; 0·7 g., 65%) which solidified on cooling, and after four crystallisations from light petroleum (b. p. 60—80 °), had m. p. 47—48° (Found: C, 57·3; H, 5·2. $C_8H_8O_2S$ requires C, 57·1; H, 4·8%). [f] King and Nord, *J. Org. Chem.*, 1949, **14**, 405. [g] Peter, *Ber.*, 1884, **17**, 2644. [h] Biedermann, *Ber.*, 1886, **19**, 1854. [i] Goldschmidt and Zanoli, *Ber.*, 1892, **25**, 2588. [j] Weinstein, *J. Amer. Chem. Soc.*, 1955, **77**, 6709. [k] Biedermann, *Ber.*, 1886, **19**, 638. [l] Johnson and May, *Org. Synth.*, 1938, **18**, 1. [m] Meyer and Stadler, *Ber.*, 1884, **17**, 2648.

Substituent Bands.—Most of the remaining bands with $\varepsilon_A > 10$ could be assigned to substituent absorption, but the bands shown by No. 1 at 1163 cm.$^{-1}$ (30), by No. 2 at 955 cm.$^{-1}$ (15), by No. 12 at 1016 cm.$^{-1}$ (20), and by No. 13 at 1433 cm.$^{-1}$ (25) were anomalous.

Previous Work.—Hidalgo[2d] measured six 2-substituted thiophens (as liquid films) (substituents; Me, Et, Br, Cl, Ac, CH:CH$_2$) and recorded twelve bands as characteristic of the nucleus. Three of these occur below 800 cm.$^{-1}$; eight of the remaining nine correspond to those given in the Table, cols. 1—6, 8—9. There is good overall agreement between results, but the frequency ranges quoted by Hidalgo are mostly considerably greater than ours. We have not found the band quoted[2d] at 1355—1236 cm.$^{-1}$; Hidalgo does not report the band that we find at 938—923 cm.$^{-1}$.

Hochgesang,[5] who summarises early work, recorded the spectra of ten 2-substituted thiophens (Me, Et, CH:CH$_2$, Pr^n, Bu^n, Bu^t, Cl, Br, Ac, and SH), mainly as liquid films. The positions agree well with those in this paper; no precise intensities were quoted. The generalisations made are, as far as they go, in accord with the present results.

Experimental.—See Ref. 1 for conditions of measurement.

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[5] Hochgesang, in Hartough, " Thiophene and its Derivatives," Interscience Inc., 1952.