Effect of Molecular Structure on Infrared Spectra of Six Isomers of Bipyridine

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Interpretation of infrared absorption data, according to substitution patterns, indicates that the position and number of infrared absorption bands for the six bipyridine isomers may be attributed largely to contributions from each ring. One inter-ring mode is found in the analysis of spectra from 1600 to 350 cm^{-1}.

Six bipyridine isomers exist, but the chemistry and spectroscopy of only one, 2,2′-bipyridine, has been investigated extensively. Infrared absorption spectra over various frequency ranges have been recorded in the literature for five isomers: 2,2′-bipyridine (*3, 13, 16, 19, 20*), 2,4′-bipyridine (*17*), 2,3′-bipyridine (*13*), 3,3′-bipyridine (*13, 20*), and 4,4′-bipyridine (*13, 20*). Vibrational assignments on the basis of frequency values were reported for a few of the principal infrared absorption bands of 2,2′-bipyridine (*12, 15*) and 4,4′-bipyridine (*15*). To make meaningful comparisons for the bipyridines, the infrared spectra from 1600 to 350 cm^{-1}, for each of the six isomers, have been recorded and analyzed. The results are organized according to substitution patterns, and are reported here.

EXPERIMENTAL

2,2′-Bipyridine, obtained from Aldrich Chemical Co., Inc., was used without further purification. The 2,3′-bipyridine and 3,3′-bipyridine were synthesized according to Smith (*9*) and purified by vacuum distillation. The 2,4′- and 3,4′-isomers were prepared by the method of Kuffner and Straberger (*11*). Treatment of the 4,4′-bipyridine dihydrochloride, also from Aldrich Chemical, with aqueous potassium hydroxide, was followed by extraction with benzene. The 4,4′-bipyridine compound (mp 113°–115° C) was recovered from this extract.

Infrared spectra were recorded on a Perkin-Elmer 521 infrared spectrophotometer at the Sadtler Research Laboratories, Inc., Philadelphia, Pa. KBr wafer technique was used for the 2,2′- and 4,4′-bipyridines. The remaining isomers, which were liquids or easily melted solids, were measured as thin films between CsBr plates.

RESULTS AND DISCUSSION

Assignments for the infrared spectra of nitrogen-heterocyclic compounds have been based upon the vibration modes assigned to benzene. Thus, pyridine has been related to monosubstituted benzenes (*4*), and monosubstituted pyridine compounds to disubstituted benzenes (*8*). A logical extension of such reasoning is the analogy between the diazines, monosubstituted pyridines, and disubstituted benzenes (*14*).

The six bipyridine isomers are dimers of pyridine. Since there are no other substituents present, the infrared spectra of the bipyridines presumably should show absorption bands due to vibrational modes connected with the rings themselves. These absorption bands are characteristic for the position of the substituent, so the symmetrical isomers should exhibit the characteristic pattern of only one substitution type. The spectra of the unsymmetrical isomers would be essentially the sum of the characteristic patterns of the two substitution types present in each dimer. Furthermore, vibrational absorptions due to the interaction between the rings might be expected.

Earlier investigations of symmetrical dimers have also shown that the infrared spectra of such compounds are affected by both the contributions of each individual ring and the interactions among the rings. Both Cheuychit and coworkers in their study of 2,2′-bipyridine derivatives (*3*), and Lippincott and coworkers in their examination of biphenyl infrared spectra (*7, 23*) found that the spectra were accounted for chiefly by independent action of each ring in the dimer. Inter-ring vibrations do occur also, but in the spectral region under consideration here, only the stretching frequency should be found (*7*).

Vibrational assignments made for pyridine and the diazines (*8, 14*) and frequency ranges correlated with vibrational modes given for monosubstituted pyridine compounds (*8*) were used to assign the absorption frequencies for each bipyridine. Vibration numbers are given according to Wilson, as quoted by Katritzky (*8*). The assignments are given in Table I for the CH vibration modes, and in Table II for the ring vibration modes. To clarify the assignments for the unsymmetrical bipyridines, the assignments are separated further into the 2-, 3-, or 4-substituted pyridine ring contributions. To determine frequencies corresponding to one vibration mode for an unsymmetrical isomer—for example, the 2,3′-bipyridine—both the 2-substituted and the 3-substituted pyridine ring contributions must be ascertained from the tables.

Since the expected absorption regions overlap in some cases, arbitrary decisions had to be made in the assignment of an absorption line to a particular substitution type. With the exception of lines attributed to binary combination bands, or to overtones, all lines observed in the bipyridine spectra have been recorded in the tables.

The appearance of several unexpected lines of appreciable intensity was noted. Except for one instance in the 4,4′-

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Table I. CH Vibration Modes[a]

Vibration Type	Frequency, Cm^{-1}							
	γ				β			
					A. 2-Substitution			
Vibration number[b]	11	10a	5	17a	18a	15	9a	3
Pyridine[c, d]	700^c	886^c	937^c	980^c	1068^d	1148^d	1218^d	1217^d
Pyridazine[e]	760	842	938	861	1129	1063	1150	1283
Range for 2-substit. pyridines[f]		780- 740			1048±5	1093 ± 14	1147 ± 3	1279 ± 14
2.2′-	660	760	896	960vw	1066	1090	1140	1250
2,3′-	632	745	890	958	1068	1097	1154	1245
2,4′-	645sh	775	874	965	1065	1096	1154	1248
					B. 3-Substitution			
Vibration number[b]	11	10b	5	17a	18b	15	9a	3
Pyridine[c, d]	700^c	886^c	937^c	980^c	1068^d	1148^d	1218^d	1217^d
Pyrimidine[g]	804	719	993	870	1075	1154	1138	1223
Range for 3-substit. pyridines[f]	820- 770	730- 690		920- 880	1038 ± 7	1124 ± 5	1103 ± 5	1202- 1182
3,3′-	790 766	712	925	876vw 822	1042	1128	1103	1238? 1191
2,3′-	770	710	930	822	1050	1122	(1097)	1192
3,4′-	795 767	713	925	870	1028	1125	1100	1190
					C. 4-Substitution			
Vibration number[b]	11	10a	5	17a	18a	15	9a	3
Pyridine[c, d]	700^c	886^c	937^c	980^c	1068^d	1148^d	1218^d	1217^d
Pyrazine[h, i]	804^h	757^h	919^h	950^h	1135^i	1063^i	1230^h	1118^h
Range for 4-substit. pyridines[f]	~725		850- 790		1067 ± 3		1232- 1208	
4,4′-	733	745	810	962	1072		1215	
2,4′-	737	745sh	840	(965)	(1065)		1215	
3,4′-	745sh	748	837	955	1070		1220	

[a] Abbreviations: vw = very weak, sh = shoulder; β = in-plane; γ = out-of-plane vibrations; parentheses indicate that the band has been assigned to more than one vibration. [b] Numbering for pyridine and diazines, Ref. 8 and citations therein. [c] See Ref. 10, verified by Ref. 2. [d] See Ref. 25, verified by Ref. 2. [e] See Ref. 24. [f] See Ref. 8 and references cited therein. [g] See Ref. 18. [h] See Ref. 21. [i] See Ref. 1.

bipyridine spectrum (vibration 6b), these anomalous lines are associated with the 3-pyridyl ring in 3,4′-bipyridine (vibration 11) and 3,3′-bipyridine (vibrations 3, 6a, 11, 14, 17a). All possible fundamentals for the bipyridines are accounted for in the assignments of the other lines, except for four CH stretching vibrations around 3000 cm^{-1}, and for 5 ring-ring modes. These ring-ring modes (*7, 23*) would appear at frequencies below 350 cm^{-1}, and so are not likely to be responsible for the anomalies. The lines are not accounted for by simple binary combination tones nor by overtones. Finally, similar lines were observed in the work of other investigators (*13, 20*), so that the lines cannot be explained easily as experimental artifacts.

Few chemical or spectral investigations have been made on these isomers, further complicating the explanation of these lines. Possibly inter- or intramolecular effects have generated the lines. One can speculate that the effect is intramolecular, since many of the anomalous lines have been found also in the spectra recorded by Shindo (*20*) in CS_2 solution.

The data reported here demonstrate that the number and positions of vibrational bands for both symmetrical and unsymmetrical bipyridines originate mainly from individual contributions from each ring. This finding confirms earlier reports on other symmetrical systems (*3, 7, 23*). Only one vibration, occurring between 1270 and 1294 cm^{-1}, could be ascribed specifically to inter-ring activity. This band was attributed to inter-ring stretching, in accordance with Cheuychit (*3*).

The absence of information on the steric configuration of some of the bipyridine isomers makes it worthwhile to examine this inter-ring stretching vibration more closely. Theoretical calculations of permanent dipole moments have been made for all the isomers (*5, 6*). The moments were calculated for planar structures in both cis and trans configurations, for the three isomers (2,2′-, 3,3′-, 2,3′-bipyridine) in which such forms are feasible. Experimentally determined moments agreed well with theoretical values, but were not available for the 2,3′- and 3,3′-isomers (*5, 6*). The intensity of the inter-ring stretching vibration reflects the magnitude of change in dipole moment as the vibration is carried out. If it is assumed that no extreme change in configuration occurs during the vibration, then the intensity may be qualitatively compared to the magnitude of the permanent dipole. Both parameters are related to the configuration of the bipyridines. No inter-ring band was found for the 4,4′-isomer, presumably because of its symmetrical structure, just as the theoretical dipole moment for this compound was zero (a small experimental moment was attributed to atom polarization) (*5*). The 2,2′-isomer could have a cis or trans configuration, the planar trans form yielding a dipole moment of zero. Actually, a very small amount is found for the 2,2′ compound, and this was attributed to the noncoplanarity of its rings in the trans configuration. Possibly due to the same reason, the inter-ring band is very weak for 2,2′-bipyridine. The remaining isomers have medium intensity inter-ring vibrations of about equal magnitude except for the strong band observed for 2,3′-bipyridine. Theoretical dipole moments calculated for the planar trans form are zero (3,3′-bipyridine), or less than one-half the cis form (2,3′-bipyridine). The moments of the cis forms, and of the

Table II. Ring Vibration Modes[a]

Vibration Type	Frequency, Cm^{-1}												
	γ			β		Breathing		ν					
						A. 2-Substitution							
Vibration number[b]	16a	16b	4	6a	6b	1	12	14	19b	19a	8b	8a	Inter-ring
Pyridine[c, d]	375[c]	405[c]	744[c]	605[d]	652[d]	992[d]	1029[d]	1375[d]	1439[d]	1482[d]	1572[d]	1580[d]	. . .
Pyridazine[e]	410	370	753	630	667	964	1032	1347	1417	1450	1566	1572	. . .
Range for 2-substit. pyridines[j]						994 ± 4		1293–1250[j]	1433 + 5	1471 + 6	1572 ± 4	1615-1585	
2,2′-	410		744	623	(660)	995	1042	1310vw	1417	1458	1560	1580	1270
2,3′-	425sh		776sh	620	656	990	1028sh	1298	1434	1460	1565	1585	1282
2,4′-	408		762sh	618	670	996	1040	1296	1433	1466	1575	1586	1284
						B. 3-Substitution							
Vibration number	16a	16b	4	6a	6b	1	12	14	19b	19a	8b	8a	Inter-ring
Pyridine[c, d]	375[c]	405[c]	744[c]	605[d]	652[d]	992[d]	1029[d]	1375[d]	1439[d]	1482[d]	1572[d]	1580[d]	. . .
Pyrimidine[g]	394	344	709	677	621	993	1068	1355	1466	1402	1559	1570	. . .
Range for 3-substit. pyridines[j]							1025 ± 2		1427-1414	1485-1465	1577 ± 5	1595 + 5	
3,3′-	405	360vw	658	628 619	558	994	1023	1326 1392	1422	1460	1565	1585	1293
2,3′-	410	. . . .	660	612	558	(990)	1016	1332	1405	1470	1575sh	1590	1282
3,4′-	406	370	670	614	570	992	1013	1370sh	1422	1472	1576	1595	1294
						C. 4-Substitution							
Vibration number[b]	16a	16b	4	6a	6b	1	12	14	19b	19a	8b	8a	Inter-ring
Pyridine[c, d]	375[c]	405[c]	744[c]	605[d]	652[d]	992[d]	1029[d]	1375[d]	1439[d]	1482[d]	1572[d]	1580[d]	. . .
Pyrazine[h, i]	340[h]	416[h]	703[h]	596[h]	516[h]	1015[h]	1021[i]	1346[i]	1418[h]	1484[h]	1524[h]	1578[h]	. . .
Range for 4-substit. pyridines[j]						993 ± 2			1415 ± 4	1520-1480	1561 ± 8	1603 + 5	
4,4′-	380	400	672	608	572 500?	988	1037	. . .	1403	1488	1530	1588	. . .
2,4′-	345	. . . .	636	600vw	567	990sh	(1040)	1328	1405	1495	1553	1595	1284
3,4′-	(370)	455	640	608sh	555sh	(992)	1020sh	1320	1400	. . .	1545	1602	1294

[a] Abbreviations: sh = shoulder, vw = very weak; β = in-plane, γ = out-of-plane, ν = stretching vibrations; parenthesis indicate that the peak has been assigned to more than one vibration. [b-i] See corresponding footnotes in Table I. [j] See Ref. 9.

2,4′-, and the 3,4′-bipyridines are similar in value, though the 2,3′ cis value is by far the largest. Thus, it can be inferred that the cis form is preferred for the 2,3′- and the 3,3′-bipyridines, at least as a first approximation.

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RECEIVED for review September 15, 1969. Accepted June 29, 1970.

Methyl Esters of Camphoric and Isocamphoric Acids

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Conclusions of earlier investigators regarding the structure and configuration of a number of the methyl esters of camphoric and isocamphoric acid are corrected. The monomethyl esters of racemic isocamphoric acid are described for the first time. NMR data are presented for all of the methyl esters of racemic camphoric and isocamphoric acid. A GLC procedure for the separation of a mixture of camphorates and isocamphorates and improved method for the partial conversion of dimethyl camphorate to dimethyl isocamphorate are given.

IT is generally believed that when *d*-camphoric acid, (+)-1, is esterified by methanol in the presence of sulfuric acid, the monomethyl ester (m.p. 76° C.), α-methyl hydrogen *d*-camphorate, (+)-2, is obtained along with the dimethyl *d*-camphorate, (+)-3. Saponification of (+)-3 with a limited quantity of base yields the monomethyl ester (m.p. 87° C.), β-methyl hydrogen *d*-camphorate, (+)-4. Similarly, it is generally believed that when *l*-isocamphoric acid, (−)-5, is esterified, the monomethyl ester (m.p. 90° C.), α-methyl hydrogen *l*-isocamphorate, (−)-6, is obtained along with the dimethyl *l*-isocamphorate, (−)-7. Partial saponification of (−)-7 yields the monomethyl ester (oil), β-methyl hydrogen *l*-isocamphorate, (−)-8.

In 1932, Quadrat-I-Khuda (*8*) claimed that the monomethyl esters melting at 76° and 87° C., respectively, were stereoisomers rather than structural isomers. Specifically, he stated that both were β-methyl esters and that the higher melting one should be shown as the epimeric isocamphorate, 8. Qudrat-I-Khuda was aware of the dextro optical rotation of both esters. No reference was made

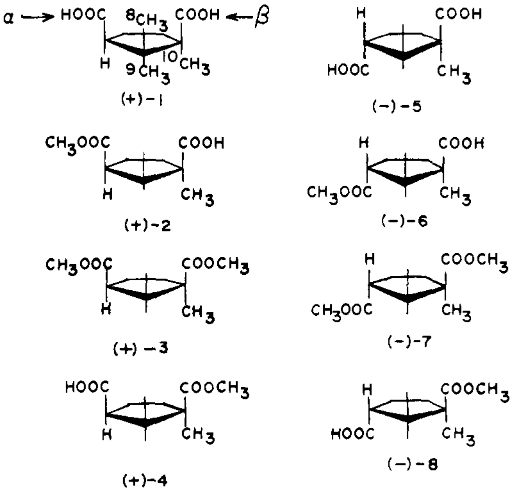

Figure 1. Configurational formulas