1131. *Studies in Furan Chemistry. Part I. The Infrared Spectra of 2,5-Disubstituted Furans*

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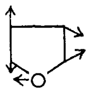
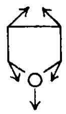
The infrared spectra of fourteen 2,5-disubstituted furans have been recorded. The positions and assignments of ten characteristic bands are discussed.

THE classical work on the infrared spectrum of pyrrole,[1] and on furan and thiophen [2] resulted in the assignment of the normal vibrations of these molecules. A recent study [3] of deuterated furans confirmed the earlier assignments, which may be classified as follows: (*a*) CH stretching near 3000 cm.$^{-1}$; (*b*) ring stretching modes between *ca.* 1600 and 1400 cm.$^{-1}$; (*c*) CH in-plane deformations at *ca.* 1300—1000 cm.$^{-1}$; (*d*) ring breathing near 1000 cm.$^{-1}$; and (*e*) CH out-of-plane deformations and ring deformations below 1000 cm.$^{-1}$. This work has been extended to 2-monosubstituted furans,[4] thiophens,[5] pyrroles,[6] and 2,5-disubstituted thiophens.[7]

We have studied the infrared spectra of 2,5-disubstituted furans in carbon tetrachloride between 2000 and 850 cm.$^{-1}$, and in carbon disulphide between 850 and 710 cm.$^{-1}$. The CH stretching vibrations at *ca.* 3000 cm.$^{-1}$ and two ring deformations below 700 cm.$^{-1}$ were not studied. The positions and intensities of ten characteristic bands have been measured and are discussed.

Ring Stretching Modes.—For furan in the vapour phase these bands occur at 1586, 1490, 1460, and 1384 cm.$^{-1}$.[3] The band which corresponds to mode (III) is absent from the solution spectra of furan and 2-monosubstituted furans.[4] We have detected only three bands in 2,5-disubstituted furans, at 1600—1569, 1481—1435, and 1388—1336 cm.$^{-1}$ (ε_A 36—159, 21—760, and 30—425) (Table 1, columns 1—3), which we assign, on this basis, to modes (I), (II), and (IV), respectively.


(I)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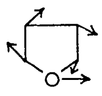
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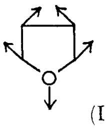
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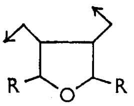
Hydrogen In-plane Deformations.—A five-membered heteroaromatic ring with only two adjacent hydrogen atoms is expected to show two in-plane, (V)—(VI), and two out-of-plane deformation modes (VIII)—(IX). All the 2,5-disubstituted furans examined show bands at 1253—1202 and 1208—1171 cm.$^{-1}$ (ε_A 51—259 and 22—219) (Table 1, columns 4 and 5). Comparison with the values obtained for 2-monosubstituted furans indicates that these bands correspond to the two CH in-plane deformations [modes (V) and (VI), respectively].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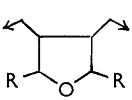
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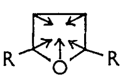
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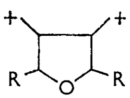
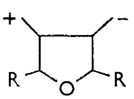

(VIII)


(IX)

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Ring Breathing Mode.—The band at 995 cm.$^{-1}$ in the vapour-phase spectrum of furan,[2,3] and at 1025—1006 cm.$^{-1}$ in the solution spectra of 2-monosubstituted furans[4] has been assigned to the ring breathing mode (VII). The 2,5-disubstituted furans exhibit a corresponding band at 1022—1013 cm.$^{-1}$ (ε_A 96—187) (Table 1, column 6). This band is notable for its ease of detection and the insensitivity of its frequency to variation in substituents.

TABLE 1

		1		2		3		4		5	
Substituents		Ring stretching modes						CH in-plane deformations			
2-	5-	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
Br	NO_2	1582	104	1458	760	1349	393	1239	139	1185	22
Br	CHO	 1578	 84	1452 1459	525 433	1342 1349	59 55	 1219	 71	 1200	 57
CHO	NO_2	1585	115	—		1348	373	1253	216	1171	219
CO_2Me	$ClCH_2$	1598	62	1438	154	1388	46	1215	284	1195	156
CHO	Me	1591	36	1438	21	1354	30	1209	86	1194	58
COC_6H_5	Br	 1581	 89	1449 † 1460	234 900	 1360	 142	 1208	 109	1176 1189	71 42
COC_6H_5	I	 1569	 127	1442 † 1453	554 518	 1352	 146	 1202	 129	1172 1188	85 52
Br	CO_2Me	 1589	 82	1472 1476	532 532	 1360	 103	 1212	 201	 1195	 96
CO_2Me	I	1589	98	1462	550	1355	118	1210	235	1197	88
CHO	I	 1570	 83	1445 1452	**442** 304	1336 1342	44 43	 1216	 51	 1195	 42
Br	CN	 —		1469 1481	339 127	 1342	 35	 1221	 84	 1208	 67
CO_2Me	Me	1599	48	1438	135	1369	61	1212	295	1194	143
CO_2Et	$ClCH_2$	1600	53	1435	21	1380	51	1215	226	1178	148
I	NO_2	1577	159	1441	745	1343	425	1233	156	1179	28

		6		7		8		9 *		10 *	
Substituents		Ring breathing		CH out-of-plane deformations				Ring deformation modes			
2-	5-	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A	cm.$^{-1}$	ε_A
Br	NO_2	1014	119	964	75	922	111	794	215	733	100
Br	CHO	 1019	 147	954 962	103 66	 925	 103	791 796	15 179	752 758	219 191
CHO	NO_2	 1018	 140	963 972	84 68	 —		 812	 326	738 747	121 241
CO_2Me	$ClCH_2$	1020	147	973	66	931	60	805	125	761	215
CHO	Me	 1021	 158	 969	 31	 944	 30	789 793	164 154	754 764	157 147
COC_6H_5	Br	 1017	 155	 978	 181	 925	 88	787 † 802	133 166	 724	 133
COC_6H_5	I	 1017	 172	 977	 210	913 920	91 61	786 † 803	60 163	 723	 37
Br	CO_2Me	 1016	 96	 990 ‡	 72	923 935	137 40	 794	 210	 756	 230
CO_2Me	I	 1020	 98	 991 §	 55	913 924	98 80	 796	 315	 757	 350
CHO	I	 1018	 112	954 962	63 115	 912	 86	 794	 160	747 754	210 196
Br	CN	1018	109	954	96	925	57	786	130	—	
CO_2Me	Me	1022	187	954	33	923	60	794	180	757	195
CO_2Et	$ClCH_2$	1021	187	974	60	—		803	120	758	200
I	NO_2	1013	128	961	95	909	110	795	250	733	110

* Columns 9 and 10 refer to carbon disulphide solutions, and columns 1—8 refer to carbon tetrachloride solutions. † One of the bands in each of these doublets is due to phenyl absorption; see L. J. Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, ch. 5. ‡ Appears as a doublet at 982 and 986 cm.$^{-1}$ in carbon disulphide. § Appears as a doublet at 981 and 987 cm.$^{-1}$ in carbon disulphide.

Hydrogen and Ring Out-of-plane Deformations.—There is some confusion in the literature regarding the assignment of these bands which occur below 1000 cm.$^{-1}$.

Thompson and Temple[2] made the following assignments for furan: (*a*) CH deformations at 872 and 837 cm.$^{-1}$; (*b*) ring deformations at 744, 724, and 605 cm.$^{-1}$. Bak *et al.*[3] reported bands in this region at 874, 838, 744, 720, and 601 cm.$^{-1}$. They further commented that two of the three bands at 874, 1181, and 1268 cm.$^{-1}$ could be CH deformations. Katritzky and his co-workers [8,9] re-assigned the band at *ca.* 870 cm.$^{-1}$, without discussion, to a ring deformation. However, in their Paper [4] on 2-monosubstituted furans they make no mention of ring deformations in this region but report three bands at 945—910, 887—881, and 837—below 800 cm.$^{-1}$, which they assign to CH out-of-plane deformations by analogy with vicinal trisubstituted benzenes. In the case of 2,5-disubstituted furans we have observed four bands, at 991—954, 944—909, 812—786, and 764—723 cm.$^{-1}$ (ε_A 33—210, 30—137, 53—326, and 37—350) (Table 1, columns 7—10). Empirical correlations for substituted benzenes [10] indicate that, as the number of adjacent hydrogen atoms decreases, the CH out-of-plane bands move to higher frequency. This would indicate that the bands at 991—954 and 944—909 cm.$^{-1}$ are CH deformation modes whilst the band relatively insensitive to substitution, at 812—786 cm.$^{-1}$, for the disubstituted furans, is a ring deformation mode. In order to obtain positive evidence on this point and on the assignment of the band at 764—723 cm.$^{-1}$ the spectra of three tetrasubstituted furans and tetrachlorothiophen were studied (Table 2).‡ The evidence from these spectra, although not conclusive, indicates that the bands at 812—786 and 764—723 cm.$^{-1}$ are due to ring deformation modes, whilst those at 991—954 and 944—909 cm.$^{-1}$ are CH deformation modes.

TABLE 2

Infrared spectra in carbon disulphide

	Substituent				Bands below 900 cm.$^{-1}$		
	2	3	4	5			
Furans	Co_2Et	Co_2Et	Co_2Et	Co_2Et	858	828	774
	Br	Co_2Me	Co_2Me	Me		809	775
	Me	Co_2Me	Me	NO_2	855, 865	802	778
2,3,4,5-Tetrachlorothiophen						804	783

Other Infrared Work.—Various workers [11-14] have reported characteristic bands in the spectra of 2,5-disubstituted furans but few assignments have been made. Ring deformation modes have been assigned to bands at 1250—1243 [11] and 1224—1214 cm.$^{-1}$.[12] From arguments advanced previously [4] it seems more likely that these bands are CH in-plane deformation modes. The ring breathing mode for various 2,5-disubstituted furans has been assigned to a band at 1032—1020 cm.$^{-1}$,[11,12] which is in agreement with our results. It has been suggested that bands at 986—973 [12] and 806—776 cm.$^{-1}$ [13] are due to CH out-of-plane modes. The former assignment is in agreement with our observations but the presence of the latter band in the spectra of tetrasubstituted furans and tetrachlorothiophen suggest that it is probably a ring deformation mode.

In summary, the general spectral features expected for 2,5-disubstituted furans, as compared with furan and monosubstituted furans, such as the decrease in number of the CH deformation modes and the tendency of these bands to move to higher frequency, have been observed. The ring modes, whose frequencies are relatively insensitive to substituents, have been assigned. A study of several tetrasubstituted furans and tetrachlorothiophen suggests that a band at *ca.* 800 cm.$^{-1}$ previously assigned to a CH out-of-plane mode is a ring deformation.

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‡ We thank a Referee for this suggestion.

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EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus. Light petroleum had b. p. 60—80°. Electronic spectra were determined on a Unicam S.P. 700 spectrophotometer (*) or a Cary model 14-50 spectrophotometer, and refer to ethanol solutions. The infrared spectra were determined for dilute solutions in carbon tetrachloride and carbon disulphide in a 0·426 or a 0·193 mm. compensated potassium bromide cell, on a Unicam S.P. 100 spectrophotometer fitted with a prism-grating double monochromator. The intensities quoted (ε_A) are the apparent values as observed with a spectral slit width of about 2 cm.$^{-1}$. The compounds studied were made by standard methods and were recrystallised or redistilled before use. N.m.r. spectra were determined in carbon tetrachloride solution with an A.E.I. RS2 spectrometer or a Perkin-Elmer spectrometer (†) operating at 60 Mc./sec., with tetramethylsilane as internal standard.

2-*Bromo*-5-*cyanofuran*.—2-Bromo-5-carbamoylfuran [15] (51 g.) and sodium chloride (19 g.) were stirred for 15 min. on a steam-bath in 1,2-dichloroethane (120 ml.). Phosphorus oxychloride (120 ml.) was added and the mixture heated under reflux with stirring for 3·5 hr. The solution was decanted from some polymeric material which had formed, and the residue was extracted with boiling 1,2-dichloroethane (60 ml.). Removal of the solvent and fractionation under reduced pressure gave the *nitrile* as an oil, b. p. 78·5—79°/14 mm. (34·2 g., 75%), n_D^{22} 1·5399 (Found: C, 34·5; H, 1·45; N, 8·0. C_2H_5BrNO requires C, 34·7; H, 1·75; N, 8·1%), $\lambda_{\text{max.}}$* 252·5 mμ (ε 15,500), $\lambda_{\text{infl.}}$ 213 mμ (ε 2700); τ 2·91 (4-proton; doublet J = 4·0 c./sec.), and 3·50 (3-proton; doublet J = 4·0 c./sec.).

2-*Benzoyl*-5-*bromofuran*.[16]—2-Benzoylfuran (27 g.) was heated at 100° and stirred while bromine (27·6 g.) was added during 0·5 hr., and the heating and stirring were continued for a further 0·5 hr. The mixture was cooled and diluted with ether (200 ml.), and the solution was washed with water (2 × 50 ml.), saturated sodium hydrogen carbonate solution until effervescence ceased, with water (50 ml.), and dried ($MgSO_4$). Removal of the solvent, followed by three crystallisations (charcoal) of the residual oil from ether–light petroleum, gave the *bromo-compound* (12 g., 30%) as pale yellow prisms, m. p. 43—44° (Found: C, 52·85; H, 3·1; Br, 32·0. $C_{11}H_7BrO_2$ requires C, 52·6; H, 2·80; Br, 31·85%), $\lambda_{\text{max.}}$ 298 mμ (ε 18,500), $\lambda_{\text{infl.}}$ 263 mμ (ε 8000); τ 1·94—2·59 (phenyl protons; multiplet), 2·84 (3-proton; doublet J = 3·5 c./sec.), and 3·49 (4-proton; doublet J = 3·5 c./sec.).

2-*Benzoyl*-5-*iodofuran*.—The foregoing bromo-compound (11·5 g.) and potassium iodide (10 g.) in glacial acetic acid (150 ml.) were heated under reflux for 0·5 hr. The mixture was cooled and diluted with water (200 ml.), and extracted with ether (3 × 100 ml.). The ether solution was washed with water (2 × 50 ml.), saturated sodium hydrogen carbonate until effervescence ceased, and with saturated brine (50 ml.), and dried ($MgSO_4$). Removal of the solvent left an oil which was recrystallised twice from ether–light petroleum, and finally from methanol, to give the *iodo-compound* (11·8 g., 86%) as colourless prisms, m. p. 58—59° (Found: C, 44·4; H, 2·7; I, 42·3. $C_{11}H_7IO_2$ requires C, 44·3; H, 2·4; I, 42·6%), $\lambda_{\text{max.}}$ 309 and 258 mμ (ε 19,000 and 7600), τ † 1·94—2·74 (phenyl protons; multiplet), 2·92 (3-proton; doublet J = 4·5 c./sec.), and 3·27 (4-proton; doublet J = 4·5 c./sec.).

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