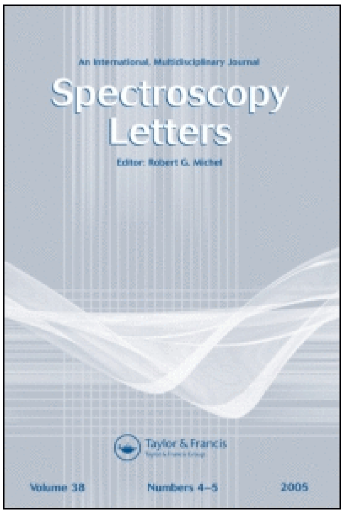

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Matrix Isolation Infrared Spectroscopic and Density Functional Theory Study of the 1:1 Complex of Bromocyclohexane with NH_3: Evidence for a Weak C-H–N Hydrogen Bond

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ABSTRACT The hydrogen-bonded bromocyclohexane–ammonia complex has been isolated and characterized for the first time in argon matrices at 16 K. Coordination of the proton adjacent to the Br substituent on the cyclohexane ring to the amino nitrogen was evidenced by distinct blue shifts of bending modes involving the H-C_1-Br unit. In particular, C-C_1-Br, H-C_1-Br, and C-C_1-H bending modes produced blue shifts ranging from 2.8 to 12.2 cm^{-1}. Density Functional Theory (DFT) calculations at the B3LYP/6–31 + G(d, p) level yield an essentially linear Br-C_1-H–NH_3 hydrogen bond with a C-H–N distance of 2.412 Å and a hydrogen bond energy of 2.95 kcal/mol.

KEYWORDS: Matrix isolation, hydrogen-bonding, Density functional theory, Molecular spectroscopy

INTRODUCTION

The concept of the hydrogen bond is important to fields such as chemistry, biology, biochemistry, and physics as well as phenomena that lie at the interface of these areas.[1] Examples of such interdisciplinary areas include molecular recognition,[2] crystal engineering,[3] and the structure and stability of biomolecules.[4] The textbook definition of a hydrogen bond is "the interaction of a partially positive charged proton situated between two highly electronegative atoms such as N, O, or F." Hydrogen bonds involving the C-H group, which do not fit this traditional definition, were documented as early as 1960,[1] and in 1982 the first crystallographic evidence of C-H–X (X=O, N, etc.) hydrogen bonds was published.[5] Since then, studies involving weak hydrogen bonds have been prolific.[6] Despite their importance, these types of hydrogen bonds elude undergraduate chemistry textbooks and are rarely mentioned in the undergraduate curriculum.

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There are abundant examples in the literature of research involving C-H–O hydrogen bonds,[7] especially with regard to the role of C_α-H–O in stabilizing protein structures.[8] C-H–N hydrogen bonds, however, have not been studied to the same extent, although there are numerous published studies, both experimental[9] and theoretical.[10] Some of these studies involve hydrocarbon–ammonia complexes, and in fact ammonia is ideal for the study of C-H–N linkages, as it has been demonstrated to act as a Lewis base that interacts through its lone-pair electrons rather than donating a proton.[11,12]

Very few studies of C-H–N hydrogen bonds involve a carbon that is sp^3-hybridized. Previously in our laboratory, we formed complexes between bromocyclopropane and the nitrogen bases ammonia and trimethylamine. The resulting C-H–N hydrogen bonds are some of the weakest formed in a matrix to date and represent the first complexes in which a cyclopropane is shown to donate a proton in hydrogen bond formation and only the second example of an alkane taking part in a C-H–N hydrogen bond.[13] Another study from our lab involves cyclopentadiene with N and O bases and presents the first example of an sp^3-hybridized carbon that is not adjacent to a carbonyl (i.e., a non-α-carbon) or other electron withdrawing substituent taking part in a C-H–N(O) hydrogen bond.[14]

This study builds on previous work and provides an interesting comparison with cyclopropane and bromocyclopropane. Cyclopropane, c-C_3H_6, exhibits unusual chemical properties because of the high degree of ring strain and behaves more like an olefin than an alkane.[15,16] Cyclohexane (c-C_6H_{12}), on the other hand, eliminates all ring strain by adopting nonplanar conformations such as the boat, chair, and twist-boat.[17] This conformational flexibility makes cyclohexane a prototypical example in organic chemistry. In addition to being interesting in its own right from both an experimental and theoretical standpoint, cyclohexane rings play important roles in organic crystals[18] and intercalataing drugs, where hydrogen-bonding interactions involving ring substituents act as an anchor.[19] Monosubstituted cyclohexanes, although locked in the chair form, are also conformationally flexible, as they can exist as axial or equatorial conformers. Such conformers have recently been isolated in a pure state as inclusion complexes in host compounds such as thiourea.[20]

The matrix isolation technique, combined with infrared spectroscopy, is ideal for the study of weak hydrogen bonds. Furthermore, it provides undergraduate students with a research experience that reinforces—yet goes beyond—concepts and skills learned in the undergraduate curriculum.

MATERIALS AND METHODS

All of the experiments conducted in this study were carried out in a completely stainless steel vacuum system, with Nupro (Solon, OH) Teflon-seat high vacuum valves. Pumping was provided by a model 1400B Welch (Niles, IL) vacuum pump, and either a Varian (Lexington, MA) HSA diffusion pump with a liquid nitrogen trap or a turbomolecular pump (Varian V301). Pressures of the order 10^{-7} mm Hg at the gauge (cold cathode; Varian) were attained using this apparatus. Cryogenics were supplied by a model 22 closed cycle helium refrigerator (CTI Cryogenics, Inc., Mansfield, MA), which operates down to 10 K. Gas samples were deposited from 2-L stainless steel vessels through a precise metering valve onto the cold surface, which is a CsI window mounted with indium gaskets to a copper block, which is in turn mounted with indium gaskets on the second stage of the CTI Cryogenics refrigerator's cold head. Deposition of the gas samples was perpendicular to the cold surface. Temperatures at the second stage of the cold head were controlled and monitored by a LakeShore (Westerville, OH) 321 digital cryogenic temperature controller. The vacuum vessel was equipped with CsI windows and sat in the sample beam of a Nicolet Nexus 670 infrared spectrometer for the duration of the experiment, and the sample was monitored during the entire deposition. The matrix isolation apparatus described here is standard and has been described thoroughly elsewhere in the literature.[21]

The liquid reagents employed, cyclohexane (Ch) and bromocyclohexane (BrCh) (both Acros Organics, Waltham, MA), were used without further purification. The gaseous reagent, ammonia (NH_3) (Matheson, Newark, CA), was subjected to one or more freeze-thaw cycles at 77 K prior to sample preparation, and argon (Matheson; 99.999%) was used without further purification as the matrix gas in all experiments.

Samples were deposited in the twin-jet mode (i.e., the two reactants were codeposited from separate vacuum lines). Ch/Ar samples were prepared by standard manomeric techniques in which Ch vapor is added to the vessel with the argon. BrCh on the other hand is relatively involatile, thus we attached a side arm to the deposition line, separated by a valve, to hold the BrCh. The argon then entrained the vapor from the side arm. This technique is commonly used with samples whose vapor pressure is less than 1 mm Hg at room temperature. The drawback to such a technique is that it is difficult to vary and measure matrix ratios. Samples were deposited at rates ranging from approximately 0.5–2 mmol/h, for times ranging from 22 to 30 h, and at temperatures ranging from 10 to 20 K. Survey scans and high-resolution scans were recorded at resolutions of 0.5, 0.25, and 0.125 cm^{-1}. Some samples were annealed to approximately 32 K, recooled to 16 K, and additional spectra were obtained.

Computations were carried out using the Gaussian 98 package to confirm complex assignments.[22] The B3LYP density functional method was used for all calculations, and the electronic density of all atoms were represented by a 6–31 + G(d, p) all electron basis set. Geometries were fully relaxed during optimization, and initial starting orientations were given such that the CH···N angle was nearly collinear. The interaction energy was computed as $\Delta E_{\text{int}} = E_{\text{complex}} - (E_{\text{acid}} + E_{\text{base}})$. Vibrational frequencies were calculated analytically from second derivatives of the potential surface, and all energy values reported include zero-point energy corrections. To evaluate hydrogen-bond interaction energies, basis set superposition error was corrected by the counterpoise method. We note that in the case of BrCh-NH_3, the computations described here were performed for both axial and equatorial conformers of BrCh.

EXPERIMENTAL RESULTS

Prior to any codeposition studies, blank experiments were carried out on the parent molecules, Ch, BrCh, and NH_3. The resulting spectra were in excellent agreement with literature spectra[23–28] as well as with spectra recorded previously in this laboratory. In addition, to ensure a precise comparison between parent and complex spectra, blank experiments were performed at each different concentration of base such that argon (but no BrCh in plug) was deposited from one vacuum line and NH_3/Ar from the other line so that the experiment was exactly duplicated but with no BrCh. In all experiments, we found that an NH_3/Ar ratio of 1/250 with BrCh cooled slightly to lower its vapor pressure yielded best results.

***Ch + NH*$_3$.** Ch/Ar and NH_3/Ar were codeposited in many experiments at concentrations ranging from 1000/1/1 (Ar/Ch/NH_3, meaning Ar/Ch at 500/1 was co-deposited with Ar/NH_3 at 500/1) to 200/1/1, and no new product absorptions and hence no evidence of complex formation was noted.

***BrCh + NH*$_3$.** The codeposition of samples of BrCh/Ar with NH_3/Ar gave rise to new infrared absorptions that could not be ascribed to either parent species. Some of these spectral features were distinct new bands, totally separate but in close proximity to parent vibrational modes, where as others were shifted only slightly from parent modes and still within the envelope of the parent absorption. In particular, absorptions in the former category were observed at 1466.5, 1332.0, 1266.3, 1123.8, and 919.8 cm^{-1}, and those in the latter category were observed at 2961.2, 2855.9, and 1452.1 cm^{-1}. In addition, many shifts in the range 0.5–1.0 cm^{-1} were noted, however, such shifts are on the order of those caused by matrix effects and thus are not used as evidence for hydrogen bond formation. We note that there are many very intense parent bands in the region 2920–2940 cm^{-1}, making it difficult to draw conclusions about any shifts in this region, and we emphasize in section 5 that these bands are not important to our analysis. These bands are still present in the codeposition spectrum but are now broad and much less intense. In general in matrix spectra, that some parent bands seem to disappear can be explained by the fact that some of the sites in the parent matrix may not be present in the codeposition matrix. Representative spectra are shown in Figs. 1–3.

COMPUTATIONAL RESULTS

Chemical properties indicating the strength of a hydrogen bond include bond energy, bond lengths and angles, and relative vibrational shifts from parent to complex. Because the frequency calculations were performed mainly to rationalize the experimental observations of the BrCh-NH_3 complex, only the

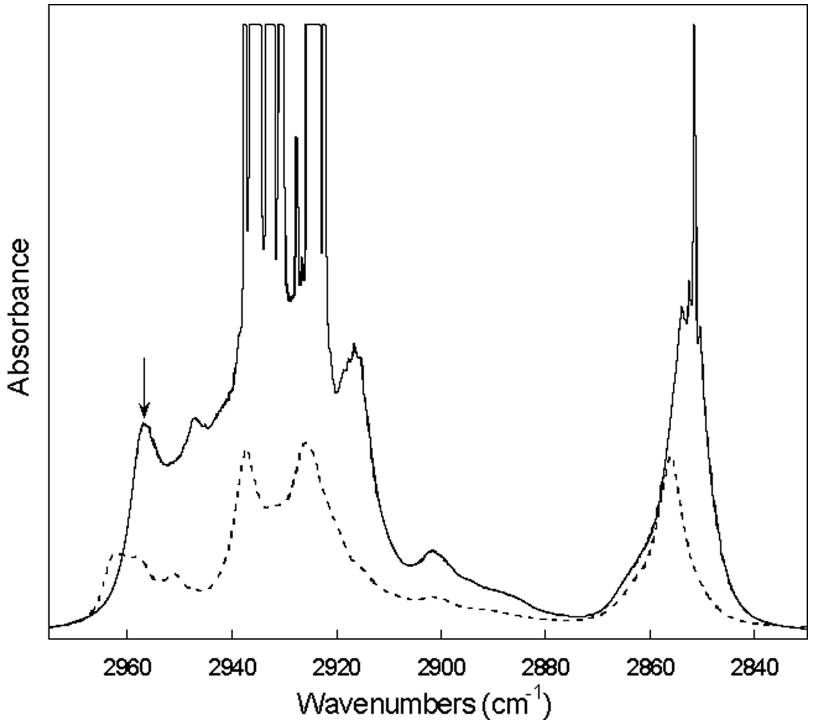

FIGURE 1 Infrared spectra (0.250 cm^{-1} resolution) in the C_1-H stretching region for parent BrCh/Ar (solid trace) and codeposition mixture BrCh/NH_3/Ar (dashed trace) on CsI at 16 K. There are no NH_3 absorptions in this region. Parent fundamental that shifts is marked with an arrow.

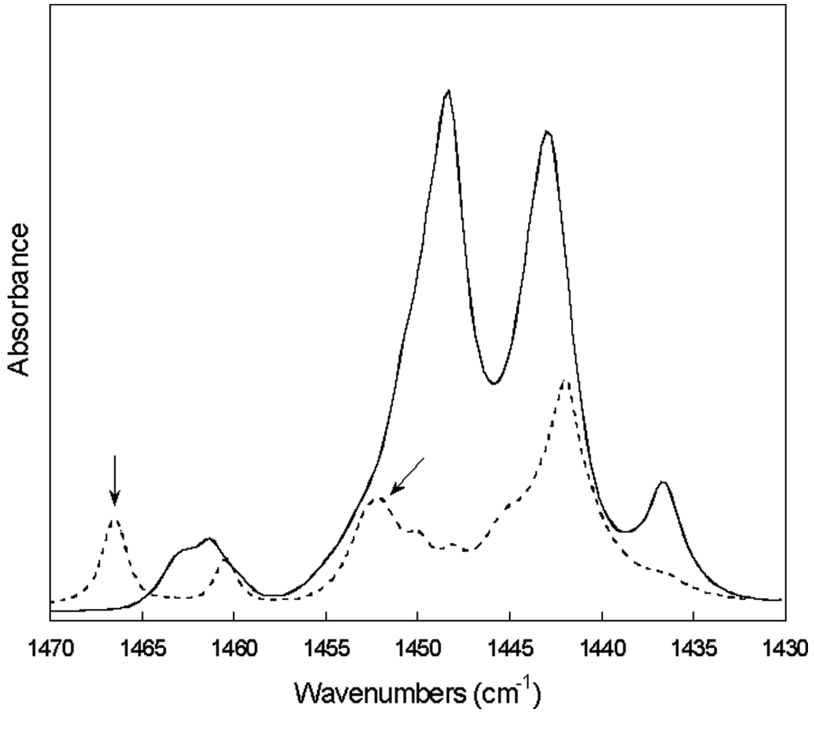

FIGURE 2 Infrared spectra (0.250 cm^{-1} resolution) for parent BrCh/Ar (solid trace) and BrCh/NH_3/Ar codeposition mixture (dashed trace) on CsI at 16 K. The product band at 1466.5 cm^{-1} is near the parent C-C-H and H-C-H bend, and the product band at 1452.1 cm^{-1} is near the parent C-C_1-Br bend. New product bands are marked with arrows. There are no NH_3 absorptions in this region.

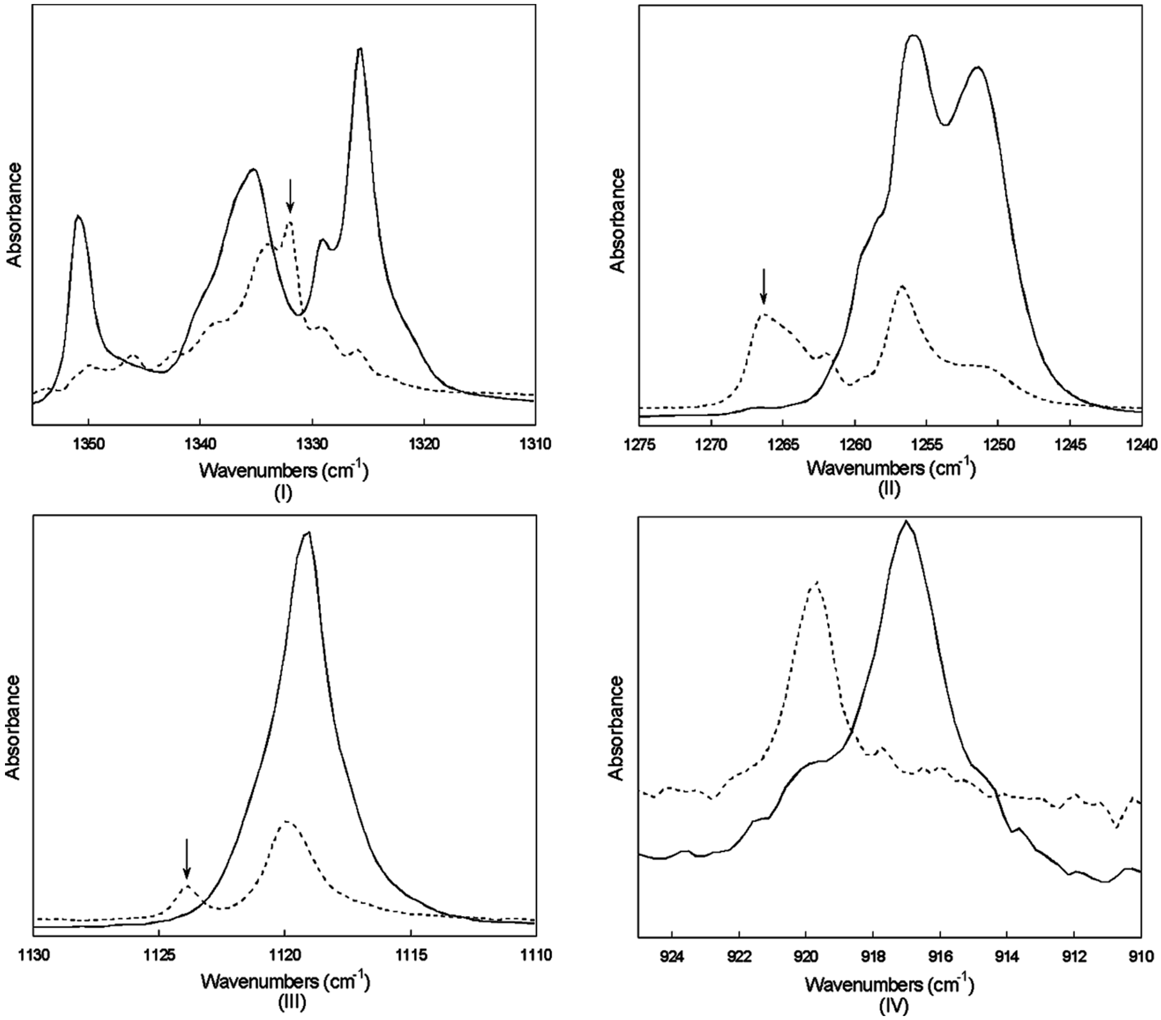

FIGURE 3 Infrared spectra (0.250 cm^{-1} resolution) of parent BrCh/Ar (solid traces) and codeposition mixture BrCh/NH_3/Ar (dashed traces) on CsI at 16 K. There are no NH_3 absorptions in these regions. Product bands (marked with an arrow) fall to the blue of the following parent modes: Panel I: C-C_1-Br, H-C_1-Br, C-C_1-H bends. Panel II: H-C_1-Br and C-C-H bends. Panel III: H-C_1-Br and C-C-H bends. Panel IV: H-C_1-Br bend, C-C-H bend, C-C stretch.

TABLE 1 Observed and Calculated Vibrational Frequencies Associated with the Bromocyclohexane Fundamentals[a]

Observed			Calculated[c]	
BrCh	BrCh-NH_3	Fundamental[b]	BrCh	BrCh-NH_3
2956.8	2961.2 (+4.4)	C_1-H or C_1-H(Br) stretch[e]	3110.1	3112.1 (+2.0)
2852.5	2855.9 (+3.4)	C-H stretch	3018.8	3022.3 (+3.5)
1461.4	1466.5 (+5.1)	C-C-H bend, H-C-H bend	1386.5	1411.9 (+25.4)
1448.4	1452.1 (+3.7)	C-C_1-Br bend	1378.0	1381.0 (+3.0)
1325.7	1332.0 (+6.3)	C-C_1-Br, H-C_1-Br, and C-C_1-H bends	1332.3	1336.4 (+4.1)
1254.1[d]	1266.3(+12.2)	H-C_1-Br bend, C-C-H bend	1121.1	1243.4 (+22.3)
1119.9	1123.8 (+4.7)	H-C_1-Br bend , C-C-H bend	1141.1	1150.6 (+9.5)
917.0	919.8 (+2.8)	H-C_1-Br bend, C-C-H bend, C-C stretch	930.2	937.2 (+7.0)

[a] Wavenumber in cm^{-1}. Values in parentheses represent the frequency shifts with respect to the isolated BrCh.

[b] Reference [23].

[c] Unscaled frequencies. Calculated at the B3LYP/6–31+G(d, p) level.

[d] Doublet, mean value reported.

[e] C_1 denotes the carbon with the Br substituent.

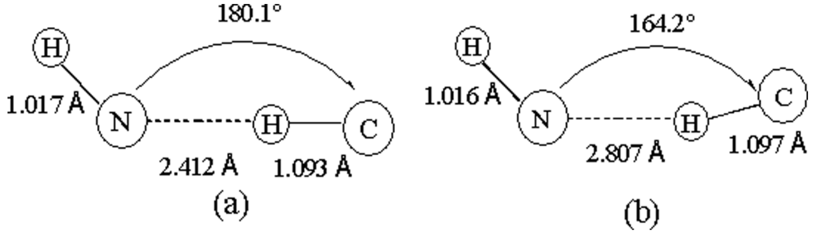

FIGURE 4 Important geometrical values of the (a) BrCh-NH_3 and (b) Ch-NH_3 complexes computed with the B3LYP/6-31 + G(d,p) density functionals. All bond lengths are in angstroms, and angles are in degrees.

relevant BrCh modes and corresponding frequency shifts upon complexation are summarized in Table 1. Because only relative frequency shifts are of interest, unscaled frequencies are reported. Furthermore, we report the results for the equatorial conformer in Table 1, as this is the preferred conformer in the matrix and the conformer for which there is superior agreement between experiment and theory. A study of the individual conformers is beyond the scope of this study and, as discussed later, does not provide additional, useful information about the C-H–N hydrogen bond.

The Ch-NH_3 and BrCh-NH_3 complexes were calculated to have binding energies of 0.63 and 2.95 kcal/mol and C-H–N bond distances of 2.807 and 2.412 Å, respectively. To be consistent with notation that follows, we note for clarity that C-H–N is actually C_1-H—N, thus emphasizing that the proton taking part in the hydrogen bond is attached to the same carbon as the Br subsitutuent (i.e., C_1). Furthermore, the C-H (i.e., C_1-H in the case of BrCh) bond length for both Ch and BrCh was predicted to remain the same (1.097 and 1.093 Å, respectively) upon complex formation. In the Ch-NH_3 complex, the amino nitrogen was located above the ring, interacting with the axial hydrogens. In contrast, in the BrCh-NH_3 complex, the amino nitrogen interacted entirely with the H-C_1-Br unit, resulting in a linear C-H–N hydrogen bond angle (180.1°) for BrCh-NH_3 compared with that of 164.2° for Ch-NH_3 (Fig. 4).

DISCUSSION

Evidence for hydrogen-bonding interactions between the cyclohexanes and ammonia comes from a direct comparison of the infrared spectra of the isolated hydrocarbon acids and bases (i.e., the blank or parent spectra) with those spectra obtained in the codeposition experiments. When Ch was deposited with NH_3, there was no evidence of complex formation. This result is not surprising, as Ch is an extremely weak carbon acid with a pK_a of 45.[16] When cyclopropane, which has a pK_a of 39[16] and significant ring strain, was codeposited with ammonia, there was no evidence of complex formation.[13] In addition, although cyclopropane was shown to form a hydrogen-bonded complex with all of the hydrogen halides,[29,30] cyclohexane was shown to form a hydrogen-bonded complex with HBr but not with HCl, and relevant frequency shifts were much smaller, thus reflecting a weaker hydrogen bond in the case of cyclohexane.[31] The hydrogen bond formed in these situations is between the electron density of the ring and the proton on the hydrogen halide. Our DFT calculations yield for Ch-NH_3 a hydrogen bond strength of 0.63 kcal/mol, and our previous work yields a hydrogen bond strength of 1.00 kcal/mol for bromocyclopropane-NH_3,[13] which agrees quite well with other published work.[32] These small interaction strengths could possibly explain the lack of observation of such complexes.

When BrCh was codeposited with NH_3, new, distinct bands located near parent BrCh modes were observed, as well as new bands that appeared within the envelope of parent BrCh modes (Figs. 1–3). The proximity of the product absorptions to modes of the parent species suggests that the BrCh and NH_3 retain their structural integrity, and therefore the product is not the result of addition, elimination, or rearrangement of the subunits. Although some of the spectral changes are small, the product bands are distinct and easily observable. Furthermore, the intensities of the product absorptions were directly proportional to the concentration of the reagents, and the product bands were observed over the entire range of concentrations studied. These observations point to a single product species with 1:1 stoichiometry. This is expected, as addition of the Br substituent makes the proton attached to that same carbon (i.e., C_1) the most acidic proton and therefore the most likely site for hydrogen bond formation. Also, as NH_3 interacts through its lone-pair electrons,[11,12] we can be certain that the acidic proton of BrCh hydrogen-bonds to the N atom of NH_3, thus forming a C_1-H—N linkage (Fig. 4). This is supported by DFT, which predicts that when the Br substituent is added to the ring, the amino nitrogen interacts entirely with the H-C_1-Br unit, forming a linear hydrogen bond. This is in contrast with the situation for Ch-NH_3 where the amino nitrogen sits above the ring and interacts with the axial hydrogens. Strikingly similar results were obtained in our previous study of cyclopropane and bromocyclopropane.[13]

The observable most commonly used in the characterization of hydrogen-bonded systems is the shift of the parent C-H stretch that involves the hydrogen-bonded hydrogen (ν_s). Numerous studies involving alkynes[33–35] and alkenes[36,37] confirm that this shift, commonly referred to as $\Delta\nu_s$ in the hydrogen-bonding literature, is a reliable measure of the strength of interaction. For example, for the acetylene-NH_3 complex,[34] $\Delta\nu_s$ is 122 cm^{-1}, whereas for ethylene-NH_3 it is 14.[37] Often, however, this region of the spectrum is obscured by intense parent C-H stretching modes. It is fortuitous for us that the BrCh parent C_1-H stretching mode (where H is the "acidic" proton on the same carbon as the Br substituent) at 2956.8 cm^{-1} is the highest energy C-H stretch, and therefore we were able to observe a product band at 2961.2 cm^{-1}, 4.4 cm^{-1} to the blue of the parent band. Although one could argue that this spectral feature is simply a broadening of the parent band, DFT calculates a 2.0 cm^{-1} blue shift for this mode, thus supporting that this may in fact be a true shift rather than a matrix effect. Typically, ν_s shifts to lower energy, with greater shifts denoting a stronger hydrogen bonding interaction. This normally corresponds with a C_1-H bond distance that is slightly elongated in the complex relative to the parent, indicating that this C_1-H bond is weakened by its interaction with NH_3, implying a red shift upon complexation. In the case of BrCh, the C_1-H bond distance of 1.093 Å remains unchanged upon complexation. Likewise, in our bromocyclopropane study, the C_1-H distance (designated C-H(Br) in that study) was essentially unchanged, and a blue shift of 6.9 cm^{-1} was predicted. We did not observe such a shift in that system, as the C-H stretching region of the spectrum was obscured by several weak and overlapping parent bands.[13] Finally, we also observed a blue shift of 3.4 cm^{-1} in a BrCh C-H stretching mode at 2852.5 cm^{-1} that does not involve the H-C_1-Br proton. DFT predicts a 3.4 cm^{-1} blue shift in this mode. We note that although blue shifts in ν_s are not commonly observed, several published studies report that they occur in certain C-H–O hydrogen bonds.[38,39]

A second important category of vibrational modes providing strong evidence for hydrogen bond formation is that of H-C-X bending modes. Past matrix studies of alkenes with nitrogen bases reveal product absorptions occurring near and to the blue of the parent C-H_2 or H-C-X bending modes.[18] It is interesting to note that our *only* evidence for hydrogen bond formation in the bromocyclopropane-NH_3 complex comes from changes in the C-H(Br) bending modes. Specifically, we observed a 12 cm^{-1} blue shift in the in-plane bend and a 6 cm^{-1} blue shift in the out-of-plane bend.[13] Notably, four of our five most distinct product absorptions for BrCh-NH_3 (Fig. 3) involve bending of the H-C_1-Br "corner" of the molecule. By this we mean that these modes involve H-C_1-Br bends as well as C-C_1-Br and C-C_1-H bends. Each product absorption lies to the blue of a parent mode, and thus these results are consistent with what has been previously observed. In addition to these distinct bands, we observed a product band at 1452.1 cm^{-1}, 3.7 cm^{-1} to the blue but still within the envelope of the parent C-C_1-Br bend at 1448.4 cm^{-1} (Fig. 2). DFT predicts a 3.0 cm^{-1}blue shift in this mode, thus supporting that this may in fact be a new product band.

Additional modes of BrCh were perturbed by hydrogen bond formation. This is characteristic of hydrogen bond formation, because, if a vibrational mode causes the region of the molecule associated with the hydrogen bond to be displaced then there is likely to be a perturbation in this mode. We observe a new product band at 1466.5 cm^{-1}, shifted 5.1 cm^{-1} to the blue of the parent band at 1461.4 cm^{-1}. This band is reported in the literature as being a C-C-H bend and an H-C-H bend and not specifically involving the H-C_1-Br unit. Notably, this fundamental corresponds with our largest calculated shift (+25.4 cm^{-1}). We are not sure why we observe a much smaller shift than that calculated. We note upon viewing the animated vibration for this mode that this vibration causes very large displacements in the atoms involved (i.e., these bends involve large sweeping motions). Perhaps this range of motion is restricted in the argon lattice, and thus there is not as much of a change in the dipole moment derivative upon hydrogen bond formation as is calculated. Thus, this discrepancy could possibly reflect that DFT cannot account for matrix effects.

Another interesting feature of BrCh is that it can exist either in the axial (*a*) or equatorial (*e*) form. It is well-known that in the liquid phase, the *e*-conformer is more stable, and that upon cooling the liquid, the *e*-conformer should be even more preferred.[40,41] Based on previous infrared studies, we conclude that we may have some of the *a*-conformer in the matrix. Our evidence for this comes from the fact that although most of the parent bands are identical for the *a*- versus *e*-conformer, there are a few bands for which the *a*-conformer's fundamental does not overlap with that of the *e*-conformer.[23–25] One such example is our parent doublet (mean value 1254.1 cm^{-1}), with individual maxima at 1256.2 and 1252.1 cm^{-1}, which coincide with literature values of 1256 (both *a*- and *e*-conformers) and 1251 cm^{-1} (*a*-conformer only). Our band at 1252.1 cm^{-1} is quite strong, as reported in the literature,[23] and thus we have this conformer in the matrix. We note, however, that our DFT results for axial BrCh predict a large red shift (−38.1 cm^{-1}) for this mode, which we do not observe. Furthermore, the correlation between our equatorial BrCh calculations and experimental results is much better than that of the axial DFT results. It is also important to note that DFT predicts identical hydrogen bond strengths for both conformers, and we therefore feel confident in focusing this study on the *e*-conformer. In addition, the important conclusions drawn from this work are based on a close comparison of parent to complex and not on a comparison of the two conformers.

In general, the theoretical frequencies summarized in Table 1 support our experimental results. We note that our largest experimental shift of 12.2 cm^{-1} corresponds with a calculated shift of 22.3 cm^{-1}, which is the second largest calculated shift. It is interesting that for this bending mode as well as those at 1119.9 and 917.0 cm^{-1} (all of which involve a H-C$_1$-Br bend), the calculated shifts are approximately twice the observed experimental shifts, which is precisely the case with the two bending modes in the bromocyclopropane-ammonia complex. We are not sure why this is the case, but raise it as an interesting comparison. Also, the experimental and calculated shifts for H-C-X bending modes for BrCh are very similar in magnitude to those for bromocyclopropane, thus demonstrating that these two systems behave quite similarly.

The calculated hydrogen bond strength for BrCh-NH$_3$ is 2.95 kcal/mol, which is higher than our published value for the bromocyclopropane-NH$_3$ complex (2.35 kcal/mol, MP2). We repeated this calculation using the same computational methods employed here for BrCh (B3LYP/6-31 + G(d, p)) and obtained a similar result of 2.50 kcal/mol. Although we are somewhat surprised, based on relative carbon acid strengths, that the hydrogen bond strength is higher for the BrCh-NH$_3$ complex, we feel evidence is emerging that may show that carbon acidity is not the most important factor in determining hydrogen bond strength. For example, our previous cyclopentadiene work yields a hydrogen bond strength of 2.40 kcal/mol (MP2) for the cyclopentadiene-NH$_3$ complex, and in fact this energy is divided equally between a C-H–N and an NH–π interaction.[14] Thus, the strong carbon acid cyclopentadiene, which has a pK_a of 15—close to that of acetylene's value of 16[16]—forms a C-H–N hydrogen bond that is weaker than that of BrCh-NH$_3$ and about equal to that of bromocyclopropane-NH$_3$. We also note that the calculated hydrogen bond strength for the acetylene-NH$_3$ complex calculated at the B3LYP level is 2.2 kcal/mol. In fact, Radom and Hartmann studied the effect of a variety of theoretical methods and basis sets on the calculated binding energy of the acetylene-NH$_3$ dimer, and demonstrated that, for small hydrogen-bonded systems, the B3LYP level of calculation (with scaled zero-point vibrational correction) reproduces the energies calculated at the highest level of calculation.[10] They show that while hydrogen bond strengths differ based on the level of calculation and basis set used, moving "down" in level yields *lower* interaction strengths. Therefore, our value of 2.95 for the BrCh-NH$_3$ complex is more likely to be on the low end of the possible range of values one could possibly obtain.

It is worth mentioning that although absolute frequencies are typically higher than experimental values at our level of calculation, there are two fundamentals listed in Table 1 (1461.4 and 1448.4 cm^{-1}) for which the corresponding calculated frequency is significantly lower (1386.5 and 1378.0 cm^{-1}). We are confident as a result of viewing the animated vibrations that these correspond well with the descriptions of these fundamentals given in the literature. However, the infrared spectra of halocyclohexanes are quite complex, as many of the vibrations are not well localized,[23] and perhaps these effects contribute to this discrepancy.

Finally, we did not observe any significant changes in base modes upon hydrogen bond formation. The "umbrella" mode of NH_3 has been shown to be sensitive to complex formation in previous matrix studies.[33,34] In our bromocyclopropane-NH_3 study, we did not observe a shift in this mode, but a blue shift of 60 cm^{-1} was calculated.[13] In contrast, in the pentachlorocyclopropane-NH_3 complex, this mode was blue-shifted by 45 cm^{-1}, and DFT predicted a shift of 93 cm^{-1}.[42] For BrCh, DFT predicts a blue shift of 68 cm^{-1}. That we do not observe such a shift for either bromocyclopropane or BrCh is perhaps indicative of a weaker C-H–N hydrogen bond compared with the highly substituted pentachlorocyclopropane, which has a C-H–N hydrogen bond strength of 4.00 kcal/mol (B3LYP/6-31 + G(d, p)). However, we cannot be certain about this, as in both systems the predicted position of the product band falls underneath strong parent absorptions.

CONCLUSIONS

This work represents the first detailed matrix isolation study of Ch and BrCh with NH_3. Whereas there is no evidence of complex formation between Ch and NH_3, complex formation between BrCh and NH_3 results in significant changes in H-C_1-Br bending modes. The shifts in these modes, which range from $\sim$3 to 12 cm^{-1}, are quite similar to those observed for the C-H(Br) bending modes of bromocyclopropane, which are $\sim$6 and 12 cm^{-1} for the in-plane and out-of-plane bending modes, respectively. This work provides an interesting comparison with other hydrocarbons studied and serves, in a comparative way, to elucidate the effect of electron withdrawing substituents, ring size, and carbon acidity on the nature and strength of the important C-H–N hydrogen bond.

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