# Identification of N-Methylbenzylamine Hydrochloride, N-Ethylbenzylamine Hydrochloride, and N-Isopropylbenzylamine Hydrochloride

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**ABSTRACT:** N-Methylbenzylamine hydrochloride, N-ethylbenzylamine hydrochloride, and N-isopropyl-benzylamine hydrochloride have recently been utilized to adulterate or mimic illicit methamphetamine hydrochloride (especially "Ice" methamphetamine). The characterizations of these three alkylbenzylamines by color testing, melting point determination, GC/MS, FTIR/ATR, and $^{1}$H-NMR are presented.

**KEYWORDS:** N-Methylbenzylamine, N-Ethylbenzylamine, N-Isopropylbenzylamine, "Ice" Methamphetamine, GC/MS, FTIR/ATR, $^{1}$H-NMR, Forensic Chemistry

### *Introduction*

Over the past 18 months, DEA and other forensic laboratories have received increasing numbers of suspected or purported high purity bulk methamphetamine hydrochloride exhibits that subsequent analyses showed to actually be a high purity alkylbenzylamine or less commonly, methamphetamine adulterated with an alkylbenzylamine [1-3]. Most of these exhibits were seized along or near the southwest border, or along the usual trafficking routes in the American southwest. In some cases, the alkylbenzylamine or methamphetamine/alkylbenzylamine mixtures

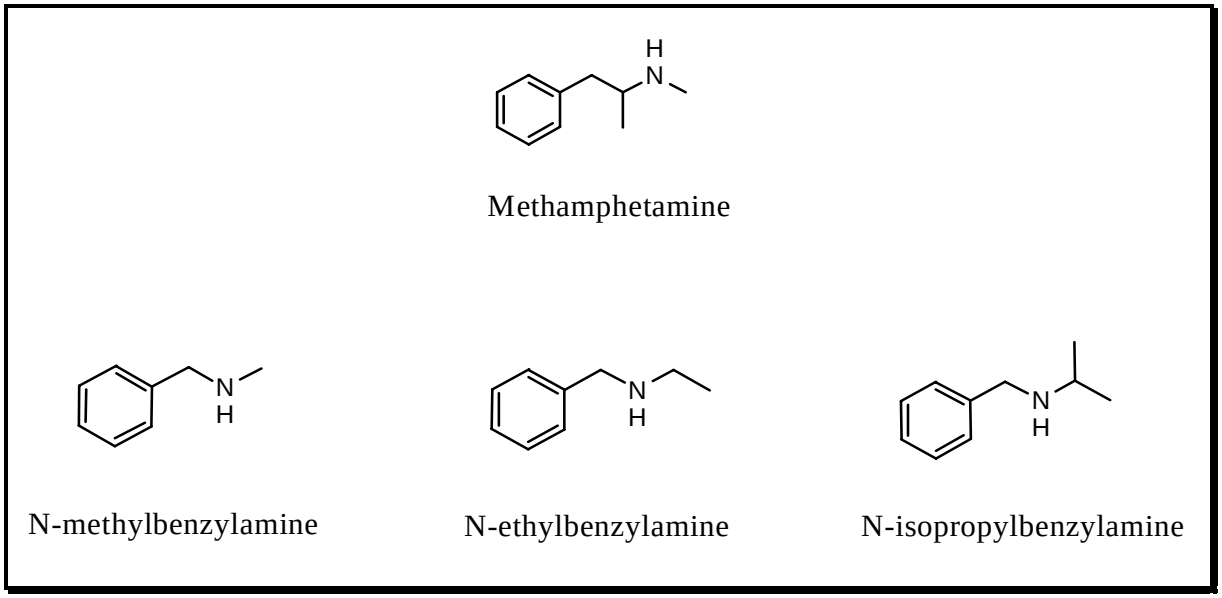



**Figure 1.** Structures of Methamphetamine and the N-Alkylbenzylamines.

were further diluted with dimethyl sulfone (a common methamphetamine "cut"). The first of these compounds encountered at this laboratory, N-methylbenzylamine hydrochloride, was submitted in early 2007. N-Ethylbenzylamine hydrochloride began to appear during the summer of 2007, and N-isopropylbenzylamine hydrochloride began to appear in late 2007 [Figure 1]. In 2008, to date (and for reasons unknown), N-isopropyl-benzylamine hydrochloride appears to have become the dominant alkylbenzylamine among these submissions.

In most cases, the alkylbenzylamines were crystalline shards or cystalline powders that visually resembled "Ice" or "crystal" methamphetamine (e.g., see Photos 1 - 3). In addition, bulk exhibits (i.e., more than 2 kilograms) were packaged similarly to what is typically encountered for bulk methamphetamine (e.g., in plastic food-storage containers wrapped in cellophane and tape or in large ziplock plastic bags, etc. (e.g., see Photo 4)). And further, the bulk exhibits were smuggled similarly to other illicit drugs - and in some cases were co-smuggled with packages of other (actual) illicit drugs. For these reasons, it is widely accepted that they are being used as methamphetamine mimics (that is, as "rip-off"/sham narcotics), as opposed to "decoys" intended to divert law enforcement attention. In fact, all three alkylbenzylamines have been identified in retail (street-level) samples.

Photo 1 - Typical Exhibit of
N-Methylbenzylamine HCl [1]


Photo 2 - Typical Exhibit of
N-Ethylbenzylamine HCl

Photo 3 - Typical Exhibit of
N-Isopropylbenzylamine HCl [2]

Photo 4 - N-Isopropylbenzylamine HCl
Exhibits in Food-Storage Containers [2]

Not surprisingly, the analytical characteristics of the alkylbenzylamines are both similar and dissimilar to the simple phenethylamine drugs. One significant issue is that the various spectra may or may not be included in the libraries installed in the instruments present at most forensic laboratories. The characterization of N-methylbenzylamine, N-ethylbenzylamine, and N-isopropylbenzylamine by melting point, color testing, GC/MS, FTIR/ATR, and $^{1}$H-NMR are presented herein.

## *Experimental*

Reagents

*Alkylbenzylamines*: N-Methylbenzylamine base, N-ethylbenzylamine base, and N-isopropylbenzylamine base were obtained from Sigma-Aldrich (St. Louis, MO). The respective hydrochloride salts were prepared by dissolving the free bases in acetone and adding concentrated hydrochloric acid. The resulting crystals were filtered, washed multiple times with acetone/ether (50/50), and air dried.

*Other Reagents*: Methamphetamine hydrochloride, amphetamine sulfate, phenethylamine sulfate, and dimethylsulfone were all obtained from this laboratory's reference collection.

*Test Solutions*: Two test solutions were prepared for GC/MS Analyses: (A) Test Solution A contained approximately 0.5 mg/mL each of dimethylsulfone and the respective bases of the three alkylbenzylamines, methamphetamine, phenethylamine, and amphetamine, in diethyl ether (prepared from their respective salts by basification with 1 M NaOH followed by extraction with diethyl ether). (B) Test Solution B contained approximately 0.5 mg/mL each of dimethylsulfone and the respective salts of N-methylbenzylamine, N-ethylbenzylamine, methamphetamine, phenethylamine, and amphetamine, in methanol.

Instrumentation

*Melting Points*: Melting points for the respective hydrochloric salts were determined using an Stanford Research Systems Opti - Melt Model MPA-100 melting apparatus (Sunnyvale, CA), and are reported in Table 1.

*GC/MS*: Mass spectra (70 eV EI) were obtained using a 5975B Agilent Technologies Inert Mass Selective Detector equipped with a 6890N Gas Chromatograph. Two different columns were used: (a) An Agilent Technologies DB5-MS, 15 m, 0.25 mm i.d., fused-silica capillary column with 0.25 μm film thickness; or (b) An Agilent Technologies HP5-MS, 30 m, 0.25 mm i.d., fused-silica capillary column with 0.25 μm film thickness. Helium was used as the carrier gas with an average linear velocity of 45 cm/sec (constant flow). The injection port and ion sources were set at 280$^{O}$C and 230$^{O}$C, respectively. For analysis, 1 μL of the respective Test Solution was injected in split mode (50:1). The oven temperature was programmed as follows: 90$^{O}$C for 1 minute, ramped at 30$^{O}$C per minute to 150$^{O}$C, then held there for 2.0 minutes (total run time = 5.00 minutes). The spectra were obtained by scanning over an *m/z* range of 40 - 500.

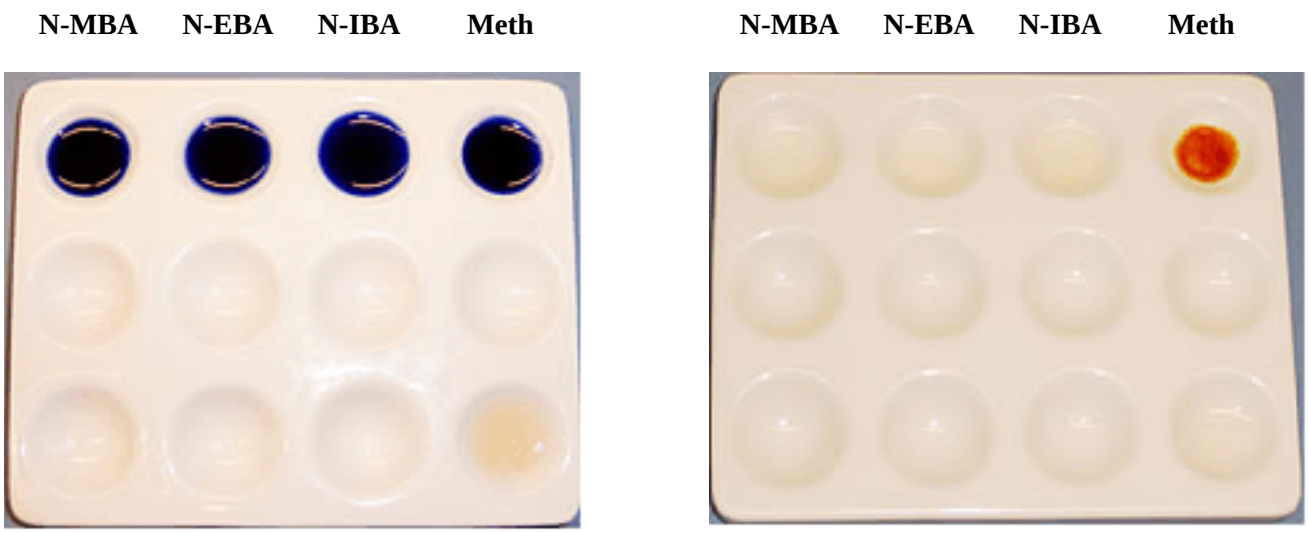
*FTIR/ATR*: Spectra were obtained using a Nicolet Avatar 370 FTIR Spectrophotometer operated in the ATR mode. Sixteen scans were collected at a resolution of 4.0 cm$^{-1}$.

$^{1}$*H-NMR*: Spectra were obtained using a Varian Mercury 400 MHz NMR. The compounds were analyzed as the hydrochloride salts in $D_2O$ (approximately 30 mg/mL) containing TSP as the 0 ppm reference (Note that the spectra are incorrectly labelled with "TMS" - TSP was actually used). Eight scans were collected, using a 90$^{O}$ pulse and a 2 second relaxation delay. Spectra were processed using 1.0 Hz line broadening.

## *Results and Discussion*

The high purity and clean appearance of the various alkylbenzylamine submissions suggest that they were industrially (not clandestinely) produced. However, the large crystal forms of some submissions (especially N-isopropylbenzylamine hydrochloride) indicates that clandestine operators are recrystallizing them in order to better mimic large "Ice" methamphetamine crystals. All three alkylbenzylamines have melting points slightly higher than methamphetamine (see Table 1). Interestingly, the DEA Western Laboratory (San Francisco, CA) reported that the N-isopropylbenzylamine hydrochloride crystals in one bulk submission crushed noticeably more easily than typical "Ice" methamphetamine crystals [2]. A similar propensity was noted during this study;

however, it is unknown if that finding is universal for all three alkylbenzylamines, or instead is an anomaly for recrystallized N-isopropylbenzylamine hydrochloride from one clandestine source. Color testing by sodium nitroprusside gave positive (blue) results for all three alkylbenzylamines; however, testing with the Marquis reagent gave negative results (see below).




**Sodium Nitroprusside Test** **Marquis Reagent Test** [1]

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[1] Caution: Depending on the concentration and the age of Marquis reagent, the alkylbenzylamines can give a presumably "false" or weak positive after approximately 30 seconds (a positive Marquis test usually takes less than 10 seconds).

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The total ion chromatogram (TIC) for the analysis of Test Solution A on the 15 m DB-5 column is shown in Figure 2a. All compounds were baseline separated with the exception of amphetamine and N-ethylbenzylamine. The TIC for the analysis of Test Solution B on the 30 m HP-5 column is shown in Figure 2b; the 30 m HP-5 column was able to partially resolve amphetamine and N-ethylbenzylamine. Figures 3 through 5 show the mass (GC/MS), infrared (FTIR/ATR), and nuclear magnetic resonance ($^1$H-NMR) spectra, respectively, for N-methylbenzylamine hydrochloride, N-ethylbenzylamine hydrochloride, N-isopropylbenzylamine hydrochloride.

The simple alkylbenzylamines are traditionally used as intermediates in organic syntheses. None of the three alkylbenzylamines are controlled, and none are believed to have appreciable CNS stimulant effects at typical methamphetamine dosage levels. The pharmacological effects of high dosages on humans are unknown [4].

**Acknowledgments**

The author thanks the following personnel (all of this laboratory): Jason A. Bordelon (Senior Forensic Chemist) for mentoring and valuable contributions; James L. Jacobs (Forensic Chemist, who was the first to identify N-methylbenzylamine hydrochloride at the laboratory) for standard preparations; and Michael M. Brousseau (Forensic Chemist) for acquiring the $^1$H-NMR spectra.

[Note: References are posted on Page 43.]

**Table 1.** Melting Points.

N-Methylbenzylamine hydrochloride, mp = 180.1 - 181.4$^{O}$C
N-Ethylbenzylamine hydrochloride, mp = 183.7 - 184.5$^{O}$C
N-Isopropylbenzylamine hydrochloride, mp = 192.0 - 193.3$^{O}$C

[Note: *d*-Methamphetamine hydrochloride, mp = 172 - 174$^{O}$C]

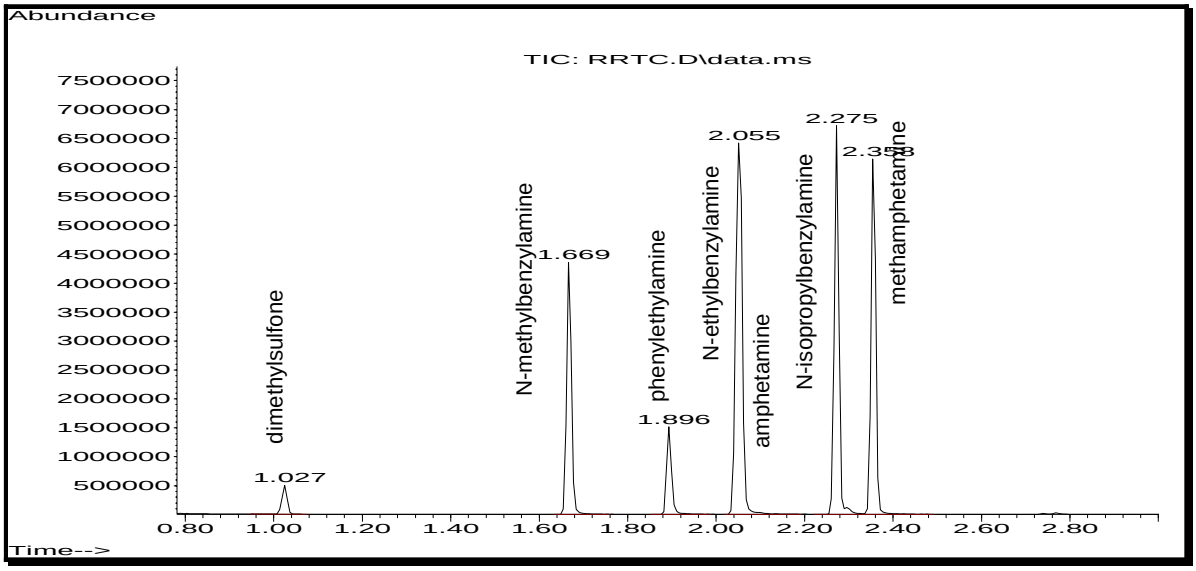


**Figure 2a.** GC/MS Total Ion Chromatogram (TIC) of the Sample Mixture A.

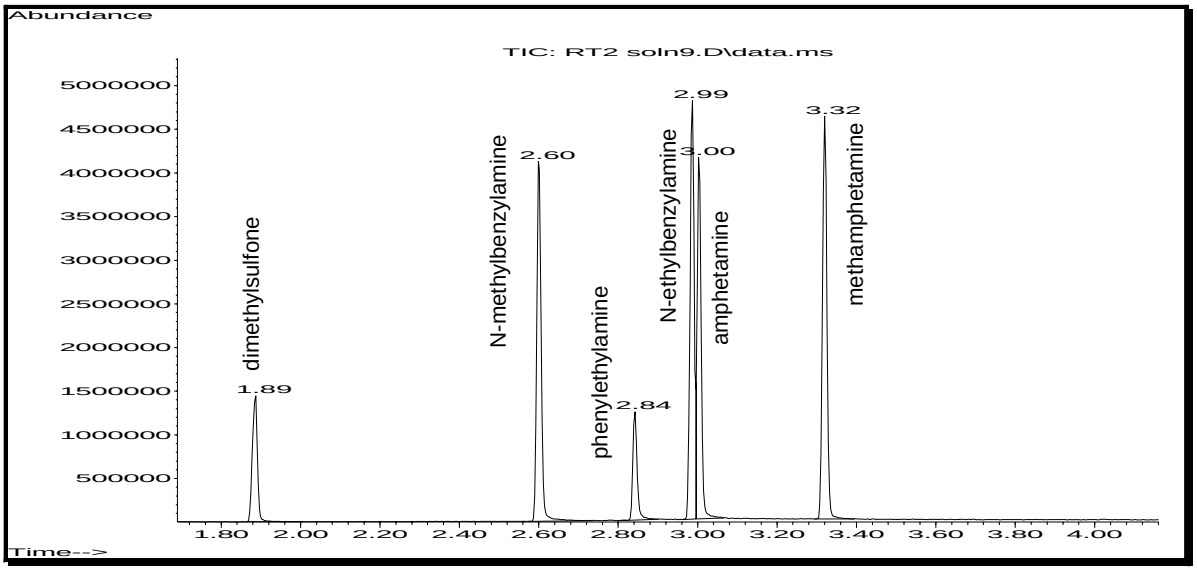


**Figure 2b.** GC/MS Total Ion Chromatogram (TIC) of the Sample Mixture B.

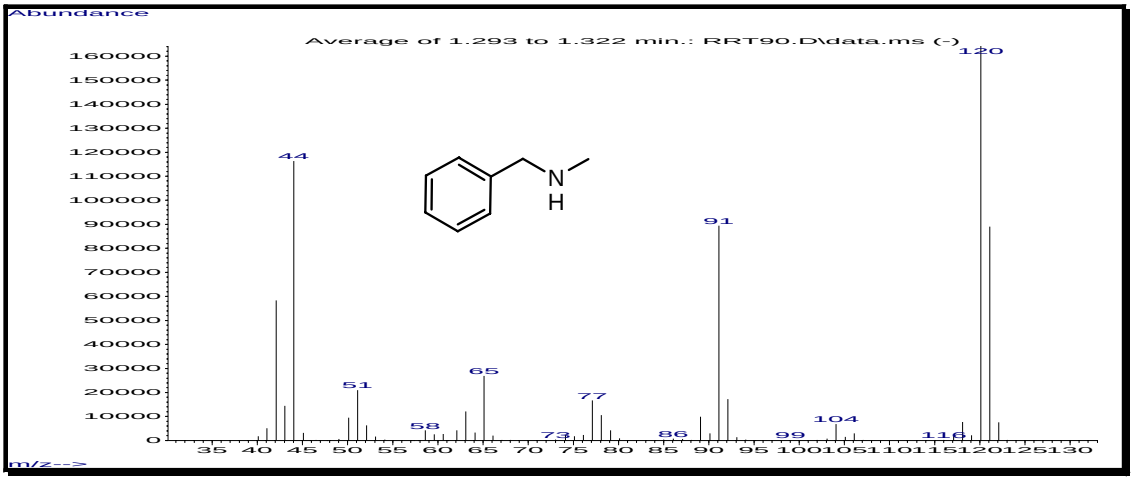


**Figure 3a.** Mass Spectrum of N-Methylbenzylamine.

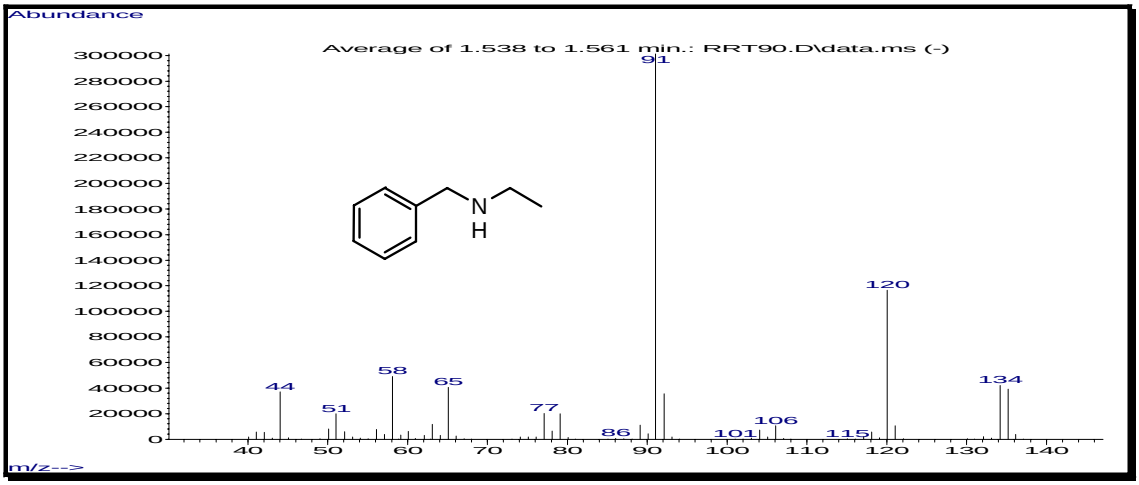


**Figure 3b.** Mass Spectrum of N-Ethylbenzylamine.

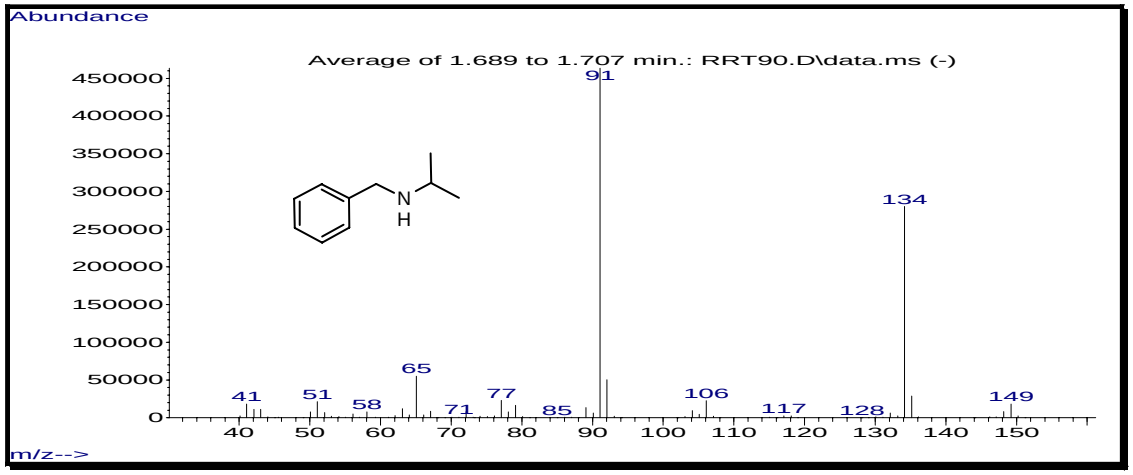


**Figure 3c.** Mass Spectrum of N-Isopropylbenzylamine.

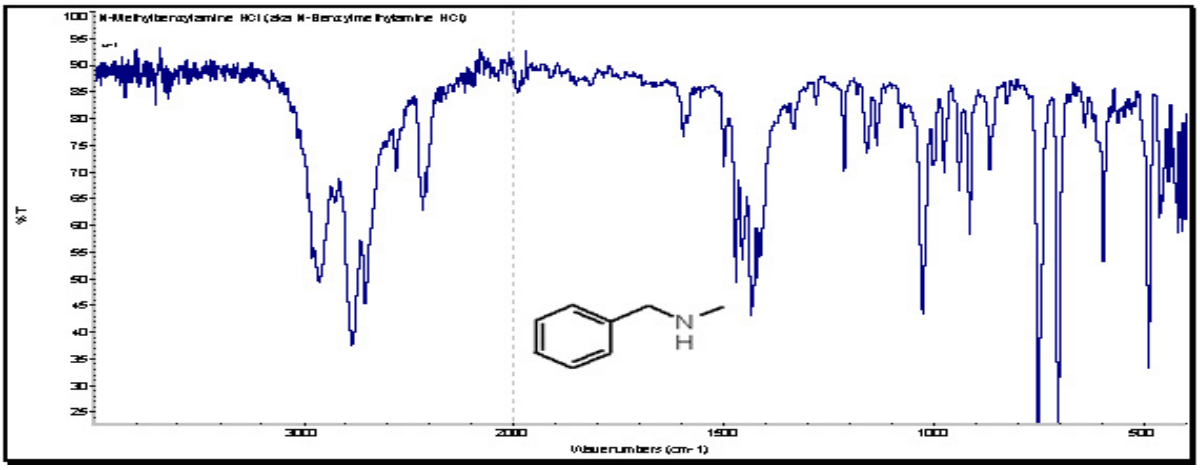


**Figure 4a.** FTIR/ATR of N-Methylbenzylamine Hydrochloride.

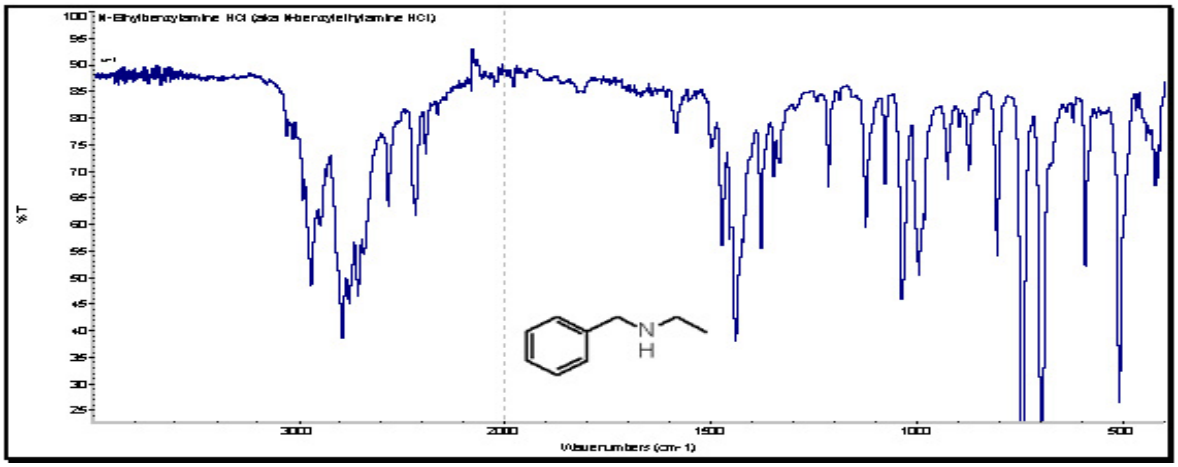


**Figure 4b.** FTIR/ATR of N-Ethylbenzylamine Hydrochloride.

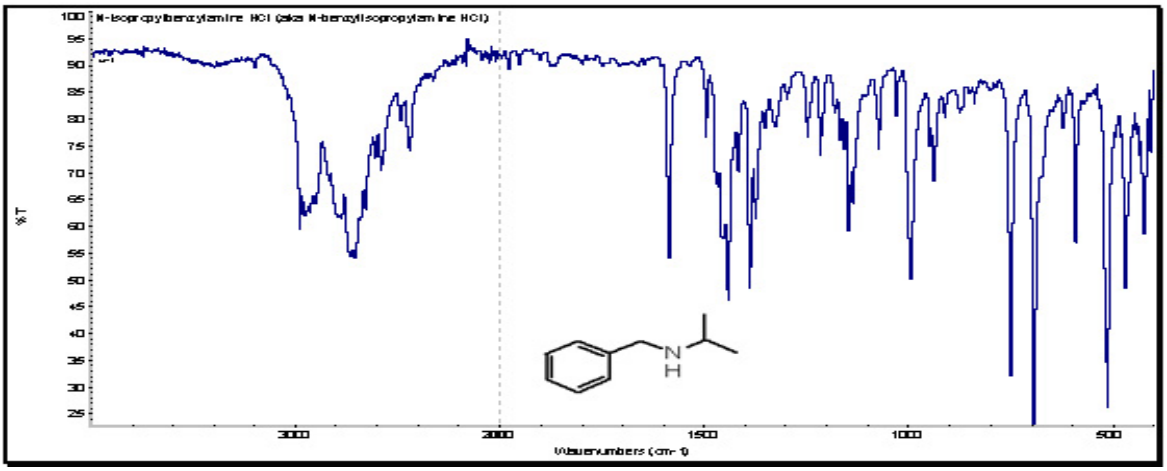


**Figure 4c.** FTIR/ATR of N-Isopropylbenzylamine Hydrochloride.

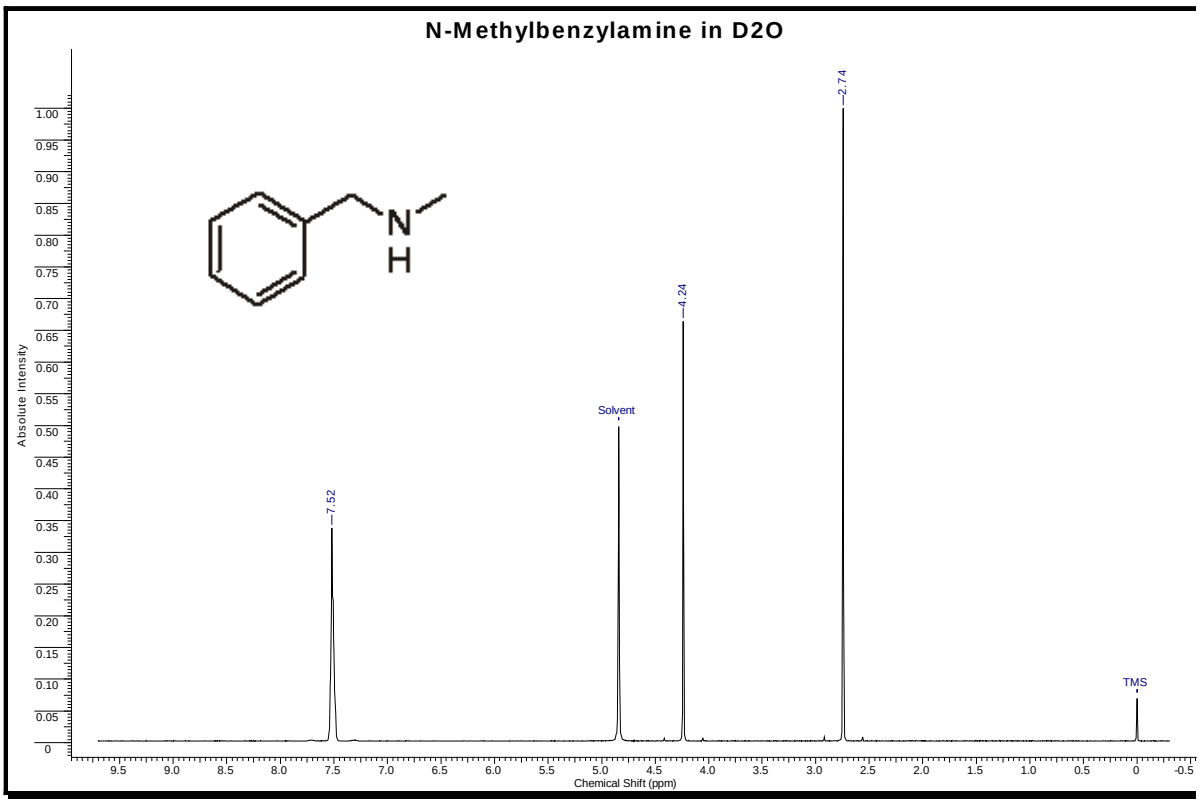


**Figure 5a.** 400 MHz $^{1}$H-NMR Spectrum of N-Methylbenzylamine Hydrochloride in $D_2O$.

[Figures 5b and 5c Follow (Next 2 Pages).]

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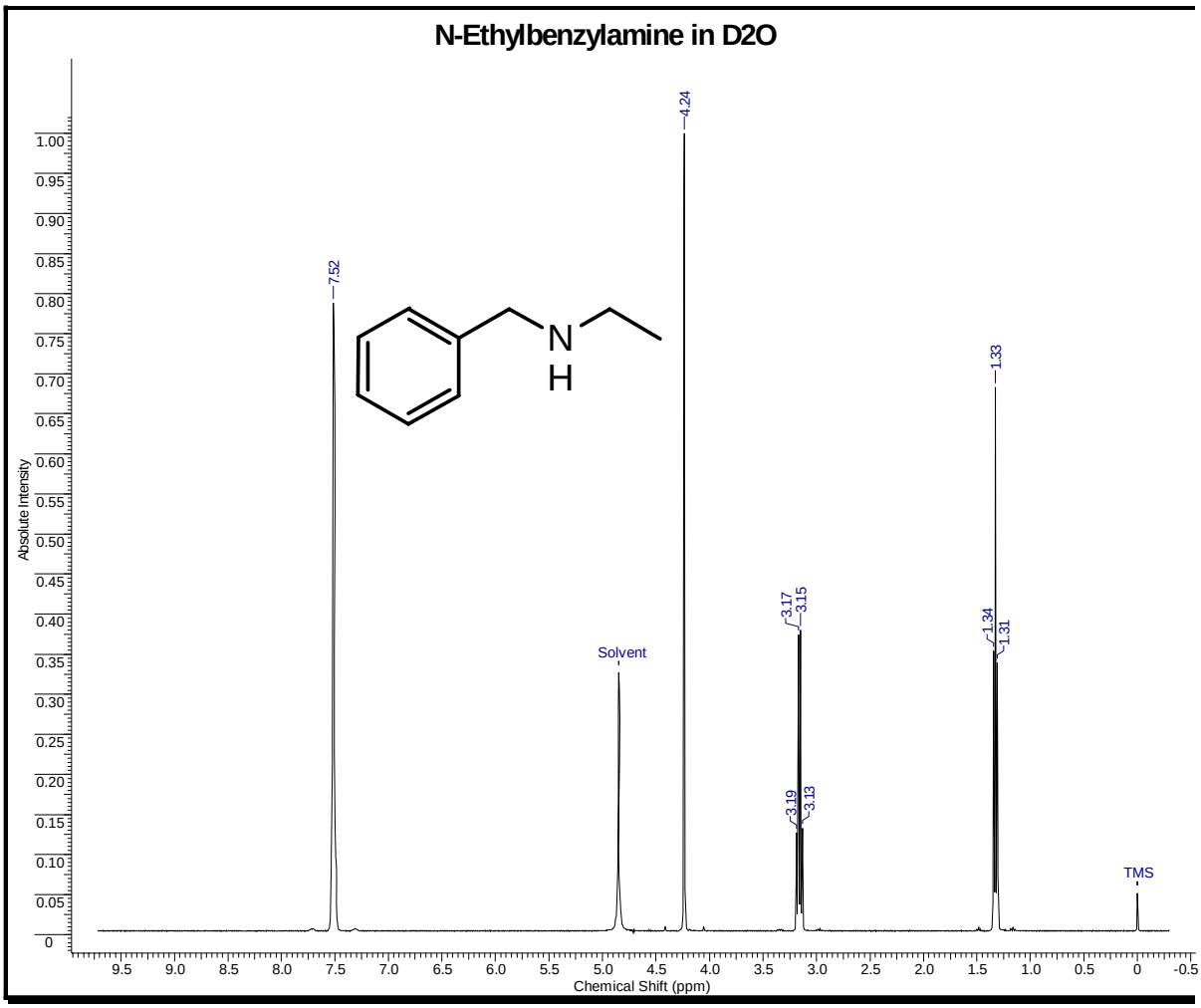
## References


1. Anonymous. N-Benzylmethylamine hydrochloride and N-benzylethylamine hydrochloride ("Ice" and crystal methamphetamine mimics) in the southwest. Microgram Bulletin 2007;40(8):79-80.

2. Anonymous. N-Isopropylbenzylamine hydrochloride (as "Ice" methamphetamine mimics) on the west coast. Microgram Bulletin 2008;41(3):31-2.

3. Anonymous. Very large seizure of N-isopropylbenzylamine hydrochloride in Bakersfield, California. Microgram Bulletin 2008;41(4):38-9.

4. Per request of the DEA Office of Diversion, the National Institute of Drug Abuse (NIDA) is currently conducting studies of the pharmacology of N-methyl-, N-ethyl-, and N-isopropyl-benzylamine.



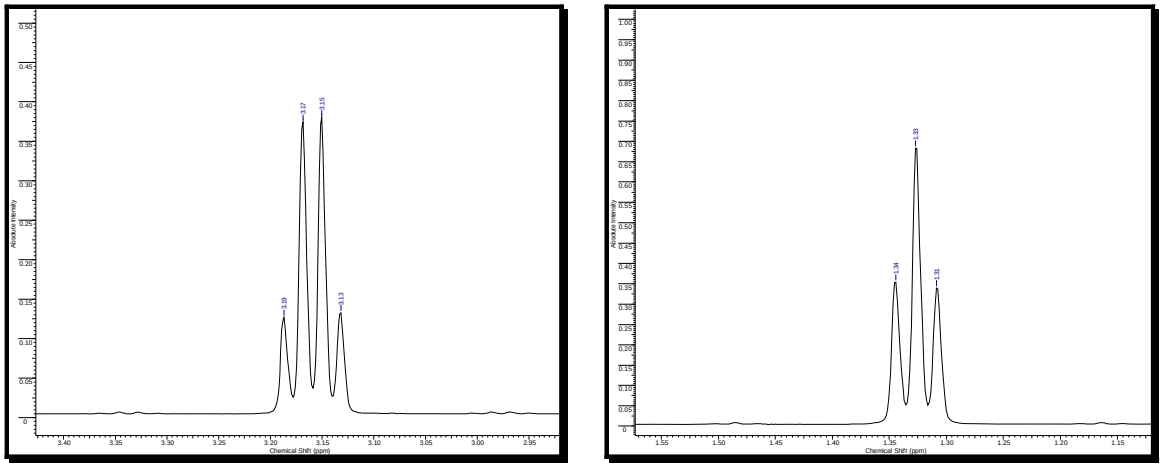
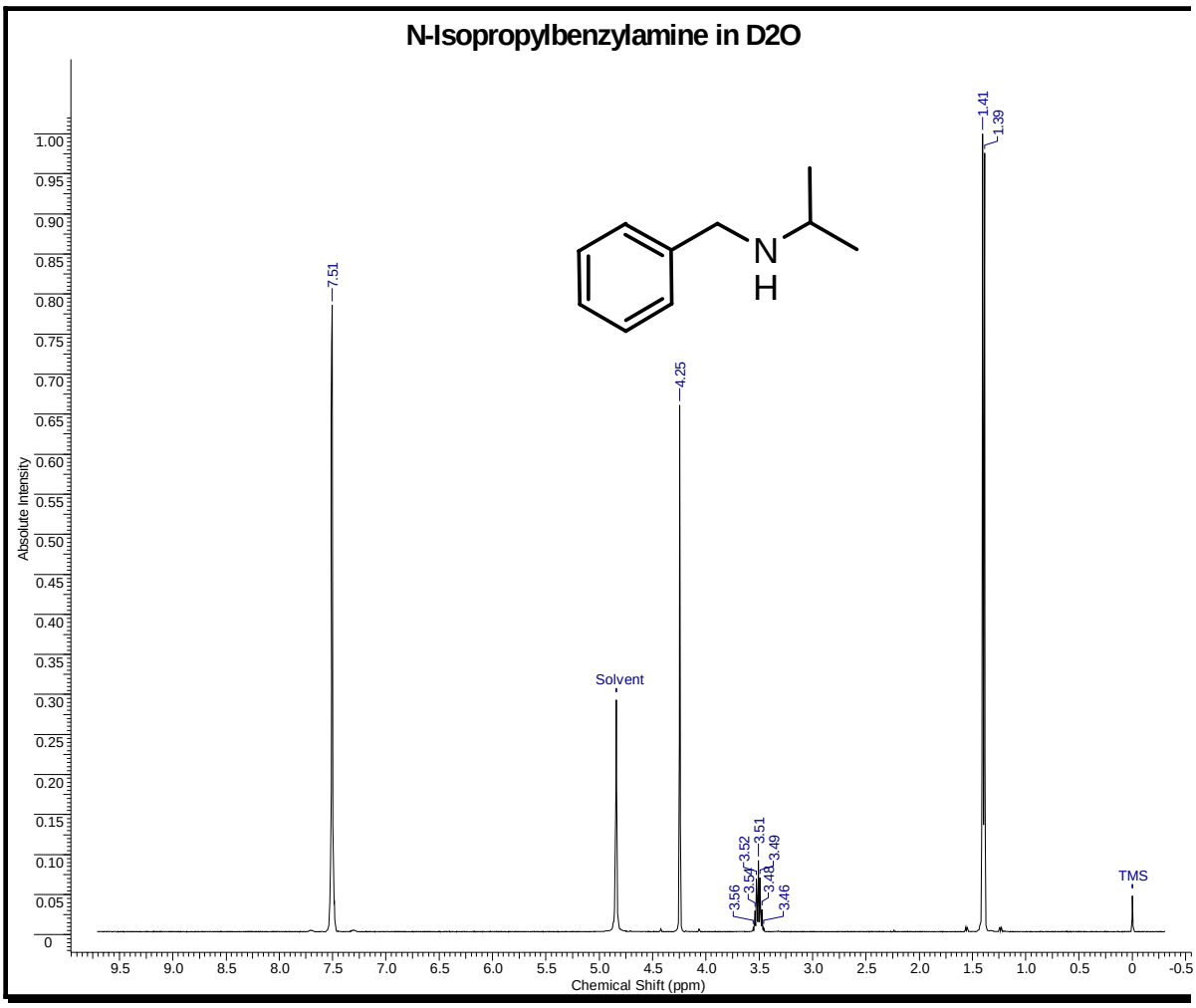



**Figure 5b.** 400 MHz $^{1}$H-NMR Spectrum of N-Ethylbenzylamine Hydrochloride in $D_2O$.



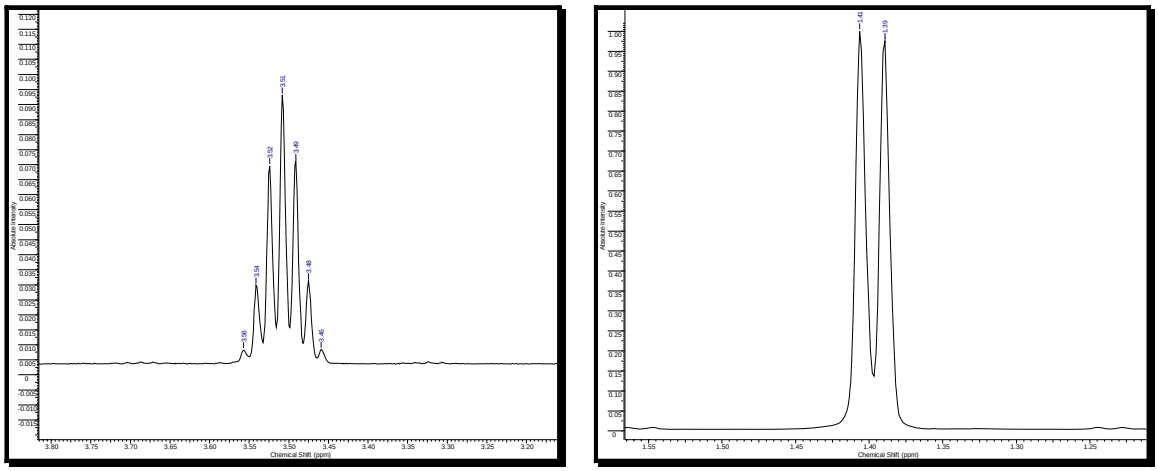



**Figure 5c.** 400 MHz $^{1}$H-NMR Spectrum of N-Isopropylbenzylamine Hydrochloride in $D_2O$.