

### 130. Infrared Absorption of Heteroaromatic, Five-membered, Monocyclic Nuclei. Part I. 2-Monosubstituted Furans.

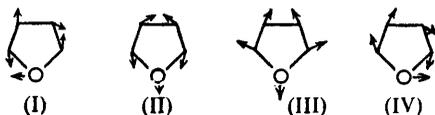
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The positions and intensities of nine characteristic infrared bands are recorded and discussed for twenty-four 2-monosubstituted furans.

ALL the infrared bands ( $\epsilon_A \geq 15$ ), with few exceptions, for monosubstituted benzenes, pyridines, and pyridine 1-oxides are characteristic of either the substituent or the nucleus. Further, any one nucleus (or substituent) shows a characteristic number of bands, the positions and intensities of which are either reasonably constant or vary with the electronic nature of the substituent (or nucleus);<sup>1</sup> mass effects are small, provided that substituents are attached to the nucleus by a carbon, nitrogen, or oxygen atom. We are now investigating five-membered heteroaromatic compounds; this paper describes the results for 2-substituted furans. For reasons given previously,<sup>1a</sup> the spectra of 0.179M-chloroform solutions were measured in a 0.112 mm. compensated cell and apparent molecular extinction coefficients recorded; the errors and approximations involved are noted in ref. 1a. Of the bands with  $\epsilon_A \geq 15$  between 2000 and 800  $\text{cm}^{-1}$ , nine were found to be characteristic of the nucleus and are recorded in Table 1.

The normal vibrations of six-membered heteroaromatic nuclei can be divided into those involving mainly (a) C-H stretching near 3000  $\text{cm}^{-1}$ , (b) C-C and C-(hetero-atom) stretching at ca. 1600—1400  $\text{cm}^{-1}$ , (c) CH in-plane deformation near 1300—1000  $\text{cm}^{-1}$ , (d) CH out-of-plane deformation at ca. 900—700  $\text{cm}^{-1}$ , (e) ring deformation below 700  $\text{cm}^{-1}$ , and (f) ring breathing (intermediate between stretching and deformation) near 1000  $\text{cm}^{-1}$ . Previous work<sup>2,3</sup> indicates that the normal vibrations of pyrrole, furan, and thiophen can also be so classified, usually with similar ranges for each vibration type: type a occurs near 3000  $\text{cm}^{-1}$ , type b at 1590—1358  $\text{cm}^{-1}$ , type c at 1270—1015  $\text{cm}^{-1}$  (except that one of the  $B_1$  vibrations in this class apparently absorbs at 872  $\text{cm}^{-1}$  for both thiophen and furan), type d at 869—711  $\text{cm}^{-1}$  (a band at 1046  $\text{cm}^{-1}$  for pyrrole is a doubtful exception<sup>2</sup>), and type e below 838  $\text{cm}^{-1}$  (all but one lie below 724  $\text{cm}^{-1}$ ), although the ring breathing vibration (type f) causes absorption at 1144, 994, and 832  $\text{cm}^{-1}$  for pyrrole, furan, and thiophen, respectively. Chloroform absorption below 800  $\text{cm}^{-1}$  obscures all vibrations of type e and some of type d. The sodium chloride prism used did not allow good resolution of type a vibrations. This paper is concerned with ring stretching and breathing and CH in- and out-of-plane deformation frequencies.

*Ring Stretching Frequencies at ca. 1600—1400  $\text{cm}^{-1}$ .*—Under our conditions, furan shows bands at 1590  $\text{cm}^{-1}$  (10),\* 1487  $\text{cm}^{-1}$  (60), and 1381  $\text{cm}^{-1}$  (25). Thompson and



Temple<sup>3</sup> assigned these to the normal modes (I—III) ( $\nu_{15}$ ,  $\nu_6$ , and  $\nu_5$  in the notation of Lord and Miller<sup>2</sup>), respectively. A fourth normal mode (IV;  $\nu_{14}$ ) is expected, but not found, in this region.

For six-membered ring compounds, substituents affect the position of bands of this

\* Apparent extinction coefficients are in parentheses, and arithmetical means and standard deviations in brackets (see ref. 1a). The intensities of shoulders and superimposed bands and the positions of shoulders are not treated statistically.

<sup>1</sup> Katritzky and his co-workers, *J.*, 1958, (a) 2182, (b) 2192, (c) 2195, (d) 2198, (e) 2202, (f) 3165, (g) 4155, (h) 4162, (i) unpublished work.

<sup>2</sup> Lord and Miller, *J. Chem. Phys.*, 1942, **10**, 328.

<sup>3</sup> Thompson and Temple, *Trans. Faraday Soc.*, 1945, **41**, 27.

TABLE 1.

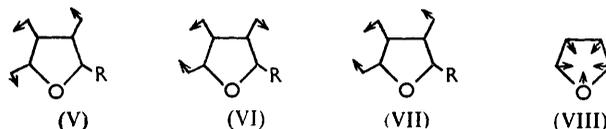
No.	Subst.	1		2		3		4		5		6		7		8		9		10	11	12	Ref.
		$\nu$ C-C { $\nu$ C-O}	$\epsilon_A$	$\nu$ C-C { $\nu$ C-O}	$\epsilon_A$	$\nu$ C-C { $\nu$ C-O}	$\epsilon_A$	$\beta$ CH cm. <sup>-1</sup>	$\epsilon_A$	$\beta$ CH cm. <sup>-1</sup>	$\epsilon_A$	ring breath cm. <sup>-1</sup>	$\beta$ CH cm. <sup>-1</sup>	$\epsilon_A$	$\beta$ CH cm. <sup>-1</sup>	$\epsilon_A$	$\gamma$ CH cm. <sup>-1</sup>	$\epsilon_A$	$\gamma$ CH cm. <sup>-1</sup>				
1	Me	1607	30	1512	40	1390	15	1145	95	1076	35	1013	85	912	90	882	15	—	—	65°	760	a	
2	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> Bu <sup>n</sup>	1602	25	1509	25	(—)	(—)	1151†	130	1077	50	1010	60	922	40	883	25	—	—	118—119	14	b	
3	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> Pr <sup>n</sup>	1605	25	1511	25	(—)	(—)	1154†	125	1079	60	1012	95	924	40	885	30	—	—	115—116	17	c	
4	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> Et	1603	20	1511	25	(—)	(—)	1155†	125	1079	55	1017	90	925	35	885	20	—	—	108	17	d	
5	CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> Me	1602	20	1510	30	(—)	(—)	1155†	100	1078	45	1014	70	924	25	887	15	—	—	90	14	e	
6	CH <sub>2</sub> NH <sub>2</sub>	1605	20	1510	30	1377	15	1151	90	1072	30	1010	100	920	50	885†	100	—	—	144—145	760	a	
7	CH <sub>2</sub> OH	1605	10	1507	35	1381†	50	1151	110	1078	25	(—)	(—)	912	60	886	40	—	—	73.5	15	a	
8	CH <sub>2</sub> O-COMe	1611	10	1506	40	1395*	25	1152	120	1078	25	1013†	190	916	90	882	50	810	50	74	14	f	
9	CH <sub>3</sub> CH-CO <sub>2</sub> Bu <sup>n</sup>	1563	45	1484	75	1393†	80	(—)	(—)	1075	55	1016	280	927	60	882	120	811	55	147	14	g	
10	CH <sub>3</sub> CH-CO <sub>2</sub> Pr <sup>n</sup>	1563	50	1482	75	1394†	85	(—)	(—)	1075	45	1016	260	927†	75	882	120	811	60	113	16	a	
11	CH <sub>3</sub> CH-CO <sub>2</sub> Et	1560	55	1484	85	1393†	85	(—)	(—)	1076	45	1018	270	927	45	884	80	810	40	124	22	a	
12	CH <sub>3</sub> CH-CO <sub>2</sub> Me	1562	55	1485	75	1392	35	(—)	(—)	1078	35	1020	260	930	65	885	80	812	40	117	23	a	
13	CH <sub>3</sub> CH-COMe	1558	135	1480	70	1392	60	1172	80	1077	20	1016	245	926	55	881	130	803	40	113	14	h	
14	CH <sub>3</sub> NOH	—	—	1494	30	1383	40	1156	90	1075	15	1018	100	931	165	885	65	—	—	74—75	i	a	
15	CMc <sup>n</sup> NOH	—	—	1498	35	1395	50	1167	110	1073	5	1006	180	942	90	(—)	(—)	—	—	104	i	a	
16	CH <sub>3</sub> N-NHPh	(—)	(—)	1485*	90	1387	5	1156	130	1069†	95	1017	120	936	50	884	100	—	—	95—96	i	a	
17	CMc <sup>n</sup> N-NHPh	(—)	(—)	1480*	65	1388	20	1164	135	1071	75	1022	110	910	65	883	75	—	—	85—86	i	a	
18	C <sub>2</sub> N	1583	5	1478	75	1384	10	1153	65	1074	45	1017	150	926	50	886	35	829	25	146—147	760	j	
19	CO <sub>2</sub> Bu <sup>n</sup>	{1576* 1577* 1585	85 65 100	1482	150	1404	105	1174*	185	1076	70	1012	140	939	60	884	100	{836* 813* 15	20	117	20	a	
20	CO <sub>2</sub> Pr <sup>n</sup>	{1576* 1585	100 100	1478	180	1405	110	1174*	165	1076	70	1013	180	945	60	883	110	835	15	112	20	a	
21	CO <sub>2</sub> Et	{1574* 1575*	70 55	1483	155	1405	95	(—)	(—)	1076	75	1010	180	932	70	884	90	{837 821	15 10	84—85	16	k	
22	CO <sub>2</sub> Me	{1585 1574	100 60	1485	175	1396	100	1169	150	1079	55	1017	95	910	55	886	75	837†	10	90.5	55	k	
23	CHO	1573	95	1470	180	1398	115	1161	55	1084	40	1021	190	930	55	884	60	835	20	52.5	12	a	
24	CO-Me	1575	145	1474	290	1400	105	{1173 1166	70	1074	20	{1025 1013	110 75	917	40	886	85	834	20	66	13	a	

TABLE 2.

Substi- tuent Type	Nos.	B <sub>1</sub> Band near 1600 cm. <sup>-1</sup>		A <sub>1</sub> Band near 1500 cm. <sup>-1</sup>		A <sub>1</sub> Band near 1400 cm. <sup>-1</sup>	
		Position Range	Intensity Statistics	Position Range	Intensity Statistics	Position Range	Intensity Statistics
H	—	1590	10	1487	60	1381	25
Sat. C	1—8	1611—1602	20 ± 7	1512—1506	20—40	1390—1377	7
C:C	9—13	1563—1558	65 ± 30	1485—1480	75 ± 5	1394—1392	1
C:N	14—18	1583	10	1498—1478	30—75	1395—1383	5
C:O	19—24	1587—1573	1581 ± 6	1485—1470	150—290	1405—1396	4

type relatively little, but the intensities are considerably changed by substituents which conjugate strongly with the ring.<sup>1</sup> The bands shown by the 2-substituted furan nucleus at 1611—1558, 1512—1470, and 1405—1377  $\text{cm}^{-1}$  (5—145, 20—290, and 15—110) (Table I, cols. 1—3) are therefore assigned to modes (I—III). The furan ring is a strong electron-donor, and, generally, the band intensities increase with increasing electron-attracting power of the substituent (Table 2). This is as expected, because increased disturbance of the  $\pi$ -electron system gives steep charge gradients and therefore large dipole-moment changes during the vibrations (cf. ref. 1*h*).

*Hydrogen In-plane Deformations at 1200—1050  $\text{cm}^{-1}$ .*—In the six-membered ring series, the number and relative orientations of the hydrogen atoms determine the positions of the in- and out-of-plane deformation modes.<sup>1</sup> A five-membered ring with three adjacent hydrogen atoms will show three in-plane and three out-of-plane deformation modes, which, by analogy, should resemble those of vicinal trisubstituted benzenes. All the 2-substituted furans absorb at 1240—1200  $\text{cm}^{-1}$  (positions and intensities cannot be measured since this region is obscured by solvent absorption), 1173—1145  $\text{cm}^{-1}$  (55—135) [ $1158 \pm 7 \text{ cm}^{-1}$  (95  $\pm$  25)]\* (overlap raises No. 22's intensity), and 1084—1069  $\text{cm}^{-1}$  (5—75) [ $1076 \pm 3 \text{ cm}^{-1}$  (45  $\pm$  20)] (Table I, cols. 4 and 5). These bands probably correspond to the three in-plane CH deformations (V—VII). Vibration modes corresponding to (VI) and (VII) for vicinal trisubstituted benzenes absorb at  $1160 \pm 5$  and  $1073 \pm 10 \text{ cm}^{-1}$ ; the mode corresponding to (V), which should absorb at somewhat higher frequencies, was not found.<sup>4</sup>



*Ring Breathing Frequency near 1000  $\text{cm}^{-1}$*  (Table I, col. 6).—The band at 990  $\text{cm}^{-1}$  (170) for furan has been assigned to mode (VIII).<sup>3</sup> All the 2-substituted derivatives show a corresponding band at 1025—1006 [ $1015 \pm 4 \text{ cm}^{-1}$ ]. The intensity (55—280) depends on the substituent type: for saturated carbon atoms (Nos. 1—8) it is (60—100) [(85  $\pm$  15)], for carbon-carbon double bonds (Nos. 9—13) (245—280) [(265  $\pm$  10)], and for carbon-nitrogen and carbon-oxygen multiple bonds (Nos. 14—24) (95—190) [(140  $\pm$  35)].

*Hydrogen Out-of-plane Deformations at 950—800  $\text{cm}^{-1}$*  (Table I, cols. 7—9)—All the 2-substituted furans show bands at 945—910  $\text{cm}^{-1}$  (25—90) [ $925 \pm 9 \text{ cm}^{-1}$  (55  $\pm$  17)] (overlap raises No. 14's intensity) and at 887—881 [ $884 \pm 2 \text{ cm}^{-1}$ ]. The intensity of the latter is (15—50) [(30  $\pm$  13)] for saturated substituents (Nos. 1—8) and (35—130) [(90  $\pm$  20)] for unsaturated ones (Nos. 9—24). Another band is obscured by solvent absorption below 800  $\text{cm}^{-1}$  for saturated substituents but occurs at 812—803  $\text{cm}^{-1}$  (40—60) [ $809 \pm 4 \text{ cm}^{-1}$  (45  $\pm$  10)] for olefins and at 837—834  $\text{cm}^{-1}$  (15—20) [ $836 \pm 1 \text{ cm}^{-1}$  (15  $\pm$  5)] for carbonyl

\* See footnote, p. 657.

<sup>4</sup> Randle and Whiffen, Paper No. 12, Report on Conference on Molecular Spectroscopy, 1954. Institute of Petroleum, London.

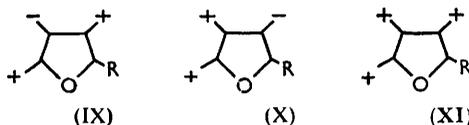
#### Footnotes to Table 1:

\* Shoulder, ‡ absorption considered to be the superimposition of two peaks, — absence of absorption, (—) band masked by stronger absorption.

<sup>a</sup> "Dictionary of Organic Compounds," edited by Heilbron and Bunbury, Eyre and Spottiswoode, London, 1953. <sup>b</sup> Found: C, 67.7; H, 8.4.  $\text{C}_{11}\text{H}_{16}\text{O}_3$  requires C, 67.4; H, 8.2%.  $n_D^{22}$  1.4570. <sup>c</sup> Found: C, 66.2; H, 8.1.  $\text{C}_{10}\text{H}_{14}\text{O}_3$  requires C, 66.5; H, 7.7%.  $n_D^{22}$  1.4618. <sup>d</sup> Kametani, Ito, and Isaka, *J. Pharm. Soc. Japan*, 1954, **74**, 1298; *Chem. Abs.*, 1955, **49**, 15896c. <sup>e</sup> Sherlin, Berlin, Serebrennikova, and Rabinovich, *J. Gen. Chem. (U.S.S.R.)*, 1938, **8**, 7; *Chem. Abs.*, 1938, **32**, 5397. <sup>f</sup> *Org. Synth.*, Coll. Vol. I, 1944, p. 285. <sup>g</sup> G.P. 851,064; *Chem. Abs.*, 1956, **50**, 8738e. <sup>h</sup> *Org. Synth.*, *op. cit.*, p. 283. <sup>i</sup> These compounds are solids, and m. p. are given. <sup>j</sup> Hughes and Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 744. <sup>k</sup> Gennari, *Gazzetta*, 1894, **24**, 249.

The approximate symmetry type is given beneath the column number, those in cols. 1—3 and 6 by analogy with unsubstituted furan, and those in cols. 4—5 and 7—10 by analogy with vicinal trisubstituted benzenes; see text.

compounds. These bands probably correspond to modes (IX—XI). The modes analogous to (IX—XI) for vicinal trisubstituted benzenes absorb at  $958 \pm 8$  (w),  $893 \pm 7$  (w), and  $770 \pm 8$   $\text{cm}^{-1}$  (vs), respectively.<sup>4</sup>



*Substituent Bands.*—With few exceptions, all the remaining bands with  $\epsilon_A \geq 15$  could be assigned to substituent absorption (cf. ref. 1a).

*Other Infrared Work.*—Early work is summarised in ref. 5. For five 2-monosubstituted furans, Cross, Stevens, and Watts<sup>5</sup> reported bands at 1248—1218, 1021—1010, 941—918, 889—878, and 763—726  $\text{cm}^{-1}$  (the first and last would be obscured by solvent in our work; the others correspond to the bands in Table 1, cols. 6—8). They assigned the band at 1248—1218  $\text{cm}^{-1}$  for 2-monosubstituted furans and that at 1180  $\text{cm}^{-1}$  for furan to the “asymmetrical C—O—C stretch,” *i.e.*, presumably to mode (IV). Although the 1180  $\text{cm}^{-1}$  band for furan is probably of this symmetry type ( $B_1$ ),<sup>3</sup> mode (IV) absorbs at 1418  $\text{cm}^{-1}$  for pyrrole,<sup>2</sup> and a large shift in position seems unlikely. The band at 1021—1010  $\text{cm}^{-1}$  was assigned to the “symmetrical C—O—C stretch;” “ring breathing” is a more conventional description of mode (VIII). Since the completion of the present work, Daasch<sup>6</sup> has published the spectra of four monosubstituted furans and suggested bands at 1597—1565, 1488—1466, 1180—1125, and 1070—1060  $\text{cm}^{-1}$  as possible additional correlations (these correspond to the bands in Table 1, cols. 1, 2, 4, and 5); Cross and Watts<sup>7</sup> accept only the first of these correlations.

*Related Raman Work.*—Han and others<sup>8,9</sup> recorded the Raman spectra of some 2-monosubstituted furans and noted that several bands were characteristic of this nucleus; no assignment of the modes was attempted. We have now treated statistically the available data for the compounds with the following substituents: Me,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ ,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$ ,  $\text{CH}_2\cdot\text{OMe}$ ,  $\text{CH}_2\cdot\text{OEt}$ ,  $\text{CH}_2\cdot\text{O}\cdot\text{COMe}$ ,  $\text{CH}_2\cdot\text{OH}$ ,  $\text{CH}_2\cdot\text{NH}_2$ ,  $\text{CH}\cdot\text{CH}_2$ ,  $\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ ,  $\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ , CN,  $\text{CO}_2\text{Et}$ ,  $\text{CO}_2\text{Me}$ , CHO. The three ring stretching frequencies are shown at 1605—1566  $\text{cm}^{-1}$  (s), 1511—1471  $\text{cm}^{-1}$  (vs), and  $[1388 \pm 4]$   $\text{cm}^{-1}$  (s); the positions of the first two bands are higher for saturated carbon substituents than for substituents capable of accepting electrons, as in the infrared spectra, but the third band is relatively constant in position.

The three CH in-plane deformation modes, the ring breathing mode, and the first two out-of-plane CH deformation modes occur at  $[1225 \pm 10$  (m),  $1153 \pm 10$  (m), and  $1079 \pm 4$  (s)  $\text{cm}^{-1}$ ],  $[1018 \pm 4$  (m)  $\text{cm}^{-1}$ ], and  $[926 \pm 6$  (m) and  $885 \pm 3$  (m)  $\text{cm}^{-1}$ ], respectively; the positions are in good agreement with the infrared spectra. A weak band found for most compounds at 837—761  $\text{cm}^{-1}$  is probably the final CH out-of-plane frequency. Mode (XI) would be expected to absorb weakly in the Raman region.

The Raman data confirm the view that the bands given in Table 1 are fundamentals of the 2-monosubstituted furan ring. Since no other characteristic bands were found in the Raman spectra in the region under consideration, and since there is only a limited number of fundamentals, our assignments are supported.

*Experimental.*—See refs. 1a and 1g for conditions of measurement, etc. The compounds, commercial products or prepared by standard methods, were redistilled or recrystallised immediately before measurement.

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<sup>5</sup> Cross, Stevens, and Watts, *J. Appl. Chem.*, 1957, 7, 562.

<sup>6</sup> Daasch, *Chem. and Ind.*, 1958, 1113.

<sup>7</sup> Cross and Watts, *ibid.*, 1958, 1161.

<sup>8</sup> Matsuno and Han, *Bull. Chem. Soc. Japan*, 1934, 9, 327; 1937, 12, 155; Han, *ibid.*, 1936, 11, 701.

<sup>9</sup> Bonino and Manzoni-Ansidei, *Z. phys. Chem.*, 1934, B, 25, 327.