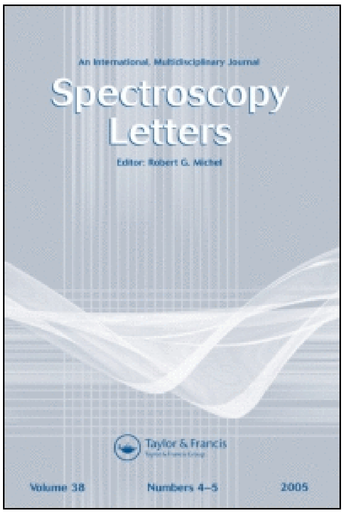

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Vibrational Spectra of 2,6-Diphenyl Pyridine, 2,2':6',2''-Terpyridine and Meta-terphenyl

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VIBRATIONAL SPECTRA OF 2,6-DIPHENYL PYRIDINE, 2,2':6',2"-TERPYRIDINE AND META-TERPHENYL

Keywords: IR, Raman, Vibrational Assignment, Splitting.

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ABSTRACT

The Raman and infrared spectra of 2,6- diphenyl pyridine, m-terphenyl and 2,2':6',2"-terpyridine have been analysed as metadisubstituted benzene or pyridine molecules. Complete vibrational assignment shows that some modes in the case of internal vibrations of substituents appear in pairs. The splitting of these modes have been attributed to the in- and out-of-phase motions arising out of interaction between phenyl or pyridine rings, as the case may be. In the case of meta terphenyl and terpyridine, two probable cases of Fermi resonance have been observed.

INTRODUCTION

Vibrational assignment of substituted pyridines have been studied by many workers [1-11] and much of these have been tabulated by Innes et al [12]. Other than 2,2'-bipyridine [13-15] most of the reported work

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are on pyridine with small substitutional groups. In a recent study [16] on the photophysics of 2,6-diphenyl pyridine it was concluded that the π-electron clouds of the side phenyl rings are bridged by the n-electron cloud. It was felt that a complete analysis of vibrational spectra of this compound would throw some light regarding the vibrational coupling between the rings. The present paper reports the analysis of Raman and infrared spectra of 2,6-diphenyl pyridine (DPP) and two similar 2,6-substituted compounds : m-terphenyl (MTP) and 2,2':6',2"-terpyridine (TP).

EXPERIMENTAL

The samples of DPP, TP and MTP were obtained from Aldrich Chemical Co., Inc. .DPP was sublimated several times under reduced pressure before use. MTP and TP were recrystallised from petroleum ether and ether in order to get pure samples. The melting point for all the molecules were checked. The ir spectra were recorded using a Perkin-Elmer model 783 IR Spectrophotometer in KBr pellets. The Raman spectra in different phases were taken with a SPEX Ramalog Spectrophotometer or a SPEX double beam monochromator model 1403 using 514.5 nm radiation from a Spectraphysics argon ion laser of 300 mw laser power. The polarization spectra were taken in CCl_4 solution or in molten state of the samples in a home designed cell. Spex Datamate 1B was used for monochromator control, data acquisition and analysis. Slit width of the source was kept around 400 micron. The spectral resolution for the IR and Raman measurements were 2 cm^{-1} and 1 cm^{-1} respectively.

RESULTS AND DISCUSSIONS

As the molecular structure of the molecules could not be found in the literature, it is very difficult to do any significant normal modes calculation. For empirical vibrational assignment, all the 2,6-substituted compounds (the central ring) may be treated as (XC_5H_3NX) for DPP, (YC_5H_3NY) for TP and (XC_6H_4X) for MTP, where X stands for the phenyl (C_6H_5) and Y stands for the pyridyl (C_5H_4N) group respectively. Considering X and Y as point masses, the 27 normal modes of DPP and TP may be [9] classified as $10a_1 + 3a_2 + 5b_1 + 9b_2$ and for MTP the 30 ring vibrations may be [9] shown as $11a_1 + 3a_2 + 6b_1 + 10b_2$, assuming all the molecules to have C_{2v} symmetry. The ring vibrations of the substituents X and Y (or the side rings) are considered separately as similar to mono-substituted benzenes [17] and 2-substituted pyridines [2,18] respectively. First we will discuss the central ring vibrations of DPP, TP and MTP frequency-range-wise, correlating the observed data of the molecules with the appropriate normal modes (Table 1). The vibrations of the side rings (substituents) will be presented subsequently in a similar fashion (Table 2).

Assignment of ring vibrations of DPP, TP and MTP.

In assigning different ring vibrations, the literature dealing with 2,6-substituted pyridines [4,8,9,11,19] and also mono and di-substituted benzenes [16,20,21] and related molecules [22-26] have generally been consulted. The Raman polarization data helped in identifying the a_1 species of vibrations.

Frequency range (3100 - 1500 cm^{-1})

The two C-H stretching vibrations falling in a_1 species for each of DPP and TP could be assigned at ν_1

TABLE 1. Assignment of fundamental vibrations of DPP, TP and MTP

Sym. Sp.	Freq. Assignment	Observed frequencies $(cm^{-1})^{**}$						Vibrational Modes
		DPP		TP		MTP		
		IR	Raman	IR	Raman	IR	Raman	
a_1	ν_1	3060 m	3060 m,p	3060 w	3063 w	3065 w	3063 s,p	ν(CH)
	ν_2	3044 m	3040 w	3050 w	3051 w,p	3030 m	3040 w,sh	ν(CH)
	ν_3	-	-	-	-	3030* m	3040* w,sh	ν(CH)
	ν_4	1590 vs	1597 vs,p	1602 w	1596 s,p	1585 vs	1600 vs,p	ν(CC)
				-	1482 m	-	-	Fermi Resonance
	ν_5	1489 m	1496 m,p	1470 m	1472 m,p	1462 vs	1461 m	ν(CC,CN) or ν(CC)
	ν_6	1312 m	1311 vs,p	1260 s	1252 m,p	1254 m	1248 m	X sens.
	ν_7	1100 m	1096 w,p	1098 s	1105 w	1096 m	1105 w,dp	β(CH)
	ν_8	999 w	997 vs,p	985 vs	996 vs,p	1008 m	1006 vs,p	Ring
	ν_9	700 vs	703 s,p	733 s	727 m,p	710 s	714 s,p	X sens.
	ν_{10}	612 m	610 w	601 m	596 vw	523 m,sh	525 w	X sens.
	ν_{11}	-	287 m,p	-	285 wb	-	279 s,p	X sens.
b_2	ν_{12}	3030 m	-	3020 m	3012 vw	3050 w	3050 m,sh	ν(CH)
	ν_{13}	1562 vs	1566 s,dp	1572 vs	1576 vs,p	-	1610 vs	ν(CC)

	ν_{14}	1450 vs	1454 vw,dp	1412 vs	1413 vw	1485 s	-	ν(CC,CN) or ν(CC)
	ν_{15}	1168 m	1172 w	1148 m,sh	1158 wb	1310 m	1312 vs,p	β(CH)
	ν_{16}	1240 w	1239 m,dp	1232 w	1228 m,dp	1272 s	1262 vw	Kekule
	ν_{17}	-	-	-	-	1164 s	1165 m	β(CH)
	ν_{18}	1155 m	1157 m,dp	1142 m	1158^{*} wb	1158 s	1155 m,sh	X sens.
	ν_{19}	821 s	825 m,dp	832 m	838 m	409 w	416 m	X sens.
	ν_{20}	-	-	-	-	836 vs	-	X sens.
	ν_{21}	522 m	520 w	520 w	529 wb	-	-	α(CCC)
	ν_{22}	-	-	-	-	519 s	-	X sens.
	ν_{23}	-	441 vvw	420 m	-	-	-	X sens.
a_2	ν_{24}	972 m	979 vvw	920 m	-	916 m	928 vw	γ(CH)
	ν_{25}	-	532 w	509 m	-	523^{*} m,sh	525^{*} w	ϕ(CC)
	ν_{26}	-	260 w	-	273 vw	-	248 w	X sens.
b_1	ν_{27}	925 m	-	891 w	-	972 m	978 w,dp	γ(CH)
		-	-	-	-	890 s	-	Fermi Resonance
	ν_{28}	-	-	-	-	885 s	-	γ(CH)
	ν_{29}	778 m	779 w,dp	768 s,sh	-	762 s	772 m	γ(CH)

contd. on next page

continuation of table 1.

ν_{30}	740 vs	-	740 s	-	690 vs	-	ϕ(CC)
ν_{31}	418 w	411 m,dp	405 m	404 w	445 s	451 w	ϕ(CC)
ν_{32}	-	234 m	-	251 w	-	-	X sens.
	-	166 m	-	168 m	-	166 m	inter-ring sciss. mode
	-	116 m	-	106 m	-	99 s	inter-ring out of plane sciss. mode
	-	85 m	-	85 m,sh	-	76 s	torsion

** symbols: s,strong; m,medium; w,weak; v,very; b,broad; sh,shoulder; p,polarized; dp,depolarized.

* frequency used more than once.

TABLE 2. Assignment of the vibrational frequencies of the substituent of DPP, TP and MTP

Sym. Sp.	Freq. Assignment	Observed frequencies (cm^{-1})**						Vibrational Modes
		DPP		TP		MTP		
		IR	Raman	IR	Raman	IR	Raman	
a'	ν_1	-	3081 w	3060* w	3063* w	-	-	ν(CH)
	ν_2	-	3081* w	3060* w	3063* w	-	-	ν(CH)
	ν_3	3060* m	3060* m,p	3050* w	3051* w,p	3065* w	3063* s,p	ν(CH)
	ν_4	3044* m	3040* w	-	-	3050* w	3050* m,sh	ν(CH)
	ν_5	3044* m	3040* w	3050* w	3051* w,p	-	3046 w,sh	ν(CH)
	ν_6	1590* vs	1597* vs,p	1572* vs	1576* vs,p	1585* vs	1600* vs,p	ν(CC)
	ν_7	1570 vs	1579 s	1550 vs	1564 m,sh	1565 m,sh 1558 vs	1571 m,p -	ν(CC)
	ν_8	1489* m	1496* m,p	1460 s	1458 m,p	1495 m,sh	1490 m	ν(CC,CN) or ν(CC)
	ν_9	1435 vs	1440 vw,sh	1445 s	1443 m,p	1472 vs	1475 vw	ν(CC,CN) or ν(CC)

contd. on next page

continuation of table 2

ν_{10}	1268 m	1266 m,dp	1358 w	-	1330 s	-	ν(CC,CN) or ν(CC)
ν_{11}	-	-	-	1324 vs,p	-	-	X sens.
ν_{12}	1256 m	-	1260* s	1252* m,p	1310* m	1312* vs,p	β(CH)
ν_{13}	1186 m	1181 m,p	-	-	-	1226 wb	X sens.
ν_{14}	1168* m	1172* w	1142* m	1158* wb	1185 s 1180 s	1190 m	β(CH)
ν_{15}	1155 m	1157 m,dp	-	-	1158* s	1155* m,sh	β(CH)
ν_{16}	1073 s	1080 vw	1075 s	1075 vw	1072 vs	-	β(CH)
ν_{17}	1027 m	-	1032 vs	1046 m,p	1040 s 1022 vs	1048 m,p 1035 w	β(CN) or β(CH)
ν_{18}	1018 m 988 m	1019 s,p 980 s,p	990 m	996* vs,p	1000 s	996 w	Ring
ν_{19}	830 m	840 vw,p	811 m	806 w	762* s	772* m	X sens.
ν_{20}	630 s	628 m,dp	655 m	658 vw	622 m	631 m	α(CCC)
ν_{21}	505 w	-	630 m 621 m	625 wb,p	460 s	453 w	X sens.
ν_{22}	382 vw	380 m,dp	383 m	388 vw	-	340 w	X sens.

a"	ν_{23}	972* m	979* vvw	970 m,sh	-	982 s	978* w,dp	γ(CH)
	ν_{24}	972* m	979* vvw	960 m	-	972* m	978* w,dp	γ(CH)
	ν_{25}	925* m	-	-	-	908 m	900 w	γ(CH)
	ν_{26}	850 vw	851 m	891* w	-	848 m	851 m	γ(CH)
	ν_{27}	755 vs	-	758 vs	-	745 vs	-	γ(CH)
	ν_{28}	699 vs	699 m,sh	733* s	727* m,p	699 vs	-	ϕ(CC)
	ν_{29}	522* m	520* w	-	-	610 vs	617 m	X sens.
	ν_{30}	418* w	411* m,dp	405* m	404* w	409* w	416* m	ϕ(CC)
	ν_{31}	-	166* m	-	228 m	-	166* m	X sens.

** symbols: s,strong; m,medium; w,weak; v,very; b,broad; sh,shoulder; p,polarized; dp,depolarized.

* frequency used more than once.

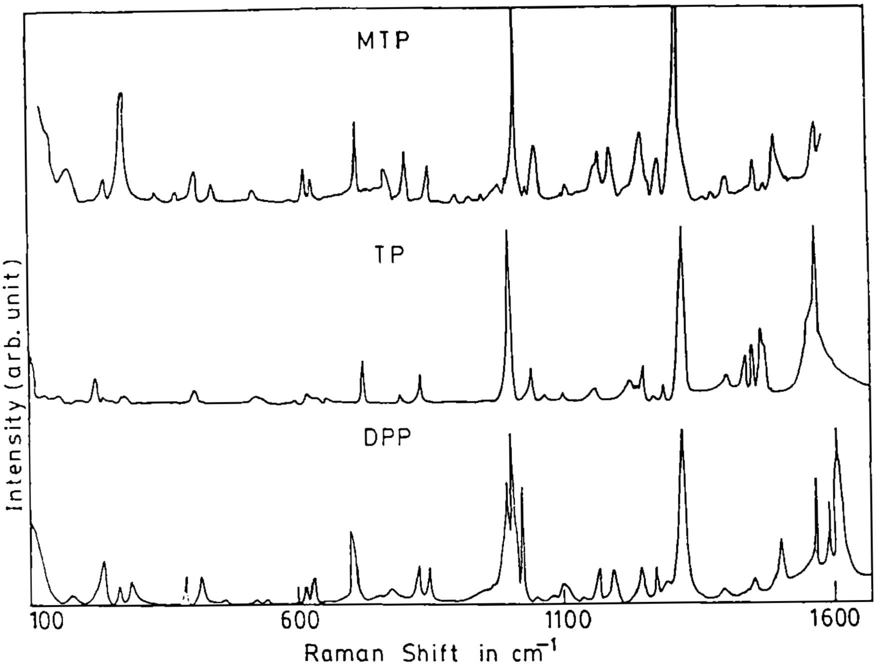

Fig.1. Raman spectra of DPP, TP and MTP in molten/solution phase.

and v_2 . But in the case of MTP, all the three in the a_1 species have been assigned taking into consideration of double assignment of 3040 cm^{-1} for v_2 and v_3. The remaining C-H stretching for all the molecules could be observed in v_{12} (Table 1). One component of the two C-C stretching vibrations, derived from e_{2g} mode of benzene was assigned to the polarized Raman lines at 1597, 1596 and 1600 cm^{-1} for DPP, TP and MTP respectively. The other component could be observed at 1566, 1576 and 1610 cm^{-1} (v_{14}, Table 1) for the said molecules respectively.

Frequency range (1500 - 200 cm^{-1})

The benzene like mode 19 [27] has partly stretching and partly bending character and according to Kovner [28], the mode is highly ir active. For DPP and MTP the first component of this mode were assigned to 1489 and 1462 cm^{-1} respectively and the other component of mode 19 could be assigned at 1450, 1412 and 1485 cm^{-1} in the case of DPP, TP and MTP. In assigning mode 19A for TP we observed two bands in Raman spectrum. We propose that the Raman band at 1482 cm^{-1} for TP may have appeared due to the interaction between $\mathbf{v_5}$ and the second harmonic of $\mathbf{v_9}$ of central pyridyl ring as Fermi Resonance. DiLella [11] made an extensive study on the assignment of deuterium substitution on pyridine at different places. They found that the 2,6-substitution on pyridine lowers the frequency of the Kekule mode 14 [27] to a large extent (around 110 cm^{-1}). In DPP and TP the Kekule mode could be ascertained at 1239 and 1228 cm^{-1} respectively, both being depolarized bands. Difficulties in assigning the Kekule mode for meta-disubstituted benzene is due to the varied opinion of different workers. Varsanyi [29] has set a frequency range 1300-1350 cm^{-1}, but we feel that in our case the band corresponding to 1272 cm^{-1} in ir should represent the Kekule mode, considering the influence of neighbouring rings. The ring breathing and the trigonal mode for all the molecules lie in the region 985 - 1008 cm^{-1}($\mathbf{v_8}$) and 700-733 cm^{-1} ($\mathbf{v_9}$) and they were identified on the basis of polarization.

The out-of-plane vibration of the unsubstituted hydrogen atom of the ring falls in the region 900 - 700 cm^{-1} and the principal factor for determining such vibrations is the number of free hydrogen atoms which are adjacent to one another [30]. 2,6-substituted pyridine should be similar to 1,2,3-trisubstituted benzenes in this regard and the assignment have been made keeping this in mind. Normally, pyridine has three a_2 modes which are infrared active, and in the case of DPP they have been assigned from Raman bands at 979, 532 and 260 cm^{-1} whereas in TP we could observe only one at 273 cm^{-1} from Raman. Strangely, we could observe two medium intensity ir bands at 920 and 509 cm^{-1} for TP in the form of γ(CH) and ϕ(CC) and one at 972 cm^{-1} for DPP which seems that they are not pyridyl mode truely. Probably the orientation of large ring substituent has an influence in that. As far as out-of-plane vibrations of MTP are concerned, the strong ir bands at 885 and 762 cm^{-1}, and medium intensity ir bands at 916 and 972 cm^{-1} have been assigned to out of plane CH bending vibrations. The pair of frequencies around ν_{28} may be due to Fermi resonance in which ν_{28} and the second harmonic of ν_{31} seem to be involved. The ring deformation vibrations are readily assigned to ν_{30} and ν_{31}.

The inter-ring scissoring mode, out-of-plane scissoring mode and a low frequency torsional mode have been assigned to 166, 116 and 85 cm^{-1} for DPP; 168, 106 and 85 cm^{-1} for TP; and 166, 99 and 76 cm^{-1} for MTP respectively, on the basis of biphenyl [31-37] and bipyridine [12].

Assignment of fundamental vibrations of side ring of DPP, TP and MTP

While considering the vibrations of the side ring, the substituents in DPP and MTP may be thought of as monosubstituted benzenes and at most the molecule may have C_s symmetry [17]. So the thirty vibrations associated with the ring, comprise of 21a'+9a" modes. Considerable guidance in making the assignments comes from a comparison with related molecules [17,29,33,38].

In the case of TP, the substituent may well be considered as meta-substituted pyridine [2,18], taking 2,2'-bipyridine as point mass. The 27 ring vibrations under C_s symmetry may be classified as 19a' and 8a" vibrations and the assignment has been made on that basis. In Table 2 we propose the assignment of the molecules correlating the data with appropriate normal modes.

In the case of DPP and TP all the CH stretching vibrations could be assigned to appropriate frequencies, but in MTP we could not observe the frequencies for mode 2 and 20b. For DPP, near the frequency of ring breathing vibration we could observe a pair of frequencies 1019 and 980 cm^{-1}, both of nearly the same intensity and polarization in molten phase. This may be attributed to the in- and out-of-plane motion arising out of the interaction between the phenyl ring and the pyridine ring like biphenyl [22] and triphenyl methyl compounds [23-25] giving rise to the pair of vibrations. We have been able to observe the splitting of one mode but actually in the event of interaction, more modes should be involved and the amount of splitting would depend on possible steric interactions and the extent of kinetic steric coupling between the rings. For a substituent sensitive (ν_{21}) mode, in the case of TP, we find pair of frequencies which may arise due to the interaction of pyridine rings. In ir spectrum, the 621 and 630 cm^{-1} (ν_{21}) bands were sharp with approximately the same intensity but the corresponding band in Raman spectrum was weak, broad and the half width was about 12 cm^{-1} . We believe that same kind of splitting in Raman spectrum could not be observed for not resolving the 625 cm^{-1} band. One C-C stretching and two C-H bending modes (ν_7, ν_{14} and ν_{17}) seemed to be involved in splitting for MTP. The ring breathing vibration could be observed for TP and MTP at 990 and 1000 cm^{-1} (ν_{18}), while the umbrella like mode for DPP, TP and MTP could be assigned to 830, 811 and 762 cm^{-1} respectively. A depolarized Raman band at 1266 cm^{-1} seemed to be the right candidate for the Kekule mode in the case of DPP. The ir absorption frequencies at 1358 and 1330 cm^{-1} in the case of TP and MTP have been associated to the Kekule mode. Regarding the vibrations of 19a and 19b, for mono-substituted benzenes, Fuson et al [39] established unequivocally that the former has a higher frequency. For DPP and MTP these components have been assigned to ν_8 and ν_9. In a previous vibrational study, Stephenson et al [40] observed that the frequency interval for mode 6a in the case of monosubstituted benzene derivatives carrying polyatomic substances should be 250 - 525 cm^{-1} . In the case of DPP and MTP this component has been assigned to ν_{21} and the other component to ν_{20} accordingly.

CONCLUSION

From the above discussion it is found that the vibrational coupling between the rings through C-C bonds has perceptible effect on a few planar modes - resulting in splitting. Most of the other normal modes seemed to be very slightly or not influenced.

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