496. *Infrared Absorption of the Furano-group in Some Polycyclic Aromatic Compounds.*

By L. H. Briggs and L. D. Colebrook.

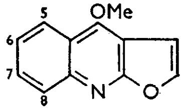
Seven infrared absorption bands characteristic of the furano-group in benzofurans, furanoquinoline alkaloids, and furanocoumarins are recorded and discussed.

Previously published studies of the infrared spectra of compounds containing the furano-group have been confined to monosubstituted or simple polysubstituted derivatives of furan. Thompson and Temple [1] have made vibrational assignments for furan. Nahum [2] has reported on the 3000 cm.$^{-1}$ region of furan and some dihydrofurans. Cross, Stevens, and Watts,[3] Daasch,[4] and Cross and Watts [5] have studied a number of 2-monosubstituted and 2,5-disubstituted furans over the range 2000—700 cm.$^{-1}$. Katritzky and Lagowski [6] have discussed nine characteristic bands for twenty-four 2-monosubstituted furans. Kubota [7] has studied the spectra of forty-three furano-compounds and has selected three bands as characteristic of this group. The compounds ranged from furan itself to a tetrasubstituted derivative but were predominantly monosubstituted furans. It has been suggested [8] that certain bands in the spectrum of a 3-monosubstituted furan are characteristic of the furanoid system. Sharp bands attributed to CH bending modes of the furan ring have been noted in the spectra of some 2,4-dinitrophenylhydrazones containing the furan nucleus.[9]

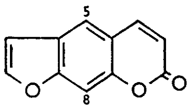
Experimental.—Spectra were determined with a Beckman IR-2 spectrophotometer, equipped with a sodium chloride prism for the range 2500—670 cm.$^{-1}$ and a lithium fluoride prism for the range 5000—2500 cm.$^{-1}$. Unless otherwise stated, the potassium bromide disc technique was used.

Results and Discussion

From a detailed examination of the spectra of three benzofurans, ten furanoquinoline alkaloids, and seven furanocoumarins seven bands, listed in the Table, have been distinguished as characteristic of the furano-group in these compounds. With the exception of dibenzofuran and dibenzofuran-2-carboxylic acid all these compounds are 2,3-disubstituted furan derivatives. The furanoquinoline alkaloids are based on dictamnine (I) and the furanocoumarins on psoralen (II).



(I)



(II)

CH *Stretching Frequencies.*—In addition to the aromatic and aliphatic CH stretching bands near 3000 and 2900 cm.$^{-1}$, respectively, the majority of the compounds exhibit bands of weak to medium intensity at 3175—3137 and 3137—3112 cm.$^{-1}$ (Table, cols. 1 and 2). The lower-frequency band usually has the higher intensity. This absorption appears to be due to the CH stretching vibrations of the furano-nucleus which occur at

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[1] Thompson and Temple, *Trans. Faraday Soc.*, 1945, **41**, 27.
[2] Nahum, *Compt. rend.*, 1955, **240**, 1898.
[3] Cross, Stevens, and Watts, *J. Appl. Chem.*, 1957, **7**, 562.
[4] Daasch, *Chem. and Ind.*, 1958, 1113.
[5] Cross and Watts, *ibid.*, p. 1161.
[6] Katritzky and Lagowski, *J.*, 1959, 657.
[7] Kubota, *Tetrahedron*, 1958, **4**, 68.
[8] Quilico, Piozzi, and Pavan, *Tetrahedron*, 1957, **1**, 177.
[9] Jones, Holmes, and Seligman, *Analyt. Chem.*, 1956, **28**, 191.

	1	2	3	4	5	6	7
				Benzofurans			
1				1284m 1242s	1104m	867w	842s
2	3152m †	3118m †	1616m †	1263m * 1247s *	1105s *	861s *	812w *
3		3124m	1616s	1258s	1105s	865s	818s
				Furanoquinoline alkaloids			
4	3145w	3115m	1626s	1266s	1088s	873s	833s
5	3155w	3125w	1621s	1261s	1094s	868m	816s
6	3161m	3125s	1623s	1253s	1089s	859s	840s
7	3146s	3123s	1618s	1263s	1104s	879w	838s
8	3145m	3112s	1621s	1271s	1094s	873w	827w
9	3164m	3126m	1626s	1259s	1089s	871m	818s
10	3165m	3135m	1623s	1264s	1099s	858s	821m
11	3165m	3135m	1618s	1272s	1100s	874m	825m
12	3175w	3135m	1623s	1259s	1109s	884m	824s
13		3121w	1626i	1256s	1109s	885m	821s
				Furanocoumarins			
14	3165m	3137m	1618s	1259s	1096s	864m	821s
15	3145w		1616s	1259s	1103s	866m	833s
16	3165w	3134m	1626s	1256s	1096s	868s	827s
17	3137s	3116s	1629s	1274m	1092s	880m	838s
18	3165m	3135s	1639s	1263s	1095s	871m	833s
19	3157m	3130s		1274m	1094s	870m	829s
20	3175w	3125w	1626i	1272m	1096s	867m	829m

Benzofurans

1 Dibenzofuran
2 Benzofuran
3 Benzofuran-2-carboxylic acid (coumarilic acid)

Furanoquinoline alkaloids

4 Dictamnine
5 8-Methoxydictamnine (γ-fagarine)
6 6,7-Dimethoxydictamnine (kokusaginine)
7 8-Methoxy-6,7-methylenedioxydictamnine (flindersiamine)
8 7,8-Dimethoxydictamnine (skimmianine)
9 5,7,8-Trimethoxydictamnine (acronycidine)
10 7-(2,3-Dihydroxy-3-methylbutoxy)-6-methoxydictamnine (evolatine)
11 7-(2,3-Dihydroxy-3-methylbutoxy)-8-methoxydictamnine (evoxine)
12 Dimethylpyranodictamnine (medicosmine)[a]
13 Methoxydimethylpyranodictamnine (acronidine)[b]

Furanocoumarins

14 5-(3-Methylbut-2-enyloxy)psoralen (isoimperatorin)
15 5-(2,3-Dihydroxy-3-methylbutoxy)psoralen (oxypeucedanin hydrate)
16 5-Geranoxypsoralen
17 8-Geranoxypsoralen
18 8-Hydroxy-5-methoxypsoralen
19 5,8-Dimethoxypsoralen (isopimpinellin)
20 8-(2,3-Dihydroxy-3-methylbutoxy)-5-methoxypsoralen (byakangelicin)

[a,b] Lamberton and Price, *Austral. J. Chem.*, 1953, **6**, (*a*) 173, (*b*) 66. s Strong, m medium, w weak, i shoulder. * In CS_2. † In CCl_4.

higher frequencies than those of ethylenic double bonds. The absence of these bands from the dibenzofuran spectrum supports this assignment. Previous reports[2,7] of absorption in this region mention only one band, presumably because a sodium chloride prism was used.

The constant position of this absorption in the spectra of all types of furan derivatives examined suggests its diagnostic value.

Ring-stretching Frequency near 1600 *cm.*$^{-1}$.—In addition to the aromatic bands between 1600 and 1500 cm.$^{-1}$, a strong, sharp band, attributed essentially to a C:C stretching mode of the furan ring, appears at 1639—1616 cm.$^{-1}$ (Table, col. 3). It is absent from the dibenzofuran spectrum. Nahum[2] has reported a band at 1621—1580 cm.$^{-1}$ due to the double bond in some dihydrofurans, and Kubota[7] two bands, at 1613—1536 and 1522—1447 cm.$^{-1}$, ascribed to the furan ring. Katritzky and Lagowski[6] have assigned bands at 1611—1558, 1512—1470, and 1405—1377 cm.$^{-1}$ to ring-stretching modes of the 2-monosubstituted furan nucleus.

The significantly higher frequency of this absorption in the benzofuran, furanoquinoline, and furanocoumarin series may, however, have diagnostic uses in some cases.

Compounds 12, 13, 14, 16, and 17 possess side chains containing unsaturated linkages, the stretching bands of which are not resolved from the furano-group absorption. Absorption due to the double bond of the pyrone moiety in compounds 14—20 is superimposed on that of the furano-nucleus.

The CO *Stretching Region.*—A doublet consisting of a medium-intensity member at 1263 cm.$^{-1}$ and a strong member at 1247 cm.$^{-1}$ appears in the benzofuran spectrum. With the exception of dibenzofuran, which exhibits single bands at 1284 and 1242 cm.$^{-1}$, all other compounds show a medium to strong band at 1274—1253 cm.$^{-1}$ (Table, col. 4). This absorption may be attributed to a furan ring-stretching mode involving the ether linkage.

The 1100 *cm.$^{-1}$ Region.*—A strong band in the range 1109—1088 cm.$^{-1}$ (Table, col. 5) appears in the spectra of all the compounds examined.

The CH *Out-of-plane Bending Region.*—The medium-intensity band at 885—858 cm.$^{-1}$ (Table, col. 6) may be assigned to a CH out-of-plane bending mode of the furan ring, in agreement with other workers.[3,6,9] A band at 867 cm.$^{-1}$ in the spectrum of dibenzofuran is extremely weak. The absence of significant absorption by this compound supports the above assignment. All the other compounds, including benzofuran-2-carboxylic acid, which has only one hydrogen atom directly attached to the furan nucleus, exhibit this absorption.

A band of variable intensity appears at 842—812 cm.$^{-1}$ (Table, col. 7). Absorption in this position has been noted[3] earlier and also assigned[6] to a CH out-of-plane bending mode. However, benzofuran shows only weak absorption while dibenzofuran unexpectedly exhibits a strong band within this range.

The 750 *cm.$^{-1}$ Region.*—Absorption at 795—730 cm.$^{-1}$ has been reported by other workers.[3,7] In simple furans this may be very intense. In the present case the spectra are complicated by absorption due to aromatic CH out-of-plane bending modes and no absorption attributable specifically to the furano-group can be observed.

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