All data taken at the Pacific Northwest National Laboratory
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Data Analysis: Tracy J. Baker

Composite spectrum for: 4-Amino-1-benzyl piperidine

- First Column: Position in wavenumber (cm^{-1})
- Second column: Real refractive index $n(\tilde{\upsilon})$ (dispersion index)
- Third column: Imaginary refractive index, $k(\tilde{\upsilon})$ (absorption index per unit length in centimeters)

Where the complex refractive index $\hat{n} = n(\tilde{\upsilon}) + ik(\tilde{\upsilon})$

Following Bertie (in the references below) we define the absorbance as $A = - \log_{10}(I/I_0)$ and the linear absorption coefficient $K = A/d$, where d is the path length. The connection between the imaginary refractive index and the absorbance coefficient arises from the following: $2.303K = 4 \pi \tilde{\upsilon} k$

See the following references for a detailed description of terms and units:

1) Bertie, J. E., Zhang, S. L., Eysel, H. H., Baluja, S., & Ahmed, M. K. (1993). Infrared Intensities of Liquids XI: Infrared Refractive Indices from 8000 to 2 cm^{-1}, Absolute Integrated Intensities, and Dipole Moment Derivatives of Methanol at 25°C. *Appl. Spec.,47*(8), 1100-1114 doi:10.1366/0003702934067973
2) Bertie, J. E., Zhang, S. L., & Keefe, C. D. (1995). Measurement and use of absolute infrared absorption intensities of neat liquids. *Vibrational Spectroscopy, 8*(2), 215-229. doi:10.1016/0924-2031(94)00038-i

Sample:

- Chemical name, formula and CAS number: 4-Amino-1-benzyl piperidine, $C_{12}H_{18}N_2$, [50541-93-0]
- IUPAC name: 1-Benzylpiperidin-4-amine
- Synonyms: 1-(Phenylmethyl)-4-piperidinamine
- Physical properties: FW = 190.28 g/mole; mp = 88 °C; bp = 306 °C; vp = 0.47 mTorr; $\rho = 0.933$ g/cm^3
- Supplier and stated purity: Sigma-Aldrich, 98% (Lot # STBK0387)
- Temperature of sample: 24 °C (+/-1 °C)
- Individual samples were measured at the following path lengths: MIR: 7.15, 15.8, 19.6, 35.7, 46.6, 92.0, 210, and 494 micrometers (μm); NIR: 92.1, 210, 495, 1006 and 2166 μm. Final data are a composite of these spectra.
- Sample cell window material: MIR = potassium bromide (KBr) except potassium chloride (KCl) for the 92.0 and 494 μm cells; NIR = KCl except KBr for the 92.1, 495 and 2166 μm cells.
- Preparation: None

NIR Instrument Parameters:

- Vertex 70, purged with UHP nitrogen
- Spectral range: 10,000 to 3,000 cm^{-1} (1 to 3.33 microns)
- NIR source: Quartz tungsten bulb
- Beamsplitter: Broadband potassium bromide (KBr)
- Detector: DLTGS at room temperature
- Aperture: 3 mm
- Folding limits: 31597.6 to 0 cm^{-1}

MIR Instrument Parameters:

- Tensor II with sample stage rotated 6 degrees, purged with UHP nitrogen
- Spectral range: 7,800 to 400 cm^{-1} (1.282 to 25 microns)
- IR source: Silicon carbide glow bar
- Beamsplitter: Potassium bromide (KBr)
- Detector: DTGS at room temperature
- Aperture: 3 mm
- Folding limits: 11664.16 to 0 cm^{-1}

NIR/MIR Instrument Parameters:

- Instrument resolution: 2.0 cm^{-1}
- Number of interferograms averaged per single channel spectrum: 128
- Apodization: Norton-Beer, Medium
- Phase correction: Mertz
- Scanner velocity: 10 kHz; 7.5 kHz (MIR)
- Interferogram zerofill: 4x
- Spectral interval after zerofilling: 0.4822 cm^{-1}

a) b)

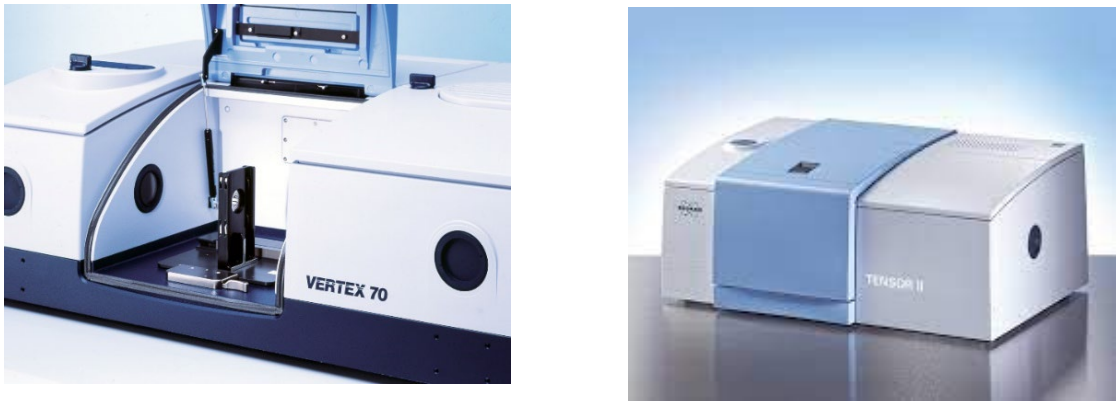

Figure 1: The Bruker Vertex 70 FTIR (a) and Tensor II (b).

Measured Refractive Index:

The refractive index for 4-Amino-1-benzyl piperidine was measured at 25 °C using an Atago model DR-M2/1550 Abbe refractometer. Notch filters were employed in front of a white light source to make measurements at multiple wavelengths. An infrared viewer from Atago was used to detect signal at 1550 nm. The temperature was controlled to match that in the sample compartment of the FTIR using a heated circulating bath.

480 nm: n = 1.5535	486 nm: n = 1.5529	546 nm: n = 1.5454
589 nm: n = 1.5418	644 nm: n = 1.5381	656 nm: n = 1.5374
1550 nm: n = 1.5168		

The refractive index, n, vs. wavelength in microns, λ, was fit to an equation similar to that of Sellmeier:

$$n(\lambda) = \{a + b/(\lambda^2 - c)\}^{1/2}$$

The resulting best-fit equation was used to find the refractive index at the highest energy data points in our experimental spectra. For 4-Amino-1-benzyl piperidine, the results were

n(7,800 cm^{-1}) = 1.5192 at 25 °C for MIR data and
n(10,000 cm^{-1}) = 1.5237 at 25 °C for NIR and merged data.

Post Processing and Related Parameters:
For the MIR, a composite spectrum was created from 8 absorbance spectra (base-10) taken at 8 path lengths: 7.15, 15.8, 19.6, 35.7, 46.6, 92.0, 210, and 494 micrometers (μm). These data were collected with the sample stage rotated by -6° to minimize artifacts resulting from back-reflection into spectrometer (see Johnson et al., *Appl. Spectrosc.*, 76(5) 620-624, 2021). For the NIR, a composite spectrum was created from 5 absorbance spectra (base-10) taken at 5 path lengths: 92.1, 210, 495, 1006 and 2166 μm. The same cells and liquid fills for the ~100, 200 and 500 μm path lengths were used for both spectral ranges. At each path length several spectra were measured and the results averaged for better signal to noise. The measured cell lengths were adjusted using Beer's law plots in which the NIR and MIR data were analyzed independently.

1) The imaginary part of the refractive index, or *k* vector, was determined for each absorbance file as per Bertie's program "RNJ46A" (see reference above). This takes into account the reflective losses due to the KBr and/or KCl windows.
2) A composite *k* vector is created via a classical, weighted, linear, least squares fit using the output files of program "RNJ46A": Intercept=0, slope is fitted, individual absorbance values weighted by T^2 (transmission squared), all absorbance values ≥ 2.5 are given zero weight. For the MIR, eight composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 210 and 494 μm cells. This *k* vector determined the final values for the range from 7800 to 3400 cm^{-1}.
   b) The second *k* vector used the results from the 92.0 and 210 μm cells. This *k* vector determined the final values for the range from 3400 to 3100 cm^{-1}.
   c) The third *k* vector used the results from the 19.6 through 92.0 μm cells. This *k* vector determined the final values for the range from 3100 to 2950 cm^{-1} and 2000 to 750 cm^{-1}.
   d) The fourth *k* vector used the results from the 7.15 through 35.7 μm cells. This *k* vector determined the final values for the range from 2950 to 2620 cm^{-1}.
   e) The fifth *k* vector used the results from the 494 μm cell. This *k* vector determined the final values for the range from 2620 to 2000 cm^{-1}.
   f) The sixth *k* vector used the results from the 7.15 through 46.6 μm cells. This *k* vector determined the final values for the range from 750 to 695 cm^{-1}.
   g) The seventh *k* vector used the results from the 35.7 through 210 μm cells. This *k* vector determined the final values for the range from 695 to 500 cm^{-1}.
   h) The eighth *k* vector used the results from the 46.6 to 210 μm cells. This *k* vector determined the final values for the range from 500 to 370 cm^{-1}.
3) A frequency correction was applied to the resulting composite MIR *k* vector.
   a) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * 0.99988 + 0.025] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
4) For the NIR, five composite vectors were created and merged by hand.
   a) The first *k* vector used the results from the 2166 μm cell. This *k* vector determined the final values for the range from 10000 to 6550 cm^{-1}.
   b) The second *k* vector used the results from the 1006 and 2166 μm cells. This *k* vector determined the final values for the range from 6550 to 4400 cm^{-1} and 4000 to 3675 cm^{-1}.
   c) The third *k* vector used the results from the 210 through 1006 μm cells. This *k* vector determined the final values for the range from 4400 to 4000 cm^{-1}.
   d) The fourth *k* vector used the results from the 92.1, 495 and 2166 μm cells. This *k* vector determined the final values for the range from 3675 to 3380 cm^{-1}.
   e) The fifth *k* vector used the results from the 92.1 through 495 μm cells. This *k* vector determined the final values for the range from 3380 to 370 cm^{-1}.
5) The resulting composite NIR *k* vector and the refractive index at 10,000 cm^{-1} were used to create the real or *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."
   a) Frequency correction (already applied): $\tilde{\upsilon}$(corrected) = [$\tilde{\upsilon}$(instrument) * 0.99998 - 0.0005] as determined by comparing measured atmospheric spectral lines (H_2O and CO_2) to values from the Northwest Infrared Spectral Library Database.
6) The MIR data were mapped onto the NIR x-axis using an interpolation routine, i.e. the Make Compatible

command in OPUS 5.5. Then the composite MIR and NIR *k* vectors were merged to generate a final composite *k* vector across the entire spectral range. The NIR data were used exclusively above 2989 cm^{-1}, and only the MIR data were used below 2955 cm^{-1}. A weighted average, with the weight of the MIR vector increasing linearly from 0 to 100% between 2989 and 2955 cm^{-1} was used in the overlapping spectral region. The resulting composite *k* vector and the refractive index at 10,000 cm^{-1} were used to create the final *n* vector using the Kramers-Kronig relation, as per Bertie's program "LZZKTB."

Photograph of Sample 4-Amino-1-benzyl piperidine:

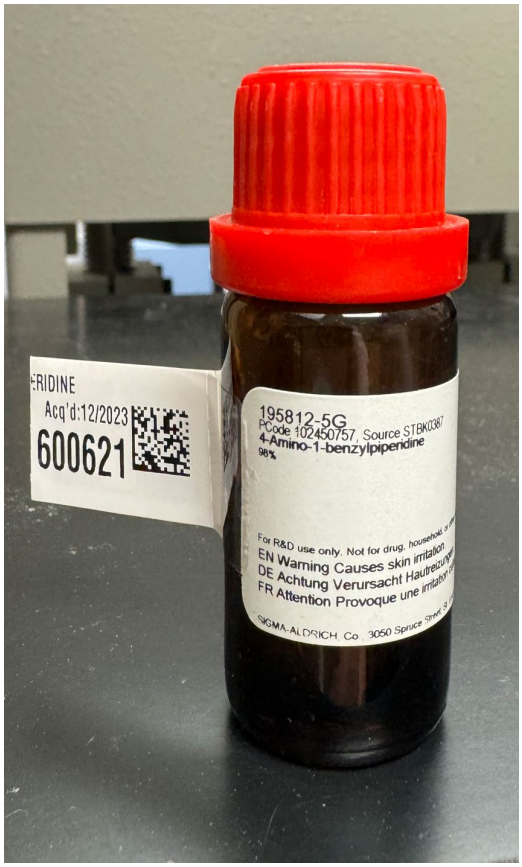

Figure 2: 4-Amino-1-benzyl piperidine in Sigma-Aldrich container for NIR and MIR measurements.