

### 869. *Infrared Absorption of Di- and Tetra-substituted 2,2'-Bipyridyls.*

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The infrared absorption of several 3,3'-, 4,4'-, and 5,5'-disubstituted and of 4,4',5,5'-tetrasubstituted 2,2'-bipyridyls is recorded. The overtone and combination bands in the 2000—1650  $\text{cm}^{-1}$  region may be used in the characterization of the bipyridyl substitution pattern. Assignments are made by analogy with similarly substituted pyridines, and a band near 1280  $\text{cm}^{-1}$  is tentatively assigned to the inter-ring stretching vibration.

ALTHOUGH the infrared spectra of substituted pyridines have been reported in detail (for a review see ref. 1), no comprehensive survey of the infrared absorption of 2,2'-bipyridyls has appeared. In this Paper we report the spectra of the following derivatives of 2,2'-bipyridyl: (3,3') dimethyl and di(ethoxycarbonyl); (4,4') dimethyl, di-n-propyl, di-n-pentyl, dibenzyl, diphenylethyl, distyryl, dichloro, and di(ethoxycarbonyl); (5,5') dimethyl, diethyl, dibenzyl, di(methoxycarbonyl), and di(ethoxycarbonyl); 4,4',5,5'-tetramethyl, 5,5'-diethyl-4,4'-dimethyl, 4,4'-diphenylethyl-5,5'-diethyl, and 5,5'-diethyl-4,4'-distyryl.

It had been observed that for monocyclic aromatic and heteroaromatic compounds the frequencies of the ring-stretching bands in the 1600—1400  $\text{cm}^{-1}$  region were not sensitive to the orientation of the substituents, but that the intensity of these bands was often altered.<sup>1,2</sup> Also, the number and position of the CH deformation bands depended upon the number and orientation of the substituents. The data obtained for the bipyridyls lead to similar conclusions and suggest that the two rings may be considered, to a certain extent, individually as polysubstituted pyridines. However, not all the vibrations will be identical with those of the monocyclic compounds, and there will be further vibrations, which may be considered to be inter-ring modes, which will not correspond to any observed fundamentals of the monocyclic compounds.<sup>3,4</sup> With the exception of the inter-ring stretching

<sup>1</sup> (a) Katritzky and Ambler, in "Physical Methods in Heterocyclic Chemistry," ed. Katritzky, ch. 10, Academic Press, New York, 1962; (b) Katritzky, *Quart. Rev.*, 1958, **13**, 995.

<sup>2</sup> Katritzky, *J.*, 1958, 4162.

<sup>3</sup> Keaton and Lippincott, *Spectrochim. Acta*, 1959, **15**, 627.

<sup>4</sup> Steele and Lippincott, *J. Mol. Spectroscopy*, 1961, **6**, 238.

TABLE 1.  
Ring-deformation frequencies in the 1600—1400 cm.<sup>-1</sup> region.

	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$
Biphenyl	1600	(70)	1573	(15)	1489	(130)	1439	(50)
2-Phenylpyridine	1592	(105)	1568	(45)	1470	(130)	1427	(60)
2,2'-Bipyridyl	1583	(190)	1565	(110)	1488	(140)	1427	(130)
3,3'-Disubstituted 2,2'-bipyridyl		ca. 1580 (50)			ca. 1452	(70)	ca. 1421	(70)
4,4'-Disubstituted 2,2'-bipyridyl *	1598—1595	(280—460) †	1564—1556	(80—140)	1470—1467	(120—210)	—	—
	[1597 ± 1	(370 ± 80)]	[1559 ± 3	(100 ± 20)]	[1468 ± 1	(165 ± 40)]	—	—
5,5'-Disubstituted 2,2'-bipyridyl	1603—1595	(25—65) †	1558—1555	(50—90)	1473—1469	(300—450) §	—	—
	[1599 ± 3	(40 ± 20)]	[1556 ±	(70 ± 10)]	[1472 ± 2	(340 ± 50)]	—	—
4,4',5,5'-Tetrasubstituted 2,2'-bi- pyridyl	1603—1598	(110—170)	1552—1548	(35—60)	1476—1473	(110—360)	—	—
	[1600 ± 2	(140 ± 25)]	[1550 ± 1	(50 ± 10)]	[1474 ± 1	(210 ± 100)]	—	—

\* Dichloro-compound: 1572 (500), 1545 (240), 1458 cm.<sup>-1</sup> (200). † Di(ethoxycarbonyl) compound:  $\epsilon = 100$ . ‡ Di(ethoxycarbonyl) compound:  $\epsilon = 420$ . § Di(ethoxycarbonyl) compound:  $\epsilon = 140$ .

TABLE 2.

In-plane and out-of-plane CH deformation frequencies.

	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$	cm. <sup>-1</sup>	$\epsilon_A$
3,3'-Disubstituted 2,2'-bipyridyl	ca. 1128	(30)	ca. 1073	(45)	ca. 850	(15)
4,4'-Disubstituted 2,2'-bipyridyl	1108—1117	(10—35)	1068—1078	(15—85)	890—918	(10—65)
	[1112 ± 3	(20 ± 10)]	[1074 ± 4	(40 ± 25)]	[905 ± 8	(30 ± 15)]
5,5'-Disubstituted 2,2'-bipyridyl	1130—1134	(25—50)	1057—1065	(30—70)	820—843	(60—70) *
	[1133 ± 2	(35 ± 10)]	[1060 ± 3	(45 ± 15)]	[832 ± 8	(60 ± 5)]
4,4',5,5'-Tetrasubstituted 2,2'-bipyridyl	...	...	1073—1080	(40—120)	829—856	(50—220)
			[1076 ± 4	(65 ± 30)]	[845 ± 11	(140 ± 60)]
					[843—858	(40—95)
					[850 ± 7	(70 ± 30)]

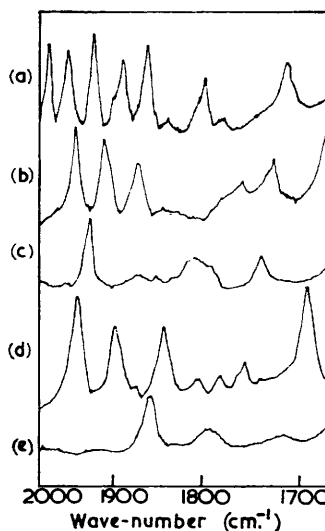
\* Dimethyl compound:  $\epsilon = 330$ .

mode, which occurs at  $1275\text{ cm}^{-1}$  for biphenyl (Raman-active only), all the inter-ring vibrations occur at a low frequency<sup>3</sup> and would not be observable under the conditions of our measurements.

**Overtone and Combination Bands.**—Absorption in the region  $2000\text{--}1650\text{ cm}^{-1}$  is due essentially to overtone and combination bands of the out-of-plane CH deformation fundamentals, but it is highly probable that the higher-frequency summation bands arise from ring-deformation fundamentals.<sup>3,5</sup> This region has been used by several workers<sup>5,6</sup> for the characterization of substituted benzene and pyridine compounds. Although absorption-band patterns for the bipyridyl compounds (see Figure) are similar within each series of compounds, the positions vary slightly. This is to be expected, as the positions of the CH deformation fundamentals are altered by electron-attracting and by heavy substituents. For bipyridyls with aromatic substituents, the summation bands arising from the monosubstituted benzene ring are also observed.

Absorption in the  $2000\text{--}1650\text{ cm}^{-1}$  region.

- (a) 2,2'-Bipyridyl.
- (b) 3,3'-Dimethyl-2,2'-bipyridyl.
- (c) 4,4'-Dimethyl-2,2'-bipyridyl.
- (d) 5,5'-Dimethyl-2,2'-bipyridyl.
- (e) 4,4',5,5'-Tetramethyl-2,2'-bipyridyl.



Although the absorption patterns of the 3,3'- and 5,5'-isomers are similar, they may be differentiated by the band which appears near  $1690\text{ cm}^{-1}$  for the 5,5'- and near  $1665\text{ cm}^{-1}$  for the 3,3'-isomer. It should be noted that the 4,4'- and the 5,5'-isomers, which have the same substitution orientation, exhibit different overtone patterns. This may be explained in terms of the different degree of interaction between the two rings, as deduced from the electronic spectra,<sup>7</sup> producing a change in the positions of the fundamentals.

**Ring-stretching Vibrations between  $1600$  and  $1300\text{ cm}^{-1}$  (Table 1).**—Four bands are observed in the spectrum of biphenyl and in that of 2,2'-bipyridyl. With the exception of the 3,3'-disubstituted compounds, only three of these bands are found in the spectra of substituted bipyridyls. The fourth band, near  $1430\text{ cm}^{-1}$ , is obscured by the stronger absorption of the third band, and, in many cases, by alkyl CH deformation bands. The positions of the bands are reasonably constant irrespective of the position of the substituents. Within each series the intensities of the bands vary slightly with the mass of the substituent, but strongly electron-withdrawing substituents ( $\text{CO}_2\text{R}$ ) cause a considerable increase in the intensities. This intensity variation has been discussed by Katritzky<sup>2</sup> in terms of the symmetry of the vibrations and the charge distribution within the ring.

<sup>5</sup> Young, DuVall, and Wright, *Analyt. Chem.*, 1951, **23**, 709; Eddy and Eisner, *ibid.*, 1954, **26**, 1428; Podall, *ibid.*, 1957, **29**, 1423; Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458; Whiffen, *Spectrochim. Acta*, 1955, **7**, 253; Pines and Wunderlich, *J. Amer. Chem. Soc.*, 1959, **81**, 2568.

<sup>6</sup> Shindo, *Pharm. Bull. (Japan)*, 1957, **5**, 472.

<sup>7</sup> Sasse and Whittle, *J.*, 1961, 1347.

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All the substituted bipyridyls investigated absorbed near  $1370\text{ cm}^{-1}$ . For the 4,4'-disubstituted compounds the intensity of the band is considerably higher ( $95\text{--}320$ ) [ $(155 \pm 50)$ ] \* than could be attributed solely to the alkyl groups. For the other isomers the intensity of the band is lower ( $25\text{--}90$ ) [ $(50 \pm 20)$ ] and may be assigned to an alkyl CH deformation. However, as the band is also observed for 4,4'-dichloro-2,2'-bipyridyl at  $1360\text{ cm}^{-1}$  (170), it must be considered as characteristic of the 4,4'-disubstituted 2,2'-bipyridyl nucleus. Absorption near  $1390\text{ cm}^{-1}$  for biphenyl and substituted benzenes has been assigned <sup>3,4,8</sup> to a fifth in-plane ring-stretching mode or to an overtone of an out-of-plane ring-deformation near  $700\text{ cm}^{-1}$ . With the available evidence it is impossible to assign completely this band for the bipyridyls.

*In-plane and Out-of-plane CH Deformation.*—By analogy with the corresponding tri- and tetra-substituted benzenes,<sup>8</sup> and di- and tri-substituted pyridines<sup>6</sup> we have assigned the bands in Table 2 to in-plane and out-of-plane deformation modes.

*Inter-ring Stretching and Ring-breathing Vibrations.*—The inter-ring stretching vibration which is infrared-inactive for biphenyl appears at  $1287\text{ cm}^{-1}$  in the Raman spectrum. Bipyridyl exists in the "trans" form. Therefore, if it were planar it would have a zero dipole, and the change in dipole during the inter-ring stretching vibration would also be zero. However, it has been shown that the system is non-planar,<sup>9</sup> and as the angle between the two rings may change during the inter-ring stretching vibration it is probable that the stretching vibration will be infrared-active to a greater or lesser extent depending upon the position of the substituent. A band at  $1270\text{--}1280\text{ cm}^{-1}$  (*ca.* 30) for the 3,3'-, 4,4'-, and 5,5'-isomers, and at  $1292\text{ cm}^{-1}$  (*ca.* 40) for the 4,4',5,5'-isomer, is tentatively assigned to the inter-ring stretching mode. However, for many compounds the band is obscured by solvent absorption and could not be measured accurately.

The ring-breathing mode absorbs at  $994\text{ cm}^{-1}$  (50) for 2,2'-bipyridyl and at  $990\text{--}997\text{ cm}^{-1}$  ( $15\text{--}90$ ) [ $994 \pm 2\text{ cm}^{-1}$  ( $50 \pm 20$ )] for 3,3'- and 4,4'-disubstituted compounds. Bipyridyls having a substituent in the 5-position have a band at  $1025\text{--}1033\text{ cm}^{-1}$  ( $20\text{--}130$ ) [ $1030 \pm 3\text{ cm}^{-1}$  ( $60 \pm 40$ )] which we assign to the ring-breathing vibration (*cf.* the assignment of the band at  $1025 \pm 2\text{ cm}^{-1}$  ( $65 \pm 35$ ) for 3-monosubstituted pyridines.<sup>10</sup>

## EXPERIMENTAL

The spectra of all compounds were measured in the region  $2000\text{--}800\text{ cm}^{-1}$  on 0.189M- or 0.378M-solutions in chloroform in a 0.106-mm. compensated cell with a Perkin-Elmer model 21 spectrometer using sodium chloride optics. The spectra were calibrated at 1601, 1028, and  $907\text{ cm}^{-1}$  with a polystyrene film.

Spectra in the region  $2000\text{--}1650\text{ cm}^{-1}$  were measured on *ca.* 10% solutions in carbon tetrachloride in a 1.0-mm. compensated cell with a Grubb-Parsons S4 spectrometer using calcium fluoride optics. Weakly soluble compounds were used as saturated solutions in *ca.* 3.0-mm. cells. Spectra were calibrated with polystyrene at 1944, 1871, 1802, and  $1601\text{ cm}^{-1}$ . All compounds were recrystallized or distilled immediately before use.

We are grateful to the Commonwealth Government for a maintenance grant to one of us (P. C.) under the Colombo Plan.

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[Received, January 23rd, 1964.]

\* Parentheses enclose apparent extinction coefficients and square brackets enclose arithmetical means and standard deviations.

<sup>8</sup> Randle and Whiffen, Report on Molecular Spectroscopy Conference, Institute of Petroleum, London, 1954.

<sup>9</sup> Fielding and Le Fèvre, *J.*, 1951, 1811.

<sup>10</sup> Katritzky, Hands, and R. A. Jones, *J.*, 1958, 3165.