

Synthesis & Characterization of Amine-Cyanoborane Adducts of Some Aliphatic Amines†

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A number of amine-cyanoborane adducts of the formula $R_3-nH_nN.BH_2CN$ ($n=0-2$; R =ethyl, *n*-propyl, *i*-propyl, *n*-butyl, and *i*-butyl) have been prepared by reacting sodium cyanotrihydroborate and amine hydrochlorides in refluxing tetrahydrofuran. The products have been characterized by elemental analyses, and infrared and 1H NMR spectra.

Synthesis of a few amine-cyanoborane adducts has been reported previously¹ by one of us. However, a literature survey shows that no aliphatic amine-cyanoborane adducts, except those of trimethyl-, dimethyl- and monomethyl-amines¹, have so far been synthesized. Both trimethylamine- and dimethylamine-cyanoboranes have shown significant anti-tumor², antiinflammatory³ and antihyperlipidemic⁴ activities in mice. Therefore, in view of the potential therapeutic utility⁵ of the amine-cyanoboranes and related compounds, we report here the synthesis of a number of aliphatic amine-cyanoboranes derived from higher and branched chain alkylamines.

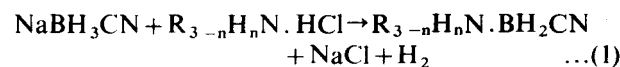
All the chemicals used were of reagent grade quality. Diethyl-, triethyl-, *n*-propyl-, *i*-propyl-, di-*i*-propyl-, tri-*n*-propyl-, *n*-butyl-, di-*n*-butyl- and di-*i*-butylamines were commercial products and were dried by refluxing over solid KOH and distilled prior to use. These were converted to their hydrochlorides by bubbling dry HCl gas through their ethereal solutions and were finally dried *in vacuo*. Ether was dried over anhydrous $CaCl_2$ followed by refluxing over metallic sodium. Tetrahydrofuran (THF) was dried by refluxing over solid KOH for 6 hr and then over $LiAlH_4$ and was distilled prior to use. Chloroform and petroleum ether were dried by the usual methods. $NaBH_3CN$ was obtained from Alfa Products, Massachusetts, U.S.A., and was used without further purification. Infrared spectra ($4000-600\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 297 or 597 spectrophotometer as thin film or as KBr pellets (for the solids).

Proton NMR spectra were recorded on a Varian T-60 or a JEOL-FX 100 spectrometer in $CDCl_3$ with TMS as the internal standard. Microanalyses of C, H and N were performed at the microanalytical laboratories of Jadavpur University and University of Calcutta. Boron was estimated volumetrically by titrating with standard alkali in presence of mannitol^{6,7}.

Synthetic procedure

Sodium cyanotrihydroborate, $NaBH_3CN$ (1.89 g, 30 mmol) and an appropriate amine hydrochloride (30 mmol) were placed in a three-necked flask fitted with a reflux condenser, a magnetic stirrer and a gas bubbler, and the assembly was flushed with dry nitrogen gas. THF (40 ml) was then added through a side arm and the mixture was refluxed for a prolonged time (see Table I). When the evolution of hydrogen gas ceased, the reaction mixture was cooled and filtered through a sintered glass funnel to remove any unreacted solid residue. The crude amine-cyanoborane was then obtained by removing the solvent in a rotary evaporator. All the amine-cyanoboranes, except V and IX (see Table I), which are solids, are liquids at room temperature. The solid compounds were purified by dissolving in chloroform and then reprecipitating by adding petroleum ether ($40-60^\circ C$). The liquid compounds were purified by dissolving them in minimum quantity of water (in order to remove water-soluble impurity) and extracting with ether, followed by drying the ether extracts over anhydrous $MgSO_4$ and evaporating under reduced pressure. Further purification of I and II was possible by vacuum distillation, whereas the rest of the compounds decomposed on attempted vacuum distillation (0.05 Torr).

The reaction leading to the formation of the amine-cyanoboranes from the amine hydrochlorides and $NaBH_3CN$ is represented in Eq. 1.



($n=0-2$, $R=C_2H_5$, *n*- C_3H_7 , *i*- C_3H_7 , *n*- C_4H_9 , *i*- C_4H_9).

The compounds II, V, VI, VIII and IX were obtained in high yields (80-90%), whereas the rest were obtained in lower yields. It has been observed that the yields for the straight chain aliphatic amines are generally lower, even after prolonged refluxing, compared to those for the branched chain aliphatic amines. This is in accordance with the stronger donor capability of the branched chain aliphatic amines owing to increased positive inductive effect. The amine-cyanoboranes are

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Table 1—Physical and Analytical Data for the Amine-Cyanoboranes, $R_3-nH_nN \cdot BH_2CN$

$R_3-nH_nN \cdot BH_2CN$ (Sl. No.)	Amine (R_3-nH_nN)	Reflux time (hr)	Yield (%)	m.p./b.p. (°C)	Anal. Data (%) Found (Calc.)
I	$(CH_3CH_2)_2NH$	80	58	120/2 Torr	C 53.30 (53.64) H 11.42 (11.62) N 24.80 (25.03) B 9.50 (9.69)
II	$(CH_3CH_2)_3N$	48	83	68/0.05 Torr	C 59.62 (60.06) H 11.80 (12.15) N 19.86 (20.02) B 7.50 (7.75)
III	$CH_3(CH_2)_2NH_2$	150	47	—	C 49.53 (49.05) H 11.30 (11.24) N 28.86 (28.61) B 10.90 (11.07)
IV	$(CH_3)_2CHNH_2$	120	55	—	C 49.50 (49.05) H 11.46 (11.24) N 28.50 (28.61) B 10.60 (11.07)
V	$[(CH_3)_2CH]_2NH$	72	77	107-108	C 59.54 (60.06) H 12.10 (12.15) N 19.81 (20.02) B 7.50 (7.75)
VI	$[CH_3(CH_2)_2]_3N$	48	80	—	C 65.05 (65.99) H 12.40 (12.64) N 15.10 (15.39) B 5.90 (5.96)
VII	$CH_3(CH_2)_3NH_2$	100	58	—	C 52.72 (53.64) H 11.36 (11.62) N 25.00 (25.03) B 9.30 (9.61)
VIII	$[CH_3(CH_2)_3]_2NH$	72	80	13.5*	C 63.93 (64.34) H 12.26 (12.51) N 16.46 (16.68) B 6.10 (6.45)
IX	$[(CH_3)_2CHCH_2]_2NH$	72	87	128-130	C 65.00 (64.34) H 12.60 (12.51) N 16.61 (16.68) B 6.42 (6.45)

*liquid at room temperature

somewhat hygroscopic, especially the liquid ones, and are soluble in water and common organic solvents such as chloroform, dichloromethane, alcohol and ether.

Characteristic infrared absorption bands and proton NMR spectral data are given in Table 2. Vidal and Ryschkewitsch⁸ reported the $\nu(C \equiv N)$ modes in the range 2185-2280 cm^{-1} , while one of us found them previously in the range 2180-2200 cm^{-1} . In the compounds studied here, the $\nu(C \equiv N)$ modes occur in the range 2175-2220 cm^{-1} , while the $\nu(N-H)$ frequencies occur in the range 3100-3160 cm^{-1} . The B-H stretching modes in the amine-cyanoboranes occur in the range 2255-2450 cm^{-1} , mostly as broad absorptions with shoulders. The B-H stretching modes in some substituted amine-boranes have been reported⁹ to occur in the range 2270-2500 cm^{-1} with

upto four absorptions due to asymmetric and symmetric $\nu(BH_2)$ vibrations⁹. The 1H NMR spectra of the amine-cyanoboranes show the presence of the aliphatic amine groups with the pattern expected for such groups. The signals (in δ ppm) for CH_3 occur at 0.96-1.43, and the signals for CH_2 and CH occur at lower fields, between 1.6 and 3.43. The absorptions due to the NH and NH_2 protons are broad singlets varying in position between 3.60 and 6.10. For the NH and NH_2 protons, and indeed for all protons, there is a close parallelism between the proton chemical shifts of the amine-cyanoboranes and those of the amine-boranes. All the corresponding amine-boranes are known¹⁰, but these have been prepared by us following the method of Greenwood⁹ for a comparative study. The NH proton signals in various amine-boranes have

Table 2—Characteristic Infrared and PMR Data for Amine-Cyanoboranes, $R_3-nH_nN.BH_2CN$

Compd.	Infrared data (cm^{-1})			PMR data (δ , ppm) ^{a,b}
	$\nu(N-H)$	$\nu(B-H)$	$\nu(C\equiv N)$	
I	3100 (s, br)	2370 (sh) 2320 (s, br)	2178 (s)	CH_3 (1.30 ^d) CH_2 (3.0 ^q) NH (5.0 ^r)
II	—	2330-2410 (s, br) 2255 (s)	2175 (s)	CH_3 (1.36 ^d) CH_2 (3.05 ^q)
III	3140 (s)	2420 (sh) 2360 (sh) 2310 (s, br)	2175 (s)	CH_3 (1.0 ^m) CH_2 (2.88 ^m) NH ₂ (6.10 ^r)
IV	3140 (s)	2380 (sh) 2345 (s, br) 2270 (sh)	2180 (s)	CH_3 (1.36 ^d) CH (3.43 ^m) NH (5.75 ^r)
V	3130 (s)	2380 (br, sh) 2300 (s, br) 2240 (sh)	2175 (s)	CH_3 (1.43 ^d) CH (3.43 ^m) NH ^c
VI	—	2410 (sh) 2322 (s, br) 2260 (s)	2180 (s)	CH_3 (1.03 ^d) CH_2 (1.82, 3.06) ^m
VII	3125 (s, br)	2410 (sh) 2360 (sh) 2300 (s)	2180 (s)	CH_3 (0.97 ^d) CH_2 (1.63, 3.12) ^m NH ₂ (4.85 ^r)
VIII	3100 (s, br)	2380 (sh) 2360 (sh) 2310 (s, br)	2182 (s)	CH_3 (0.96 ^d) CH_2 (1.56, 2.94) ^m NH (5.28 ^r)
IX	3160 (s)	2438 (sh) 2450 (s)	2220 (s)	CH_3 (1.0 ^d) CH & CH_2 2.2, 2.55, 2.85) ^m NH (3.60 ^r)

^as=singlet, d=doublet, t=triplet, q=quartet.

^bSaturated solutions in $CDCl_3$, measured at 60 MHz, except III and VI which were measured at 100 MHz.

^cCould not be observed; probably too broad to be observed.

been observed between 5.55 and 3.95¹¹. The absorptions due to BH_2 protons could not, however, be observed.

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