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Vibrational Frequencies, Assignments, and Normal-Coordinate Analysis for the Methyl Isocyanide–Borane Complex

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The infrared (4000–200 cm^{-1}) and Raman (4000–100 cm^{-1}) spectra of $CH_3NC\cdot{}^{10}BH_3$, its deuterated species, and $CH_3NC\cdot BH_3$ have been recorded for the solid state. Fundamental vibrations, except the internal torsional mode, have been assigned on the basis of C_{3v} symmetry. The $N\equiv C$ stretching frequency was found to increase ca. 150 cm^{-1} upon complex formation. Normal-coordinate analysis has been carried out in the staggered configuration. The $N\equiv C$ force constant was found to increase ca. 10% upon complex formation in agreement with the strengthening of the $N\equiv C$ bond indicated by the structural data, which is the main cause of the upward frequency shift of the $N\equiv C$ stretch. The C—B force constant was found to have a value of 2.90 mdyn/Å, which is larger than the N—B constant (2.45 mdyn/Å) in $CH_3CN\cdot BH_3$, suggesting that methyl isocyanide is a stronger base than methyl cyanide.

Introduction

Many donor–acceptor complexes of methyl cyanide with metal and nonmetal acceptors have been examined in various spectroscopic studies.[1] It was already known long before Werner's theory on the coordination complex that isocyanides, isomers of cyanides, form adducts with metal compounds. Now a number of isocyanide complexes of zerovalent metals and metal ions are known.[2] Although this implies that isocyanides act as donors, isocyanide complexes with nonmetal acceptors are somehow little known.

Recently methyl isocyanide–borane has been prepared by mixing methyl isocyanide and diborane in the gas phase at a low pressure of 1–2 torr.[3] The stability of the adduct is noticeable in the respect that methyl cyanide–borane completely dissociates in the gas phase.[4,5] Further, the structure of methyl isocyanide–borane has been determined by microwave spectroscopy, which has revealed that the $N\equiv C$ distance is shorter by 0.001 Å in comparison with that of the free isocyanide.[3]

X-ray structural studies for $CH_3CN\cdot BX_3$ (X = F, Cl) have shown a decrease in the $C\equiv N$ bond length.[6] Several complexes of methyl cyanide show an unusual upward shift of the $C\equiv N$ stretching frequency upon complex formation.[1,5,7,8] Normal-coordinate analyses for the complexes[5,7,8] have exhibited that the $C\equiv N$ force constant actually increases upon complex formation in accordance with the increased bond strength implied by the decrease in the $C\equiv N$ bond length and the upward shift of the $C\equiv N$ stretching frequency.

In expectation of similar vibrational features in methyl isocyanide–borane associated with the $N\equiv C$ bond shortening, the present study was planned to observe and to analyze the infrared and Raman spectra of the methyl isocyanide–borane complex.

Experimental Section

Methyl isocyanide was prepared, according to Stevens et al.,[3] in a sealed glass tube with a break-seal and a ground-glass joint. The tube was connected to a vacuum line by means of the ground joint, and after evacuation, the break-seal was opened. Methyl isocyanide was recovered from the silver complex by heating the mixture up to 140 °C and collecting the methyl isocyanide in a trap held at −196 °C. The crude product containing a small amount of hydrogen cyanide was purified by vacuum distillation. Methyl isocyanide was collected in a trap held at −95 °C (toluene slush) and HCN at −196 °C. The purity was checked by the infrared spectrum. Methyl-d_3 isocyanide was prepared in a similar manner with methyl-d_3 iodide (Merck Sharp and Dohme) instead of methyl iodide.

Table I. Description and Numbering of the Fundamental Vibrations of $CH_3NC\cdot BH_3$[a]

	A_1 Class		
ν_1	CH_3 sym str	ν_5	BH_3 sym def
ν_2	BH_3 sym str	ν_6	C–N str
ν_3	$N\equiv C$ str	ν_7	C–B str
ν_4	CH_3 sym def		
	A_2 Class		
ν_8	torsion		
	E Class		
ν_9	CH_3 deg str	ν_{13}	CH_3 rock
ν_{10}	BH_3 deg str	ν_{14}	BH_3 rock
ν_{11}	CH_3 deg def	ν_{15}	CNC def
ν_{12}	BH_3 deg def	ν_{16}	NCB def

[a] Abbreviations used: sym, symmetric; deg, degenerate; str, stretch; def, deformation.

Diborane(6) enriched in ^{10}B (94 atom % boron-10) was prepared, according to Shapiro et al.,[9] by the reduction of $^{10}BF_3\cdot O(C_2H_5)_2$ by lithium aluminum hydride or deuteride. Preparation of boron-10-enriched boron trifluoride etherate was described elsewhere.[5] Isotopically normal diborane(6) was prepared by the $LiAlH_4$ reduction of $BF_3\cdot O(C_2H_5)_2$ (81% ^{11}B–19% ^{10}B).

The infrared spectra (4000–200 cm^{-1}) were recorded at −196 °C with a Hitachi Model 345 infrared spectrophotometer, which was calibrated with standard gases.[10] The methyl isocyanide–borane adduct was prepared by condensing methyl isocyanide and diborane in a 2:1 mole ratio at −196 °C into a small glass tube with a stopcock and a ground-glass joint. After the stopcock was closed, the tube was allowed to warm naturally to room temperature. It was then opened to the vacuum line for a while to remove volatile substances. The tube was attached by means of the ground joint to a low-temperature cell. After evacuation, the sample was allowed to sublime onto a cooled CsI optical plate mounted in a copper block of a liquid-nitrogen reservoir end. The infrared spectra of the ^{10}B compounds are shown in Figure 1.

The Raman spectra (4000–100 cm^{-1}) were recorded on a JEOL JRS S-1 laser-Raman spectrophotometer equipped with an NEC GLG 5800 He–Ne laser with the sample in a capillary tube. The spectrometer was calibrated with the emission lines of neon. The adduct was prepared in a small glass tube with a side capillary in a manner similar to that employed in the infrared work. After the reaction tube was sealed off from the vacuum line, the adduct was collected by

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(1) Yarwood, J., Ed. "Spectroscopy and Structure of Molecular Complexes"; Plenum Press: London, 1973.

(2) (a) Cotton, F. A.; Zingales, F. *J. Am. Chem. Soc.* **1961**, *81*, 351. (b) Malatesta, L. *Adv. Inorg. Chem.* **1959**, *1*, 283.

(3) Stevens, J. F., Jr.; Bevan, J. W.; Curl, R. F., Jr.; Geanangel, R. A.; Grace Hu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1442.

(4) Emeleus, H. J.; Wade, K. *J. Chem. Soc.* **1960**, 2614.

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(9) Shapiro, I.; Weiss, H. G.; Schmich, M.; Skolnik, S.; Smith, G. B. L. *J. Am. Chem. Soc.* **1952**, *74*, 901.

(10) "Tables of Wavenumbers for the Calibration of Infrared Spectrometers", 2nd ed.; Pergmanon Press: Elmsford, NY, 1977.

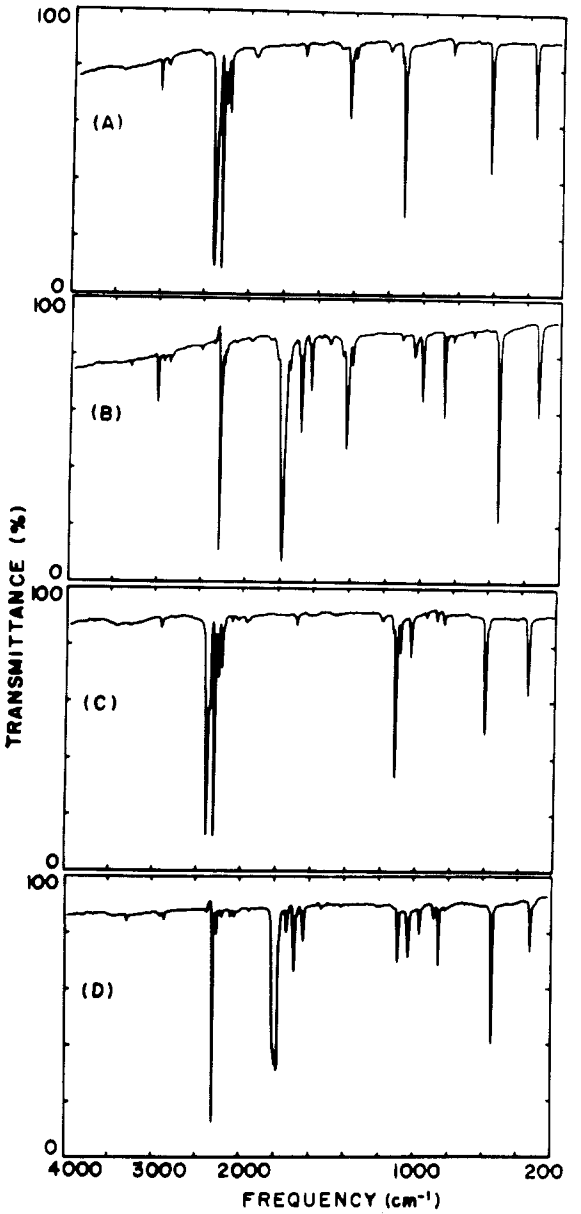

Figure 1. Infrared spectra of (A) $CH_3NC\cdot{}^{10}BH_3$, (B) $CH_3NC\cdot{}^{10}BD_3$, (C) $CD_3NC\cdot{}^{10}BH_3$ and (D) $CD_3NC\cdot{}^{10}BD_3$ recorded in the solid state at −196 °C.

sublimation into the capillary immersed in liquid nitrogen. Then the capillary was sealed off. Tiny colorless and transparent crystals grew while the capillary was stored in a refrigerator for a few days. The Raman spectra of the ^{10}B compounds are shown in Figure 2.

Vibrational Assignments

Assignments are made on the basis of C_{3v} molecular symmetry. From group-theoretical consideration, it follows that the molecule has 7 A_1, 1 A_2, and 8 E normal modes, where the A_1 and E modes are infrared and Raman active while the A_2 mode is inactive in both. The designation of the fundamentals is given in Table I.

The CH_3 and CD_3 vibrations are found in the regions of those in free methyl isocyanide and methyl-d_3 isocyanide[11,12] with small frequency shift. The methyl rocks in $CH_3NC\cdot BH_3$ and $CH_3NC\cdot{}^{10}BH_3$ are obscured in a strong band of a BH_3 deformation. The CH_3 and CD_3 rocks are too weak in intensity to be observed in the Raman spectra.

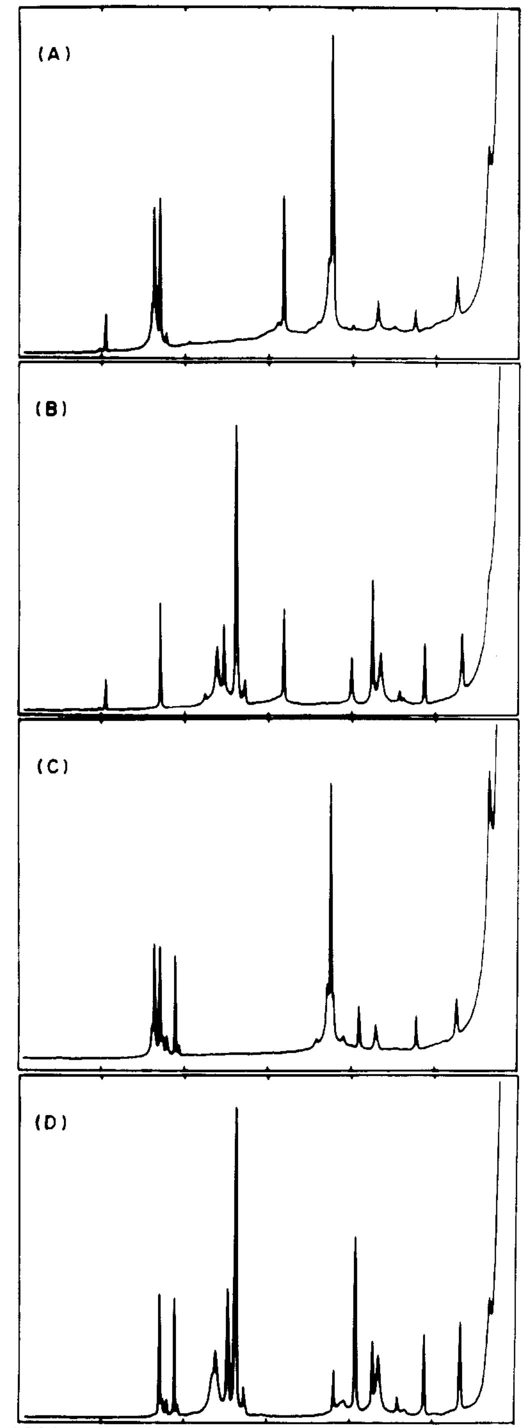

Figure 2. Raman spectra of (A) $CH_3NC\cdot{}^{10}BH_3$, (B) $CH_3NC\cdot{}^{10}BD_3$, (C) $CD_3NC\cdot{}^{10}BH_3$, and (D) $CD_3NC\cdot{}^{10}BD_3$ recorded in the solid state at ambient temperature.

A strong absorption is observed at 2312–2314 cm^{-1} in each isotopic species and assigned to the N≡C stretch, which is higher by about 150 cm^{-1} than that in free methyl isocyanide (2166 cm^{-1}).[11,12]

The degenerate $^{10}BH_3$ stretch ν_{10} is strongly observed at 2394–2396 cm^{-1} accompanying a shoulder at the low-frequency side, which is assigned to the symmetric $^{10}BH_3$ stretch ν_2. The BD_3 stretches, ν_2 and ν_{10}, are well separated. The degenerate $^{10}BD_3$ stretch ν_{10} in $CH_3NC\cdot{}^{10}BD_3$ is assigned to a strong band at 1804 cm^{-1}, and that in $CD_3NC\cdot{}^{10}BD_3$ is observed as a doublet at 1807 and 1797 cm^{-1}. The symmetric $^{10}BD_3$ stretch ν_2 is assigned to a less intense band observed at

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(11) (a) Williams, R. L. *J. Chem. Phys.* **1956**, *25*, 658. (b) Mattern, J. G.; Fletcher, W. H. *Spectrochim. Acta* **1962**, *18*, 995.

(12) Duncan, J. L.; McKean, D. C.; Mackenzie, M. W.; Pena, J. P. *J. Mol. Spectrosc.* **1979**, *76*, 55.

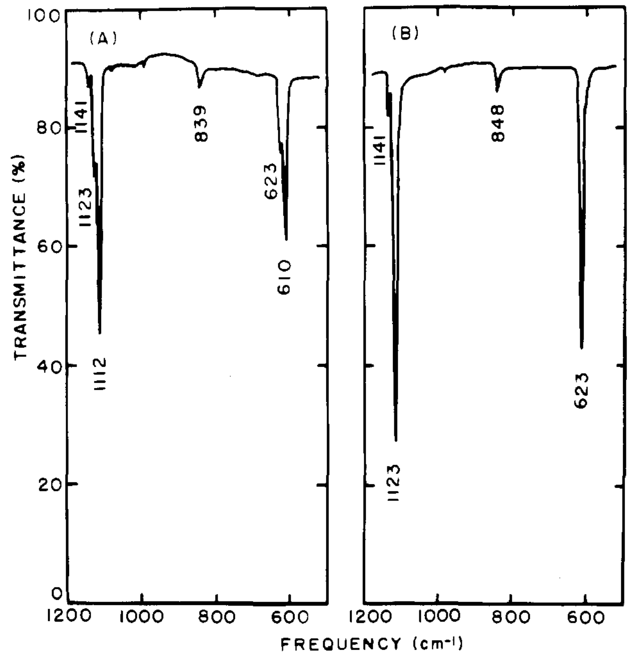

Figure 3. Infrared spectra of (A) $CH_3NC{\cdot}BH_3$ and (B) $CH_3NC{\cdot}^{10}BH_3$ in the 1200–500-cm^{-1} region recorded in the solid state at −196 °C.

1695–1698 cm^{-1}. In the Raman spectra, the relative intensities of the two BD_3 stretches ν_2 and ν_{10} are reversed: the symmetric stretch is more intense than the degenerate one.

A strong infrared band at 1123 cm^{-1} in $CH_3NC{\cdot}^{10}BH_3$ shifts to 1112 cm^{-1} in $CH_3NC{\cdot}^{11}BH_3$ (assigned in its natural isotopic abundance), while a 1141-cm^{-1} band observed in $CH_3NC{\cdot}^{10}BH_3$ shows no ^{10}B–^{11}B isotopic shift (Figure 3): therefore the 1123-cm^{-1} band is assigned to the symmetric $^{10}BH_3$ deformation ν_5 and the 1141-cm^{-1} band to the degenerate ν_{12}. In this case the symmetric deformation is more intense than the degenerate one in both the infrared and Raman spectra. Upon deuteration of the borane group these shift to around 870 cm^{-1} (880 cm^{-1} in $CH_3NC{\cdot}^{10}BD_3$ and 864 cm^{-1} in $CD_3NC{\cdot}^{10}BD_3$) and to 830 cm^{-1}, of which the higher frequency bands are more intense than the lower frequency ones. As with the BH_3 deformations, the stronger bands of high frequency are assigned to the symmetric $^{10}BD_3$ deformation ν_5 and the weaker bands of low frequency to the degenerate $^{10}BD_3$ deformation ν_{12}.

A band observed at 848 cm^{-1} in $CH_3NC{\cdot}^{10}BH_3$ exhibiting a ^{10}B–^{11}B isotopic shift (Figure 3) is assigned to the $^{10}BH_3$ rock ν_{14}, which shifts to 713 cm^{-1} upon deuteration of the borane group.

The C–N stretch ν_6 is assigned to a band observed around 1000 cm^{-1} in a variety of isotopic substitution shifting toward higher frequency upon adduct formation. This mode is weak in intensity in the infrared spectrum, contrary to that for free methyl isocyanide, whose C–N stretch mode is strong in both the infrared and Raman spectra.

A band around 600 cm^{-1} exhibiting a ^{10}B–^{11}B isotopic shift (Figure 3) is assigned to the C–B stretch, which is strongly observed in all the isotopic compounds.

Two bands are observed below 400 cm^{-1}, of which the higher frequency band is assigned to the CNC deformation and the lower frequency one to the NCB deformation.

The assignments of the fundamentals for the ^{10}B adducts are given in Tables II–V.

Infrared bands that are not attributed to fundamentals are listed in Table VI together with tenative assignments. In the spectra of the BD_3 adducts, bands not attributable to a overtone or a combination are observed in the B–H and B–D stretching regions. These will be due to BHD_2 compounds.

Table II. Observed and Calculated Frequencies (cm^{-1}) for $CH_3NC{\cdot}^{10}BH_3$ and Potential Energy Distributions[a]

	IR	Raman	calcd	PED[b]
ν_1	2948 w	2948	2947	$99S_1$
ν_2	2377 sh	2367	2374	$97S_2$
ν_3	2313 vs	2299	2312	$87S_3$, $6S_6$, $4S_7$
ν_4	1409 w	1410	1410	$95S_4$
ν_5	1123 s	1118	1124	$89S_5$, $9S_7$
ν_6	994 vw	995	996	$72S_6$, $25S_7$
ν_7	623 s	622	625	$65S_7$, $24S_6$, $10S_3$
ν_9	3014 w	3016	3016	$98S_9$
ν_{10}	2396 vs	2390	2394	$99S_{10}$
ν_{11}	1439 m	1444	1442	$87S_{11}$, $7S_{13}$
ν_{12}	1141 w	1140	1139	$95S_{12}$
ν_{13}	1126[c]		1130	$89S_{13}$, $4S_{11}$
ν_{14}	848 w	850	854	$84S_{14}$, $10S_{16}$
ν_{15}	365 s	369	367	$39S_{15}$, $40S_{16}$, $19S_{14}$
ν_{16}		180	182	$48S_{16}$, $36S_{15}$, $14S_{14}$

[a] Abbreviations used: w, weak; m, medium; s, strong; v, very. Raman intensities are not given since photomultiplier sensitivity varies in a wide range within the spectral region. [b] The potential energy distribution is defined as $PED_{ij} = 100F_{ii}L_{ij}^2/\Sigma F_{ii}L_{ij}^2$. [c] The same frequency as that of ν_{13} for $CH_3NC{\cdot}^{10}BD_3$ was assigned because this was obscured by the strong absorption of ν_5.

Table III. Observed and Calculated Frequencies (cm^{-1}) for $CH_3NC{\cdot}^{10}BD_3$ and Potential Energy Distributions[a]

	IR	Raman	calcd	PED[b]
ν_1	2646 w	2947	2947	$99S_1$
ν_2	1698 m	1693	1696	$98S_2$
ν_3	2312 vs	2300	2314	$88S_3$, $6S_6$, $4S_7$
ν_4	1409 w	1409	1410	$95S_4$
ν_5	880 m	877	880	$73S_5$, $17S_6$, $7S_7$
ν_6	1005 m	1004	1007	$52S_6$, $34S_7$, $11S_5$
ν_7	565 s	565	567	$59S_7$, $18S_6$, $11S_5$, $9S_3$
ν_9	3014 m	3017	3016	$98S_9$
ν_{10}	1804 vs	1807	1804	$98S_{10}$
ν_{11}	1438 m	1445	1442	$87S_{11}$, $7S_{13}$
ν_{12}	830 w	828	832	$98S_{12}$
ν_{13}	1126 w		1130	$92S_{13}$
ν_{14}	713 w	714	713	$68S_{14}$, $22S_{16}$
ν_{15}	336 m	338	337	$43S_{15}$, $30S_{16}$, $25S_{14}$
ν_{16}		170	168	$52S_{16}$, $26S_{15}$, $21S_{14}$

[a] See footnote *a* of Table II. [b] See footnote *b* of Table II.

Table IV. Observed and Calculated Frequencies (cm^{-1}) for $CD_3NC{\cdot}^{10}BH_3$ and Potential Energy Distributions[a]

	IR	Raman	calcd	PED[b]
ν_1	2117 w	2114	2119	$97S_1$
ν_2	2370 sh	2364	2374	$97S_2$
ν_3	2313 s	2298	2313	$85S_3$, $6S_6$, $4S_7$
ν_4	1098 m	1097	1096	$69S_4$, $27S_6$
ν_5	1124 s	1116	1124	$87S_5$, $9S_7$
ν_6	950 w	947	947	$45S_6$, $35S_7$, $17S_4$
ν_7	606 m	604	604	$60S_7$, $27S_6$, $10S_3$
ν_9	2268 m	2263	2266	$97S_9$
ν_{10}	2394 vs	2393	2394	$99S_{10}$
ν_{11}	1039 m	1044	1034	$90S_{11}$
ν_{12}	1141 w	1136	1139	$98S_{12}$
ν_{13}	892 w		892	$70S_{13}$, $15S_{14}$
ν_{14}	848 w	846	842	$62S_{14}$, $29S_{13}$
ν_{15}	357 m	360	357	$35S_{15}$, $42S_{16}$, $20S_{14}$
ν_{16}		171	172	$43S_{16}$, $41S_{15}$, $13S_{14}$

[a] See footnote *a* of Table II. [b] See footnote *b* of Table II.

Normal-Coordinate Analysis

Normal-coordinate analysis was carried out with use of the FG matrix method of Wilson[13] and a standard iterative least-squares method.[5]

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[13] Wilson, E. B., Jr.; Decius, J. C.; Cross, C. "Molecular Vibrations"; McGraw-Hill: New York, 1955.

Table V. Observed and Calculated Frequencies (cm^{-1}) for $CD_3NC\cdot{}^{10}BD_3$ and Potential Energy Distributions[a]

	IR	Raman	calcd	PED[b]
ν_1	2119 w	2114	2119	$97S_1$
ν_2	1695 m	1689	1696	$98S_2$
ν_3	2314 vs	2298	2315	$87S_3$, $6S_6$, $4S_7$
ν_4	1099 m	1109	1097	$68S_4$, $27S_6$
ν_5	864 m	861	863	$69S_5$, $23S_6$
ν_6	972 w	967	970	$19S_6$, $42S_7$, $25S_5$, $11S_4$
ν_7	533 s	549	551	$57S_7$, $21S_6$, $9S_5$, $9S_3$
ν_9	2269 w	2262	2266	$97S_9$
ν_{10}	1807 s	1806	1804	$97S_{10}$
	1797 s			
ν_{11}	1038 m	1036	1034	$90S_{11}$
ν_{12}	830 vw	825	832	$98S_{12}$
ν_{13}	893 w		883	$90S_{13}$
ν_{14}	712 vw	713	709	$68S_{14}$, $20S_{16}$
ν_{15}	329 m	329	327	$39S_{15}$, $33S_{16}$, $25S_{14}$
ν_{16}		157	159	$48S_{16}$, $31S_{15}$, $19S_{14}$

[a] See footnote *a* of Table II. [b] See footnote *b* of Table II.

Table VI. Combination and Overtone Bands (cm^{-1}) of Methyl Isocyanide-Borane(^{10}B)

$CH_3NC\cdot{}^{10}BH_3$

obsd	assigt, calcd	obsd	assigt, calcd
2930	$\nu_3 + \nu_7 = 2936$	1694	$2\nu_{14} = 1696$
2561	$\nu_{10} + \nu_{16} = 2576$, $\nu_5 + \nu_{11} =$	1498	$\nu_{12} + \nu_{15} = 1506$
	2562, $\nu_{11} + \nu_{13} = 2565$	1492	$\nu_{13} + \nu_{15} = 1491$
2530	$\nu_4 + \nu_{13} = 2535$, $\nu_4 + \nu_5 = 2532$	1212[a]	$\nu_{14} + \nu_{15} = 1213$
2270	$2\nu_{12} = 2282$	1112	$CH_3NC\cdot{}^{11}BH_3$
2227[a]	$2\nu_5 = 2246$, $\nu_5 + \nu_{13} = 2249$	740[b]	$2\nu_{15} = 738$
1978[a]	$2\nu_6 = 1988$, $\nu_{12} + \nu_{14} = 1989$		

$CH_3NC\cdot{}^{10}BD_3$

obsd	assigt, calcd	obsd	assigt, calcd
3320	$\nu_3 + \nu_6 = 3317$	1768[a]	$CH_3NC\cdot{}^{10}BHD_2$ (?)
2872	$2\nu_{11} = 2876$	1709	$\nu_5 + \nu_{12} = 1710$
2532	$\nu_4 + \nu_{13} = 2535$	1656	$2\nu_{12} = 1660$
2383	$CH_3NC\cdot{}^{10}BHD_2$ (?)	1644[a]	$CH_3NC\cdot{}^{10}BHD_2$ (?)
2292	$\nu_4 + \nu_5 = 2289$	1596	$\nu_{11} + \nu_{16} = 1608$
2267	$\nu_{11} + \nu_{12} = 2268$	1560	$\nu_6 + \nu_7 = 1570$
2246	$2\nu_{13} = 2252$	1540	$\nu_{12} + \nu_{14} = 1543$
2148	$\nu_{11} + \nu_{14} = 2151$	1463	$\nu_{13} + \nu_{15} = 1462$
1990	$\nu_5 + \nu_{13} = 2006$	1052	$\nu_5 + \nu_{16} = 1050$,
1883[a]	$\nu_5 + \nu_6 = 1885$		$\nu_{14} + \nu_{15} = 1049$
1835	$\nu_6 + \nu_{12} = 1835$,	867	$CH_3NC\cdot{}^{11}BD_3$
	$\nu_{13} + \nu_{14} = 1839$	679[b]	$2\nu_5 = 676$

$CD_3NC\cdot{}^{10}BH_3$

obsd	assigt, calcd	obsd	assigt, calcd
3297	$\nu_9 + \nu_{11} = 3307$	2065[a]	$\nu_5 + \nu_6 = 2074$
3264	$\nu_2 + \nu_{13} = 3262$,	2042	$\nu_4 + \nu_6 = 2048$
	$\nu_3 + \nu_6 = 3263$	1983	$\nu_6 + \nu_{11} = 1989$,
2912	$\nu_3 + \nu_7 = 2919$		$\nu_4 + \nu_{13} = 1990$,
2754	$\nu_{10} + \nu_{15} = 2751$		$\nu_{12} + \nu_{14} = 1989$
2227	$\nu_4 + \nu_{12} = 2239$	1691	$\nu_4 + \nu_7 = 1704$
2211[a]	$\nu_4 + \nu_5 = 2222$	1202[a]	$\nu_{11} + \nu_{16} = 1210$,
			$\nu_{14} + \nu_{15} = 1205$

$CD_3NC\cdot{}^{10}BD_3$

obsd	assigt, calcd	obsd	assigt, calcd
3297	$\nu_9 + \nu_{11} = 3307$	1817[a]	$\nu_5 + \nu_6 = 1836$
3287	$\nu_3 + \nu_6 = 3286$	1740[a]	$CD_3NC\cdot{}^{10}BHD_2$ (?)
2904	$\nu_4 + \nu_{10} = 2901$	1655	$2\nu_{12} = 1660$
2858	$\nu_3 + \nu_7 = 2867$	1644[a]	$CD_3NC\cdot{}^{10}BHD_2$ (?)
2384	$CD_3NC\cdot{}^{10}BHD_2$ (?)	1540	$\nu_{12} + \nu_{14} = 1542$
2210[a]	$\nu_2 + \nu_7 = 2248$	1425	$2\nu_{14} = 1424$
2069[a]	$2\nu_{11} = 2076$	860	$CD_3NC\cdot{}^{11}BD_3$
1957	$\nu_4 + \nu_5 = 1963$,	663[b]	$2\nu_5 = 658$
	$\nu_{10} + \nu_{16} = 1959$		

[a] These bands are also observed in the Raman spectra.
[b] Raman bands.

Table VII. Molecular Parameters and Coordinates for Methyl Isocyanide-Borane

Bond Lengths, Å[a]

$r = C{-}H = 1.10$ $\quad D = N{\equiv}C = 1.155$
$R = B{-}H = 1.22$ $\quad L = C{-}B = 1.566$
$d = C{-}N = 1.416$

Bond Angles, Deg[a]

$\alpha = HCH = 110.0$ $\quad \gamma = HBC = 105.7$
$\beta = HCN = 109.0$ $\quad \theta = CNC = 180.0$
$\delta = HBH = 113.0$ $\quad \zeta = NCB = 180.0$

Symmetry Coordinates[b]

A_1 $S_1 = (1/3^{1/2})(\Delta r_1 + \Delta r_2 + \Delta r_3)$
$S_2 = (1/3^{1/2})(\Delta R_1 + \Delta R_2 + \Delta R_3)$
$S_3 = \Delta D$
$S_4 = (1/n_1^{\,1/2})[m_1(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]^c$
$S_5 = (1/n_2^{\,1/2})[m_2(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3) - (\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3)]^d$
$S_6 = \Delta d$
$S_7 = \Delta L$
A_2 $S_8 = \Delta\tau^e$
E $S_9 = (1/2^{1/2})(\Delta r_2 - \Delta r_3)$
$S_{10} = (1/2^{1/2})(\Delta R_2 - \Delta R_3)$
$S_{11} = (1/2^{1/2})(\Delta\alpha_2 - \Delta\alpha_3)$
$S_{12} = (1/2^{1/2})(\Delta\delta_2 - \Delta\delta_3)$
$S_{13} = (1/2^{1/2})(\Delta\beta_2 - \Delta\beta_3)$
$S_{14} = (1/2^{1/2})(\Delta\gamma_2 - \Delta\gamma_3)$
$S_{15} = \Delta\theta$
$S_{16} = \Delta\zeta$

[a] Reference 3. [b] The projections of R_1 and r_1 on a plane perpendicular to the threefold axis make an angle of 180° with each other. The angle α_1 lies between r_2 and r_3 and the angle β_1 between r_1 and L, etc. [c] $n_1 = 3(m_1^{\,2} + 1)$, $m_1 = -3^{1/2}\cos\beta/\cos(\alpha/2)$. [d] $n_2 = 3(m_2^{\,2} + 1)$, $m_2 = -3^{1/2}\cos\gamma/\cos(\delta/2)$. [e] Torsion.

Table VIII. Symmetry Force Constants for $CH_3NC\cdot BH_3$[a]

A_1 class		E class	
$F_{1,1}$	5.004 (4)	$F_{9,9}$	4.719 (44)
$F_{2,2}$	3.277 (5)	$F_{10,10}$	2.979 (16)
$F_{3,3}$	18.293 (9)	$F_{11,11}$	0.564 (14)
$F_{4,4}$	0.645 (1)	$F_{12,12}$	0.389 (1)
$F_{5,5}$	0.541 (3)	$F_{13,13}$	0.794 (8)
$F_{6,6}$	4.887 (31)	$F_{14,14}$	0.422 (13)
$F_{7,7}$	2.908 (26)	$F_{15,15}$	0.293 (23)
$F_{2,5}$	0.125 (31)	$F_{16,16}$	0.381 (20)
$F_{4,6}$	−0.499 (7)	$F_{9,11}$	0.299 (61)
$F_{5,7}$	−0.304 (7)	$F_{10,12}$	−0.050 (29)
		$F_{11,13}$	−0.043 (16)
		$F_{14,16}$	0.158 (13)
		$F_{15,16}$	0.080 (11)

[a] The subscripts identify $F_{i,j}$ with symmetry coordinates *i* and *j* as defined in Table VII. Stretching force constants are in mdyn/Å, bending constants in mdyn Å/rad^2, and stretch-bend interactions in mdyn/rad. The dispersions of the force constants are given in parentheses.

G matrix elements were calculated from molecular parameters determined by the microwave study.[3] The molecular parameters and symmetry coordinates are presented in Table VII. Symmetry force constants were calculated so as to fit the calculated frequencies to the observed ones for the four ^{10}B isotopic species simultaneously. Infrared frequencies were mainly used for the calculation except ν_{16}, for which Raman frequencies were employed. The doublet frequencies observed for the $^{10}BD_3$ degenerate stretch ν_{10} in $CD_3NC\cdot{}^{10}BD_3$ were averaged. The individual eigenvalues were weighted as $w_i = 1/\lambda_i$. Since the A_2 torsional mode was not observed, no calculation was performed for it.

Initial diagonal force constants for the methyl isocyanide portion were taken from the values of free methyl isocyanide[14]

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(14) Duncan, J. L. *Spectrochim. Acta* **1964**, *20*, 1197.

Table IX. Comparison of Vibrational Frequencies (cm^{-1}) and Valence Force Constants (mdyn/Å) for the Skeletal Bonds of CH_3NC, CH_3CN, and Their $^{10}BH_3$ Adducts

	$\nu_{N\equiv C}$	ν_{C-N}	ν_{CNC}	ν_{C-B}	$f_{N\equiv C}$	f_{C-N}	f_{CNC}	f_{C-B}
CH_3NC	2166^a	949^a	263^a		16.65^b	5.40^b	0.176	
$CH_3NC\cdot{}^{10}BH_3$^{c}	2313	994	365	623	18.29	4.88	0.293	2.90
	$\nu_{C\equiv N}$	ν_{C-C}	ν_{CCN}	ν_{N-B}	$f_{C\equiv N}$	f_{C-C}	f_{CCN}	f_{N-B}
CH_3CN	2267^d	920^d	362^d		18.11^b	5.15^b	0.351^b	
$CH_3CN\cdot{}^{10}BH_3$^{e}	2354	978	404	588	18.79	5.08	0.364	2.45

[a] Reference 11. [b] Reference 14. [c] This work. [d] Nakagawa, I.; Shimanouchi, T. *Spectrochim. Acta* 1962, *18*, 513. [e] Reference 5.

and those of the BH_3 group transferred from the values of methyl cyanide–borane.[5] The initial C–B force constant was assumed to be the same value as the N–B constant in methyl cyanide–borane.[5]

An interaction constant between two vibrational modes not sharing at least one common atom was fixed at the value of zero. Other interaction constants were added in the refinement one by one, but any constant that was smaller in magnitude than its dispersion or smaller than 0.02 in magnitude or whose inclusion caused the secular equation to be ill conditioned was omitted from the refinement, being constrained to zero. This produced a good fit between the calculated and observed frequencies with an average deviation from the observed frequencies of 0.21% for the A_1 class and of 0.40% for the E including all the four ^{10}B isotopic compounds.

The calculated frequencies are given in Tables II–V, together with the potential energy distributions. The symmetry force constants and the dispersions from the last cycles of the least-squares refinement are given in Table VIII.

Discussion

Frequencies and valence force constants for the skeletal bonds of CH_3NC and $CH_3NC\cdot{}^{10}BH_3$ are collected in Table IX together with the corresponding quantities of CH_3CN and $CH_3CN\cdot{}^{10}BH_3$.[5]

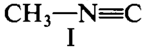
The N≡C stretching frequency increases ca. 150 cm^{-1} and also the N≡C valence force constant increases significantly (9.8%) upon adduct formation. As seen from the potential energy distributions (Tables II–V) the N≡C stretch couples with the C—N and C—B stretches, which causes the upward shift in the N≡C frequency. But since the coupling is very small, such a large frequency increase can be explained only by an increase in the force constant. The increase in the N≡C force constant is consistent with the strengthening in the N≡C bond indicated by the structural data.[3]

The C—N stretching frequency also increases upon adduct formation, but the force constant decreases contrary to the case of the N≡C bond. The potential energy distributions (Tables II–V) show that the C—N stretching mode largely couples with the C—B stretch, which leads to the elevation of the C—N frequency in spite of the decrease in the force constant. Moreover it couples with the BD_3 symmetric deformation in the BD_3 adducts whose frequency is lower than that of the C—N stretch: therefore the C—N stretching frequencies of the BD_3 adducts are higher than those of the corresponding BH_3 adducts.

The BD_3 symmetric deformation, on the other hand, couples with the C—B stretch. Accordingly, vibrational couplings exist among the C—N stretch, the C—B stretch, and the symmetric deformation of the borane group. The couplings cause these vibrations not to be observed at definite positions, but their frequencies vary from one isotope to the others.

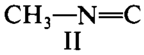
The CNC bending frequency increases ca. 100 cm^{-1} upon adduct formation. The increase in the CNC bending force constant is remarkable, reaching up to 66% upon adduct formation. This is surprising when compared with the increase in the CCN bending frequency (40 cm^{-1}) and force constant (4%) in $CH_3CN\cdot BH_3$.

If methyl isocyanide is considered to have a structure made up of contributions from resonance forms I and II, the relatively small CNC bending frequency and force constant can be explained in terms of a contribution from the bent form II.[12] When complexation occurs with borane, two extreme forms are presented as III and IV. The experimental results can fairly well be explained in terms of more contribution from the form III to a structure of methyl isocyanide–borane. An enhancement of triple-bond nature in the N≡C bond leads to a decrease in the N≡C bond length and hence to increases in the force constant and stretching frequency. A lesser importance of the bent form IV in the adduct leads to a increase in the CNC bending force constant. It is a marked difference between the borane adducts with methyl isocyanide and cyanide that there is no equivalent counterpart in methyl cyanide. The greater importance of the form III in the adduct results in a less polar C—N bond, which leads to a diminution in infrared intensity of the C—N stretch.



$CH_3—\overset{+}{N}\equiv\overset{-}{C}$

I

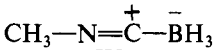


$CH_3—N=C$

II

$CH_3—\overset{+}{N}\equiv C—\overset{-}{B}H_3$

III



$CH_3—N=\overset{+}{C}—\overset{-}{B}H_3$

IV

The C—B force constant in methyl isocyanide–borane is larger (18%) than the N—B constant in methyl cyanide–borane. The strengths of the donor–acceptor bonds correctly reflect adduct stabilities since methyl cyanide–borane dissociates completely in the gas phase at room temperature to the respective components,[4,5] while no such dissociation of methyl isocyanide–borane is found when the solid film is prepared on the CsI substrate by sublimation for infrared measurement. Although further studies on complexes with various Lewis acids must be conducted for an extensive argument on the Lewis base strength of the isocyanides, it can be said that methyl isocyanide is a stronger Lewis base to borane than methyl cyanide.

Registry No. $CH_3NC\cdot{}^{10}BH_3$, 80243-27-2; $CH_3NC\cdot{}^{10}BD_3$, 80243-28-3; $CD_3NC\cdot{}^{10}BH_3$, 80243-29-4; $CD_3NC\cdot{}^{10}BD_3$, 80243-30-7; $CH_3NC\cdot BH_3$, 62630-46-0.