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Nitrogen−Phosphorus Multiple Bond Vibrational Assignments in the Infrared and Raman

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Introduction

Compounds containing NP bonds are perhaps the most extensively studied inorganic series, and a vast body of structural and spectroscopic data is available.[2] Nevertheless, assignment of NP stretching bands is complicated by the wide range of observed frequencies, the diversity of bonding characteristics for phosphorus, the sensitivity of the stretching frequency to the electronegativity of substituents, and variations in force constants.[3]

Recent syntheses and isolation of numerous derivatives of substituted NP provide an opportunity for systematic spectroscopic study. Most appropriate are the series of Mes*NP derivatives containing the sterically imposing 2,4,6-tri-*tert*-butylphenyl (Mes*) substituent, many of which have been crystallographically characterized. The NP bond lengths in these compounds are unusually short, and the bond angles at the nitrogen centers (C−N−P) are large {Mes*NPCl, 1.495(4) Å, 154.8(4)°,[4] and 1.509(2) Å, 146.4(2)°;[5] Mes*NPBr, 1.498(4)Å, 159.5(4)°,[5] and 1.499(6) Å, 161.0(6)°;[6] Mes*NPI, 1.480(3) Å, 172.5(3)°;[6] Mes*$NPCl_3$, 1.462(4) Å, 160.9(3)°;[7] Mes*$NPBr_3$, 1.46(1) Å, 160.1(3)°;[7] [Mes*NP-benzene][$GaCl_4$], 1.484(7) Å, 175.5(7)°;[8] [Mes*NP][SO_3CF_3], 1.467(4) Å, 176.4(3)°[9] }. These features imply a substantial degree of NP π-bonding, which is supported by solid state NMR features for [Mes*NP][$AlCl_4$],[10] and bodes well for a reliable group frequency distinction and comparison. Therefore, we have obtained FT-IR and FT-Raman spectra for each of the compounds listed above and have prepared[11] three samples with ^{15}N isotopic labeling. The data allow for reliable assignment of NP stretching frequencies and show a correlation between Raman intensity and the bond angle at nitrogen.

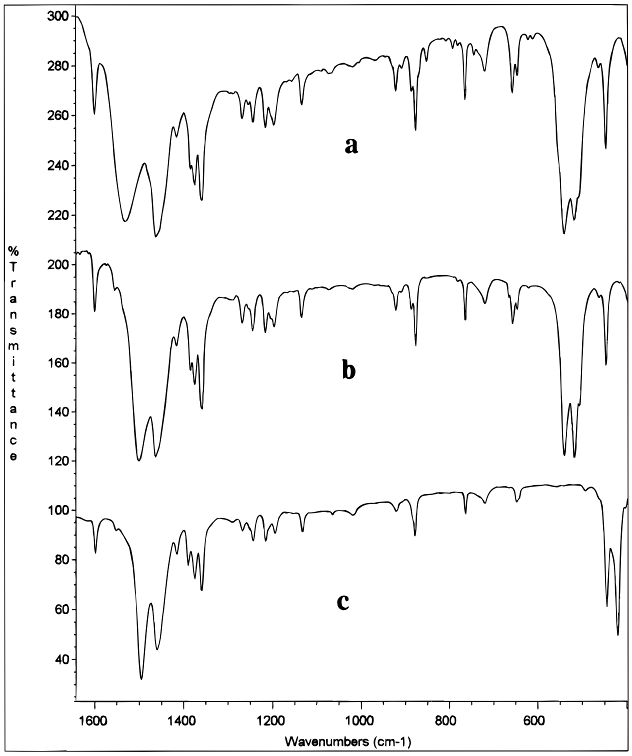

Figure 1. IR spectra (1620−400 cm^{-1}) of (a) Mes*$NPCl_3$, (b) Mes*$^{15}NPCl_3$, and (c) Mes*$NPBr_3$.

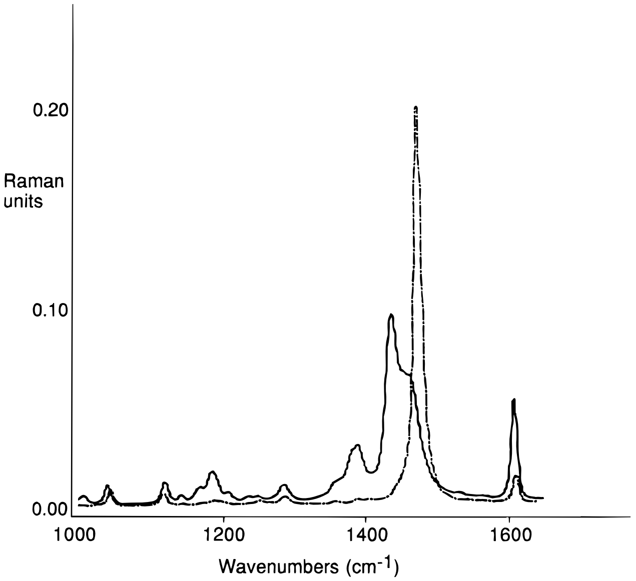

Figure 2. Raman spectra (1000−1600 cm^{-1}) of Mes*NPCl and Mes*NPI (dotted).

Experimental Procedures

The following compounds were prepared according to literature procedures: Mes*NPCl,[12] Mes*NPBr,[5,6] Mes*NPI,[6] Mes*$NPCl_3$,[7] Mes*$NPBr_3$,[7] [Mes*NP-benzene][$GaCl_4$],[12] and [Mes*NP][SO_3CF_3].[9] Infrared spectra were recorded as Nujol mulls and as dry powders between CsI plates (Table 1) on a Nicolet 510P spectrometer. Raman

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[2] See, for example: Corbridge, D. E. C. *Phosphorus: An outline of its Chemistry, Biochemistry and Technology,* Elsevier: New York, 1990. Allcock, H. R. *Phosphorus-Nitrogen Compounds*, Academic Press: New York, 1972.

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[10] See, for example: Curtis, R. D.; Schriver, M. J.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1991**, *113*, 1493−1498.

[11] Mes*NH_2 was prepared from $H^{15}NO_3$ as previously described: Burgers, J.; Hoefnagel, M. A.; Verkade, P. E.; Visser, H.; Webster, B. M. *Recl. Trav. Chim. Pays-Bas* **1958**, *77*, 491−523.

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Table 1. Infrared Data (Nujol Mulls between CsI Plates; 1620−400 cm^{-1}) for RNP Derivatives (R = Mes*) with the NP Assignment in Bold

RNH_2	RNPCl	$R^{15}NPCl$	RNPBr	RNPI	$RNPCl_3$	$R^{15}NPCl_3$	$RNPBr_3$	$[RNP][GaCl_4]$	$[R^{15}NP][GaCl_4]$	$[RNP][SO_3CF_3]$
1618m										
1599s	1598s	1598s	1598s	1603m	1603m	1602m	1601m	1595s	1594s	1595s
	1437vs	**1428vs**	**1462vs**	**1464vs**	**1534vs**	**1504vs**	**1498vs**	**1494s**	**1466sh**	**1463s**
1436vs					1418m	1419m	1418m	1419m	1420m	
1396m	1390s	1392s	1392s	1373s	1387m	1388m	1392m	1398m	1398m	1395m
1362s	1361s	1363vs	1363vs	1362vs	1361s	1361s	1362s	1366vs	1366vs	1362vs
								1341sh	1341sh	1295sh
1288m	1270m	1269m	1269m		1270m	1271m	1270m	1267m	1267m	1261m
1266m	1245s	1247s	1244m	1245m	1247m	1247m	1247m	1244m	1242m	
1238s	1219m	1218m	1218m	1218m	1219m	1218m	1218m	1219m	1218m	
1194m	1198m	1200m	1198m		1199m	1199m	1197m	1206m	1204m	1196s
	1135m	1135m	1133m	1133m	1136m	1137m	1135m	1134m	1131m	1135m
								1067m	1068m	
								1018mbr	1024m	
919m	926m	925m	925m		924m	924m	924m	928m	928m	
								909m	908m	912m
881s	889m	889m	881m	882m	888m	890m	881m	887s	886s	884s
	879s	878s			879m	879m				
770m	762s	762s	760m	770m	767m	767m	766m	764m	762m	763m
					660m	659m	650m	700s	699s	
643m	642m				649m	649m		675m	675m	630s
					543vs	542vs				583m
					520vs	520vs				530m
					509s	509s				
	410s	410s		410s	449s	449s	447s			
							422vs	403sbr	422sbr	403sbr

Table 2. Raman Data (Powders; 1600−400 cm^{-1}) for RNP Derivatives (R = Mes*) with NP Assignment in Bold

RNH_2	RNPCl	$R^{15}NPCl$	RNPBr	RNPI	$RNPCl_3$	$RNPBr_3$	$[RNP][GaCl_4]$	$[R^{15}NP][GaCl_4]$	$[RNP][SO_3CF_3]$
1615s									
1602s	1598s	1599s	1598s	1600m	1600m	1601m	1598m	1595m	1598m
	1438vs	**1427vs**	**1471vs**	**1473vs**	**1538vs**	**1499vs**	**1494vs**	**1453vs**	**1474vs**
1450s					1449m	1447m	1405m	1404m	
	1391m	1392m					1395m	1394m	1393m
		1374m					1366m	1364m	
		1356m							
1289m	1292m		1292m	1293m	1293m	1294m	1292m	1291m	1291m
							1267m	1270m	
1200m	1199m	1200m	1199m	1199m	1199m	1198m			1203m
1145m	1136m	1136m	1136m	1133m	1138m	1136m	1134m	1132m	1133m
	1060m	1058m	1060m	1064m	1076m	1067m	1067m	1068m	1069m
933m		1003m					991m	987m	
922m	926m	926m	926m		931m	927m			924m
826s	822s	823s	823m	822m	824m	823m	820m	820m	821m
566m	568m	566m	566m	565m	566m	562m	564m		562m
					450m	465m			
						429m			

spectra were obtained on powdered crystalline samples in Pyrex tubes (Table 2) on a Bruker RFS100 spectrometer. Calculations were performed using the Gaussian 94[13] package of programs.

Results and Discussion

Infrared and Raman data for a series of Mes*NP derivatives are presented in Tables 1 and 2, respectively. Spectral characteristics observed for Mes*NH_2 (presented in tables for comparison) in the 1620−400 cm^{-1} region are also evident in all of the spectra for Mes*NP-containing compounds. Most notable in the IR spectra of Mes*$NPCl_3$, Mes*$NPBr_3$, and Mes*$^{15}NPCl_3$ (compared in Figure 1) is an intense and broad band in the 1500 cm^{-1} region which shifts dramatically with isotopic labeling and halide substitution (1534 cm^{-1}, 1498 cm^{-1}, and 1504 cm^{-1}, respectively). Other shifts throughout the spectra are no more than 2 cm^{-1}. These bands correlate with the most intense band in the Raman spectra of Mes*$NPCl_3$ (1538 cm^{-1}) and Mes*$NPBr_3$ (1499 cm^{-1}).

Assignment of such high-wavenumber bands to the NP stretch is consistent with the structural features observed for these compounds and the proposed triple bond models.[7,10] Further support is provided by Glaser's theoretical studies on the diatomic molecule ^{14}NP,[14] which give a vibrational frequency of 1588.8 cm^{-1}. From the reduced masses of ^{14}N and ^{15}N we calculate a value of 1552 cm^{-1} for ^{15}NP and have confirmed this isotopic shift of 37 cm^{-1} using *ab initio* frequency calculations at the HF/6-31G* level. Vibrational frequencies calculated at this level of theory often exceed experimental frequencies.[15] Nevertheless, the calculated frequencies for the diatomic compound are surprisingly similar to the observed

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Table 3. C−N−P Bond Angles and Relative Raman Intensities (ref 16) of 1450−1550 cm^{-1} Band (NP) for RNP Derivatives (R = Mes*)

	RNPCl	RNPBr	$RNPCl_3$	$RNPBr_3$	RNPI	$[RNP][SO_3CF_3]$	$[RNP][GaCl_4]$
C−N−P (deg)	154.8(4), 146.4(2)	161.0(6)	160.9(3), 159.5(4)	160.1(3)	172.5(3)	176.4(3)	175.5(7), 177.0(3)
I_{rel}	2	3	7	8	18	16	19

values for $Mes*NPCl_3$ (1534 cm^{-1}), $Mes*^{15}NPCl_3$ (1504 cm^{-1}), and $Mes*NPBr_3$ (1498 cm^{-1}).

The IR spectra for Mes*NPCl and $Mes*^{15}NPCl$ are very similar to that for $Mes*NH_2$, and assignments are complicated by stretches for the Mes* substituent. Unequivocal assignment of the NP stretch is also precluded by masking bands of Mes* in the IR for $[Mes*NP][GaCl_4]$ (1494 cm^{-1}) and $[Mes*^{15}NP][GaCl_4]$ (1466 cm^{-1}), although these bands exhibit a substantial isotopic shift and occur to higher wavenumber than those observed for Mes*NPCl (1437 cm^{-1}) and $Mes*^{15}NPCl$ (1428 cm^{-1}).

An auxiliary feature is apparent in the Raman spectra for these compounds, which validates the NP stretch assignment. The representative Raman spectra of Mes*NPCl and Mes*NPI shown in Figure 2 illustrate a dramatic difference in the intensity of the band in the 1450−1500 cm^{-1} region, and Table 3 lists compounds according to an increasing C−N−P bond angle and shows that the relative intensity ($I_{rel} = I_{NP}/I_{1600}$)[16] of the assigned NP stretch increases with increasing angle at the nitrogen center. We interpret this correlation in terms of a larger angle at the nitrogen center, allowing for a higher degree of conjugation from NP to the Mes* substituent and therefore a greater polarizability.

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(16) Listed as an intensity ratio with respect to the intensity of the 1600 cm^{-1} band corresponding to the Mes* substituent, as illustrated in Figure 2.