Matrix Isolation Infrared and ab Initio Study of the 1:1 Complexes of Bromocyclopropane with NH_3 and $(CH_3)_3N$: Evidence for a Novel C−H···N Hydrogen Bond

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Hydrogen-bonded complexes of bromocyclopropane with the strong bases ammonia and trimethylamine have 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 cyclopropane ring to the nitrogen of the base was evidenced by distinct blue shifts of the C−H(Br) bending modes in the infrared spectrum. These shifts ($\sim$12 cm^{-1} for the in-plane bend and $\sim$6 cm^{-1} for the out-of-plane bend) are much smaller than those observed for alkenes and alkynes, suggesting a distinct but extremely weak interaction. Ab initio calculations yield an essentially linear BrC−H···NH_3 hydrogen bond with a C−H···N distance of 2.301 Å and a hydrogen bond energy of 2.35 kcal/mol, thus supporting that this hydrogen bond is one of the weakest observed thus far in a matrix. This study represents the first example of a (substituted) cyclopropane acting as a proton donor and only the second example of an alkane taking part in a C−H···N hydrogen bond.

Introduction

The concept of the hydrogen bond remains one of the frontiers of our knowledge of chemical bonding and intermolecular interactions.[1] Although studies involving hydrogen bonds are being pursued in many laboratories, few of these studies involve the characterization of weak hydrogen bonds. In particular, little is known about the way in which C−H bonds of hydrocarbons interact to form hydrogen bonds with electron donors. Since hydrogen bonds typically form with the electronegative elements N, O, and F, studies involving nitrogen and oxygen bases are useful. Characterization of the C−H···N (and C−H···O) hydrogen bond is important to the modeling of hydrophilic interactions in solution and to an understanding of the structure of organic crystals.[2] Despite this importance, little is known about C−H hydrogen bonding and its dependence on hybridization of the s and p orbitals of the carbon and on the presence of electron withdrawing substituents.

Hydrocarbon−ammonia complexes which contain a C−H···N hydrogen bond have been studied previously. Some of the most interesting results come from comparisons of spectroscopic studies of several related complexes. For example, rotational spectra of H_3N-HCN,[3] $H_3N-HCCH$,[4] and H_3N-HCF_3[5] demonstrate through comparisons of hydrogen-bond lengths and weak bonding stretching force constants that the HCN complex is most strongly bound while the HCCH and HCF_3 complexes are similar in their interaction strengths. In addition, studies[6−9] show that the hydrogen-bonding interaction between a series of alkynes with a range of bases was characterized by a red shift of 20−300 cm^{-1} for the alkynic hydrogen stretching motion. More recently, hydrogen-bonded complexes of ethylene and substituted ethylenes with strong bases were evidenced by red shifts of the C−H stretching mode in the infrared spectrum.[10] These shifts, which range from 10−150 cm^{-1}, are less than those mentioned above for the corresponding alkynic complexes.

Most of the above-mentioned studies involve hydrocarbons that are sp or sp^2 hybridized. The few hydrocarbons that do contain an sp^3 hybridized carbon in the C−H···N hydrogen bond are highly substituted (e.g., CF_3H) or have other functional groups and are therefore relatively strong acids. It is generally known that C−H bonds with high s character exhibit exceptional acidity, and this explains the fact that acetylenes as a group are among the most acidic of the hydrocarbons.[11] This same effect accounts for the relatively high acidity of the C−H bonds on cyclopropane rings.[12] Specifically, the “pinching back” of the internuclear angles at the carbons (i.e., the H−C−H angle) in small ring compounds increases the s character of the C−H bonds. 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 (cyclopropane is reported to be $sp^{2.28}$ hybridized).[13,14]

The matrix isolation technique, combined with infrared spectroscopy, is ideal for the study of weakly bound complexes.[6−10] In general, hydrogen bond formation manifests itself as a distinct shift, broadening, and intensification of the proton donor (hydrocarbon) stretching and bending modes. The nitrogen bases are ideal for such studies because they are much more likely to act as a Lewis base that interacts through its lone pair electrons rather than to donate a proton.[15,16] Little work has been done with non-hydrogen-donor moieties which act as a base and thus enable the study of cyclopropane as a carbon acid. In fact, the only matrix isolation studies of cyclopropane and substituted cyclopropanes to date involve complexation with hydrogen halides and water, which act as Lewis acids and donate

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a proton to the cyclopropane.[17−20] This study was undertaken to characterize the complexes formed when cyclopropane and bromocyclopropane were co-deposited with the nitrogen bases ammonia and trimethylamine and the oxygen base dimethyl ether in an argon matrix. A major goal of this work is a more complete understanding of the correlation between the strength of the hydrogen bond formed and the shift of the relevant hydrogen stretching and/or bending modes. This study will allow a comparison with previous work involving hydrogen bonding in alkenes and alkynes, and represents the first matrix isolation study involving bromocyclopropane with nitrogen and oxygen bases. In addition, to our knowledge, CF_3H and CCl_3H are the only alkanes that have been studied with strong bases (and even then, only with NH_3) using matrix isolation infrared spectroscopy,[21] and therefore the C−H···N hdyrogen bond formed between bromocyclopropane and $NH_3/(CH_3)_3N$ is only the second one to be formed between an alkane and a nitrogen base.

Experimental Section

All of the experiments conducted in this study were carried out in a completely stainless steel vacuum system, with Nupro Teflon-seat high-vacuum valves. Pumping was provided by a Model 1400B Welch vacuum pump, and a Varian HSA diffusion pump, with a liquid nitrogen trap. Vacuums on the order of 10^{-7} mm at the gauge (cold cathode, Varian) were attained using this apparatus. Cryogenics were supplied by a model 22 closed cycle helium refigerator (CTI, Inc.), which operates at temperatures 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 an RMC−Cryosystems model 4025 digital cryogenic temperature controller. The vacuum vessel was equipped with CsI windows and sat in the sample beam of a Nicolet Magna-IR 750 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.[22]

The gaseous reagents employed were cyclopropane(Cp), ammonia(NH_3), trimethylamine ($(CH_3)_3N$), and dimethyl ether ($(CH_3)_2O$) (all Matheson). These reagents were subjected to one or more freeze−thaw cycles at 77 K prior to sample preparation. Bromocyclopropane (Aldrich) was used without prior distillation but was subjected to several freeze−thaw cycles. Argon (Matheson) was used (without further purification) as the matrix gas in all experiments.

Samples were deposited in both the single-jet mode and twin-jet mode. In the single-jet mode, the hydrocarbon and base were premixed in a single vacuum manifold and diluted with argon, while in the twin-jet mode the two reactants were co-deposited from separate vacuum lines. Samples were deposited at rates ranging from approximately 0.5−2 mmol/h, for times ranging from 22−30 h, and at temperatures ranging from 10−20 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 an additional spectrum was obtained.

Computational Methods

Ab initio calculations were performed with the Gaussian-94 suite of programs.[23] The 6-311+G(d,p) and 6-311G(d,p) basis sets[24] were used in all calculations. Electron correlation was treated at the MP2 level of approximation.[25] The zero-point energy and thermal corrections[26] to the Gibbs free energy were evaluated at the Hartree−Fock level, due to core-memory limitations in the case of BrCp. Gas-phase acidities of Cp and BrCp were based on the free energy of the reaction

$$AH \rightarrow A^- + H^+ \qquad (1)$$

The relative difference in pK_a between Cp and BrCp (ΔpK_a) was thus

$$\Delta pK_a = 1/2.303RT\Delta[\Delta G] = 1/2.303RT\{\Delta G(BrCp^-) - \Delta G(BrCp) - [\Delta G(Cp^-) - \Delta G(Cp)]\} \qquad (2)$$

with terms involving the proton free energy canceling. Cp and BrCp complex geometries with NH_3 were optimized to a tight minimum. To evaluate hydrogen-bond interaction energies, basis set superposition error was corrected by the counterpoise method.[27] Partial atomic charges were based on the 6-311G-(d,p) self-consistent field (SCF)electron density.

Experimental Results

Initially, blank experiments were conducted with hydrocarbons and bases, and the resulting spectra were in excellent agreement with literature spectra.[28−42] In addition, since small changes from parent to complex were anticipated, blank experiments were performed whenever a new sample was prepared. This ensured a precise comparison between parent and complex spectra for every concentration of reactants studied. Once it was established that single-jet results did not provide any additional information, all experiments were performed in the twin-jet mode. All of the results provided here are from twin-jet depositions. In all experiments, band positions were reproducible within ± 0.2 cm^{-1}.

Cyclopropane Reactions. Cp/Ar and NH_3/Ar were co-deposited in many experiments at concentrations ranging from 1000/1/1 (Ar/Cp/NH_3, meaning Ar/Cp 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. The twin-jet co-deposition of Cp with $(CH_3)_3N$ gave rise to a doublet, with maxima at 2776.6 and 2775.5 cm^{-1}, shifted to lower energy from the parent C−H stretching modes of the base (2778.7 and 2777.2 cm^{-1}). In addition, a new product absorption at 2787.2 cm^{-1} appeared as a distinct shoulder on the high enery side of the doublet. These features were present in all co-deposition experiments, with concentrations ranging from 1000/1/1 (Ar/Cp/$(CH_3)_3N$) down to 200/1/1 for each reactant. Changing relative concentration of the reactants did not lead to any new features.

Cp was also co-deposited with $(CH_3)_2O$ under a wide variety of conditions, and no evidence of complex formation was observed.

Bromocyclopropane Reactions. BrCp/Ar was co-deposited with NH_3/Ar and $(CH_3)_3N$/Ar in many experiments at concentrations ranging from 1000/1/1 (Ar/BrCp/base) to 200/1/1. Deposition window temperature as well as reactant flow rates were also varied in these experiments. When BrCp was co-deposited with NH_3, several changes were noted in all experiments. A new absorption at 1281.8 cm^{-1} was observed, appearing as a moderate broad band on the high-energy side of the BrCp parent bands at 1269.5 and 1266.4 cm^{-1}. The most striking new feature was a strong new product absorption at 814.7 cm^{-1}, on the high-energy side of the parent BrCp band,

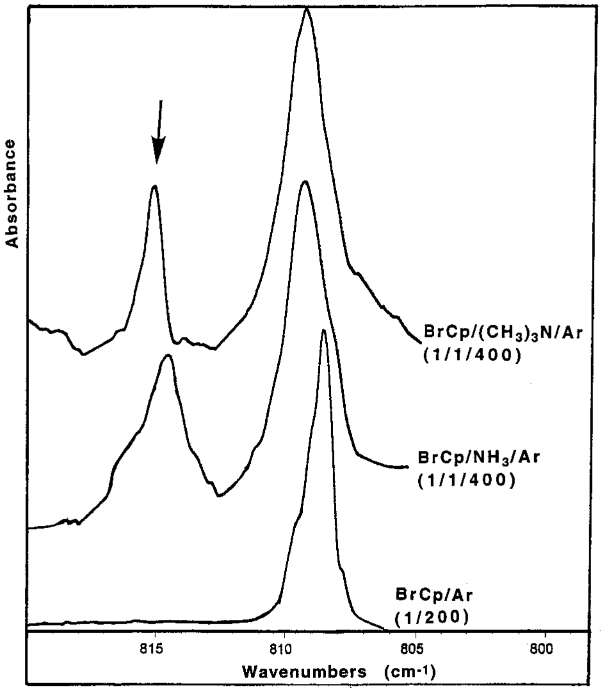

Figure 1. Infrared spectra (0.125 cm^{-1} resolution) in the CH(Br) out-of-plane bending region for parent BrCp/Ar (bottom trace) and co-deposition mixtures (upper two traces) deposited on CsI at 16 K. The new product absorption is marked with an arrow. There are no parent NH$_3$ or (CH$_3$)$_3$N absorptions in this region.

which was also slightly shifted and broadened from 808.5 (parent) to 809.3 cm^{-1} (complex). This band at 814.7 cm^{-1} was present in all experiments and was always about one-half as intense as the parent band at 809.3 cm^{-1}. This band grew slightly upon annealing. When BrCp was co-deposited with (CH$_3$)$_3$N, there was a new absorption at 1281.3 cm^{-1}. This band overlapped with a weak and broad trimethylamine band at about 1280 cm^{-1}, but it was obvious from the rate of growth of the band and from subtraction spectra that it was a product band. Again, the most striking feature in the spectrum of the complex was an intense band at 815.1 cm^{-1}, again to the high-energy side of the BrCp parent band at 809.3 cm^{-1}. This band was also present in all experiments and was always about half as intense as the parent band at 809.3 cm^{-1}. This band also grew upon annealing. In all experiments, the general features of the spectrum remained the same upon changing relative concentrations of acid and base. Figures 1 and 2 show representative spectra of the products arising from the co-deposition of BrCp with NH$_3$ and (CH$_3$)$_3$N.

BrCp was co-deposited with (CH$_3$)$_2$O under a wide variety of conditions and no evidence of complex formation was noted.

Computational Results

The MP2/6-311G(d,p)-optimized geometry of Cp (D_{3h} symmetry) was C−H 1.084 Å, C−C 1.509 Å, angle H−C−H 115.0°, and angle C−C−H 117.7°. In contrast, the MP2/6-311G-(d,p)-optimized geometry of BrCp (C_s symmetry) is shown in Figure 3. The Cp ring was distorted to an isosceles triangle with the C−CBr bond distance contracted to 1.501 Å. The H−CBr bond (1.083 Å) was only very slightly contracted, relative to Cp, and lies closer (by 2°) to the plane of the ring than the CH bonds of Cp. The methylene unit geometries, opposite HCBr, were nearly identical to those of Cp. The natural orbital hybridization[43] of these CH bonds was sp$^{2.66}$ and sp$^{2.68}$, compared to a CH bond composition of sp$^{2.68}$ for Cp. In comparison, the H−CBr bond hybridization was sp$^{2.45}$. The topography of the electrostatic potential of Cp consisted of electronegative regions in the plane of the ring, due to the C−C bonds, and electropositive regions above and below the ring

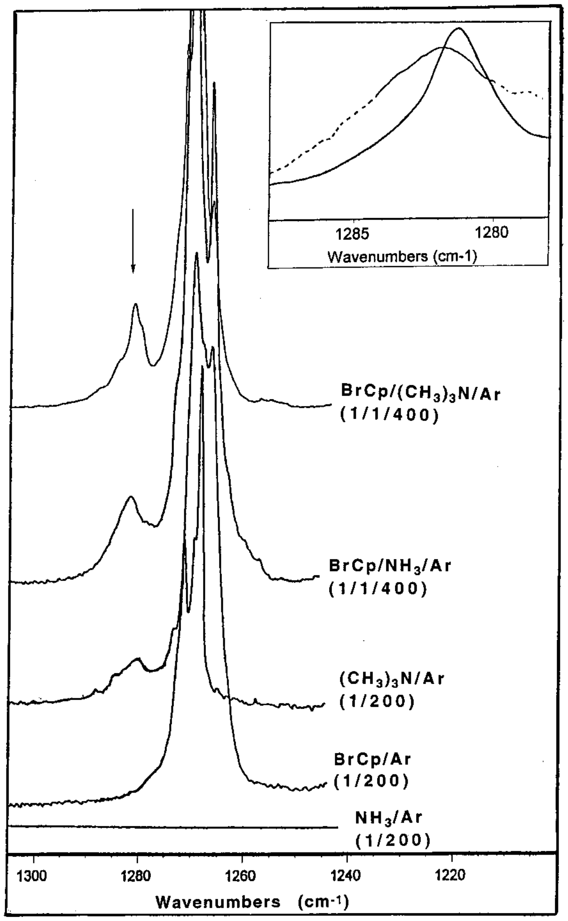

Figure 2. Infrared spectra (0.125 cm^{-1} resolution) in the CH(Br) in-plane bending region for parent depositions (lower three traces) and codepostion mixtures (upper two traces) deposited on CsI at 16 K. The new product absorption is marked with an arrow. The inset (upper right) shows an expanded view of the result of subtraction of (CH$_3$)$_3$N/Ar parent from BrCp/(CH$_3$)$_3$N/Ar (solid line) compared to BrCp/NH$_3$/Ar (dashed line).

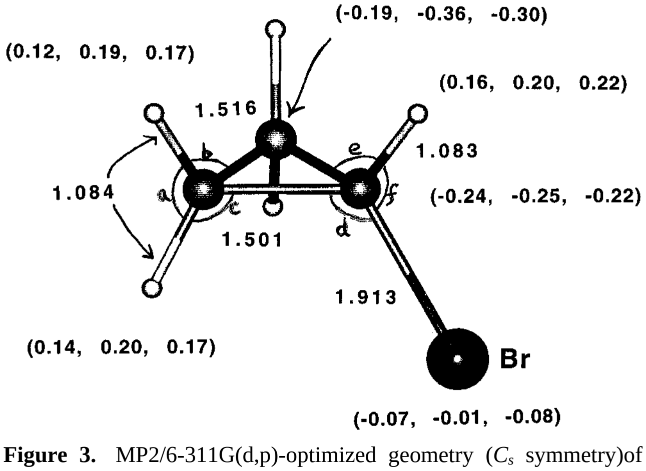

Figure 3. MP2/6-311G(d,p)-optimized geometry (C_s symmetry)of bromocyclopropane (bond distances in angstroms) and atomic partial charges. Partial charges (units e) reflect the Mulliken electronic population (M), natural orbital population (NPA), and least-squares fit to the electrostatic potential (ESP), and are listed in order of: (M, NPA, ESP). Angles are (a) 115.5°, (b) 118.2°, (c) 116.9°, (d) 119.2°, (e) 119.0°, (f) 111.4°.

due to the electropositive hydrogens, the most electropostitive sites being centered on the C_3 axis. This topography was reflected by the HF/6-311G(d,p) partial charges (unit e) of C (−0.23, −0.36, −0.30) and H (0.11, 0.18, 0.15), based on Mulliken populations[44] (M), natural orbital population analysis[43] (NPA), and least-squares fitting to the SCF electrostatic potential[45] (ESP), respectively (M, NPA, ESP). In comparison, the partial charges of BrCp are shown in Figure 3. All BrCp hydrogens are slightly more electropositive than those of Cp. The most significant difference is the H−CBr hydrogen (0.16, 0.20, 0.22), which had an increased positive charge of 0.05e overall, compared to Cp. The most electropostive region of BrCp was thus located approximately along the H−CBr axis. Given the distortion of the Cp electrostatic potential by Br, it was of interest to determine the effect of Br substitution on the hydrogen bond interaction energy of $C-H\cdots NH_3$. The MP2/6-311G(d,p)-optimized geometries of $Cp\cdots NH_3$ and $BrCp\cdots NH_3$ are shown in Figure 4. The $Cp\cdots NH_3$ potential energy minimum was extremely shallow (soft) and consisted of NH_3 located along the C_3 symmetry axis, with the NH_3 hydrogens staggered relative to the methylene hydrogens. This complex had C_{3v} symmetry, and the amino nitrogen was located 3.412 Å above the Cp ring. The CH−N distances were 2.880 Å. In contrast, the $BrCp\cdots NH_3$ minimum (C_s symmetry) was steeper and the NH_3 interacted almost entirely with the H−CBr unit. The $BrC-H\cdots NH_3$ hydrogen bond was essentially linear, and the $CH\cdots N$ distance was 2.301 Å, substantially closer than the approach of NH_3 to the Cp hydrogens, suggesting a stronger interaction. The calculated $Cp\cdots NH_3$ interaction energy, 1.00 kcal/mol (MP2/6-311G(d,p)), was very weak. In comparison, the calculated $BrCp\cdots NH_3$ hydrogen bond energy, 2.35 kcal/mol, was twice as strong. Analysis of the relative acidities of Cp and BrCp further reveals the electron-withdrawing effect of Br substitution on the Cp ring. The relative change in the free energy of deprotonation eq 1, $\Delta(\Delta G) = \Delta G$ BrCp $- \Delta G$ Cp, was calculated (MP2/6-311+G(d,p)) to be −11.69 kcal/mol, with $\Delta pK_a = -8.6$. Thus, the pK_a of BrCp was nearly 9 units lower than that of Cp.

Vibrational frequencies for isolated Cp and BrCp as well as frequencies upon complexation with NH_3 were calculated at the MP2/6-311G(d, f) level for Cp and the HF/6-311+G(d, f) level for BrCp. Since these calculations were performed mainly to rationalize the experimental observations of the BrCp−base complexes, only the relevant BrCp modes and corresponding frequency shifts upon complexation are summarized in Table 1.

Discussion

Evidence for hydrogen-bonding interactions between the cyclopropanes and the bases 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 co-deposition experiments. When Cp was co-deposited with NH_3, there was no evidence of product formation. This result is in agreement with Barnes and Paulson,[18] who were able to form complexes of Cp−hydrogen halide and Cp−H_2O in argon matrixes, but were not able to form a Cp−NH_3 complex. When Cp was co-deposited with $(CH_3)_3N$, a new product absorption appeared about 11 cm^{-1} to the blue of the C−H stretching mode of the $(CH_3)_3N$. In addition, the C−H stretching modes of the $(CH_3)_3N$ were red shifted by about 2 cm^{-1}. These changes in the parent C−H stretching modes are the only ones observed, and while this suggests some interaction between the acid and base, there is not enough evidence to characterize the interaction, especially in the absence of the perturbation of Cp modes. Recent gas-phase studies[46] of Cp−amine van der Waals complexes show that the Cp−NH_3 complex is a symmetric top with the lone pair of the nitrogen atom pointing toward the center of the Cp ring. The same structure is observed for Cp−$(CH_3)_3N$ complexes, except that the latter does not exhibit effects from internal rotation of the base subunit about the C_3 axis. Our ab initio calculations yield for Cp−NH_3 an interaction energy of 1.00 kcal/mol, which is very weak and could possibly explain our lack of observation of a Cp−base complex. We note that our calculated result is very close to the value of 0.97 kcal/mol reported by Forest et al.[46]

When BrCp was co-deposited with the nitrogen bases NH_3 and $(CH_3)_3N$, two new absorptions were noted that could not be ascribed to either parent species (see Figures 1 and 2). These product bands in the co-deposition spectra of BrCp with the bases involve vibrational modes of the CHBr “corner” of the cyclopropane ring. Specifically, the two new absorptions seen in the case of BrCp-NH_3 and BrCp-$N(CH_3)_3$ occur near and to the blue of the parent CH(Br) in-plane and out-of-plane bending modes (the Br in parentheses denotes the “acidic” proton on the same carbon as the Br substituent). The nearness of the product absorptions to modes of the parent species suggests that the BrCp and bases retain their structural integrity and therefore the product is not the result of addition, elimination, or rearrangement of the subunits. Although the spectral changes are small, the product bands are distinct and in the case of the product band near the CH(Br) out-of-plane bend, quite intense. Although product yields are low (as evidenced by the intensity of the parent bands in the co-deposition spectra), the intensities of the product absorptions were directly proportional to the concentration of each 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.

The new absorption at 1281.8 cm^{-1} (BrCp/NH_3/Ar) and 1281.3 cm^{-1} (BrCp/$(CH_3)_3N$/Ar) falls about 12 cm^{-1} to the blue of the parent CH(Br) in-plane bend at 1269.5 cm^{-1}. This absorption is broad and although not a shoulder, is very close to the BrCp parent band. In the NH_3 experiments, this product absorption is easy to study since there are no NH_3 vibrations in this region. In the case of $(CH_3)_3N$, this band falls very near BrCp parent bands which overlap with $(CH_3)_3N$ parent bands in this region. In our parent $(CH_3)_3N$ spectra, we see a very weak and broad absorption at about 1281 cm^{-1}, close to the base CH_3 rocking modes which start at about 1277 cm^{-1}. Previous studies[34,37] report a weak $(CH_3)_3N$ band at 1281 cm^{-1} in an argon matrix, but this band is not assigned to a fundamental frequency and is not identified or discussed at all. We note that at $(CH_3)_3N$/Ar concentrations lower than 1/700 and very low flow rates we do not observe this band. On the basis of concentration and annealing data as well as subtraction spectra, we feel confident that our band at 1281.3 cm^{-1} is in fact a product band and therefore corresponds to the product band that we observe in the same region upon co-deposition with NH_3. Figure 2 shows representative co-deposition spectra as well as a spectrum (inset) in which the $(CH_3)_3N$/Ar parent spectrum was subtracted from the co-deposition spectrum.

The second new absorption in the co-deposition spectra is the band which occurs at 814.7 cm^{-1} with NH_3 and 815.1 cm^{-1} with $(CH_3)_3N$. This band occurs 6.2 cm^{-1} to the blue of the parent band at 808.5 cm^{-1} with NH_3 and 6.6 cm^{-1} to the blue of the parent band with $(CH_3)_3N$. This band is always broader

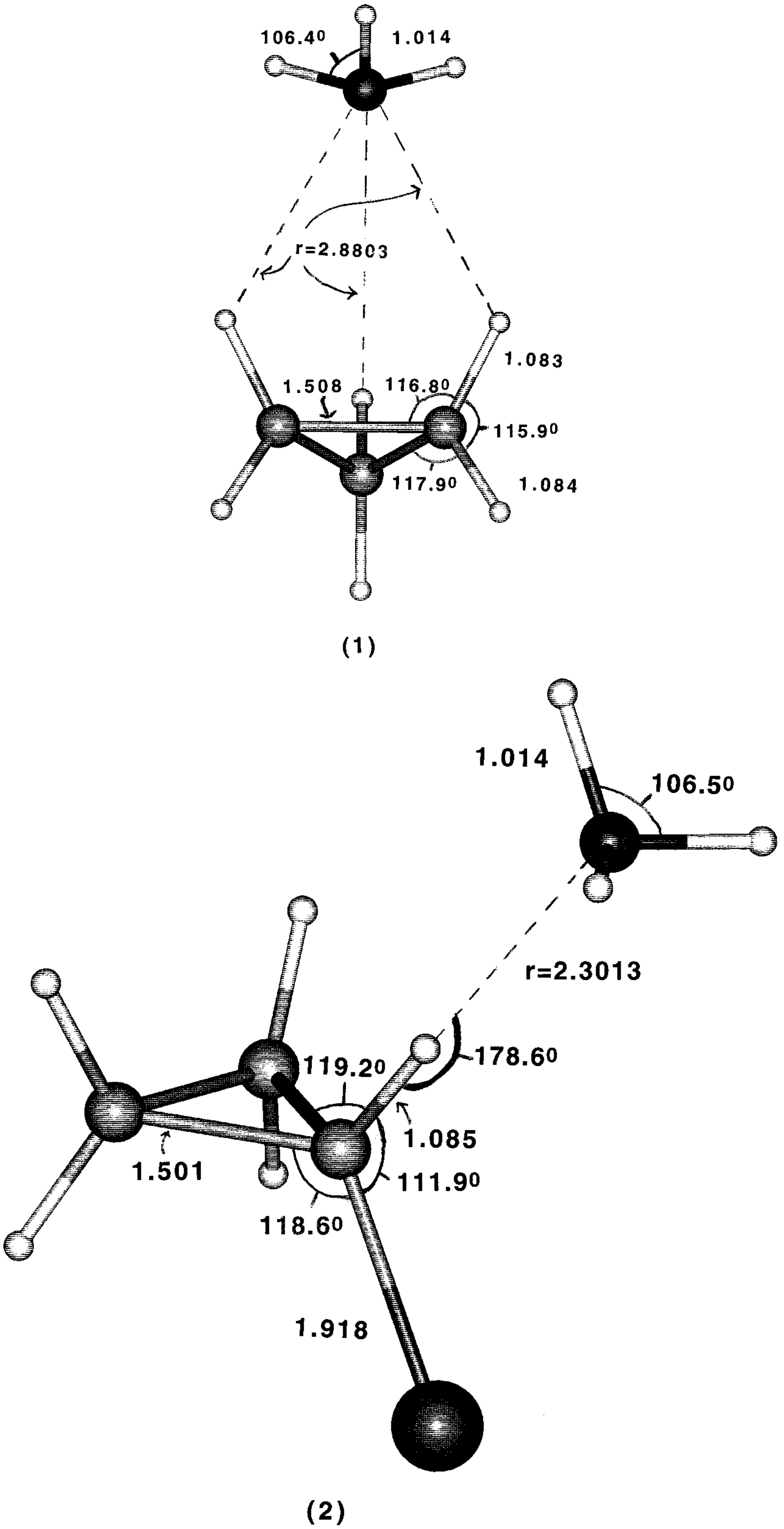

Figure 4. (1) Cp−NH_3, MP2/6-311G(d,p)-optimized geometry (C_{3v} symmetry, distances in angstroms). (2) BrCp−NH_3, MP2/6-311G(d,p)-optimized geometry (C_s symmetry).

with NH_3 than with $(CH_3)_3N$. In addition, the parent band itself is shifted by about 1 cm^{-1} with both NH_3 and $(CH_3)_3N$. There has been some controversy surrounding the assignment of this parent band at 808 cm^{-1}. While Rothschild[39] and Maillols and Tabacik[40] assign this as the CH(Br) out-of-plane bend, Hirokawa,[41] Aleksanyan,[42] and Wurrey[28] assign it as the CH_2 out-of-phase rock. We feel that our results strongly favor the former assignment for several reasons. For one, there are many CH_2 vibrations possible for BrCp, and we see no evidence of perturbations involving any of these modes. It seems very unlikely that only the CH_2 out-of-phase rock would be sensitive to complex formation when in fact it has been shown that the CH_2 wagging vibration of Cp is a mode which is very sensitive to small perturbations. Truscott and Ault[17] found that even in

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

observed			calculated[b]	
BrCp	BrCp−NH_3	fundamental(symmetry)	BrCp	BrCp−NH_3
∼3060	∼3060 (0)	CH(Br) stretch (a′)	3353.5	3360.4 (+6.9)
1269.5	1281.8 (+12.3)	CH(Br) in-plane bend (a′)	1404.3	1425.7 (+21.4)
808.5	814.7 (+6.2)	CH(Br) out-of-plane bend (a″)	878.6	892.6 (+14.0)
551.3	551.3 (0)	C−Br stretch (a′)	585.3	578.7 (−6.6)
312[c]		C−Br out-of-plane bend (a″)	334.9	337.2 (+2.3)
269[c]		C−Br in-plane bend (a′)	293.6	294.2 (+0.6)

[a] Wavenumber in cm^{-1}. Values in parentheses represent the frequency shifts with respect to the isolated BrCp. [b] Unscaled frequencies. Calculated at the HF/6-311+G(d, f) level. [c] Not observed, but solid-phase value taken from ref 28.

experiments in which they failed to form a complex between Cp and strong Lewis acids, they observed a band 12 cm^{-1} to the red of the parent CH_2 wagging vibration, suggesting that this band was the result of a weak perturbation or asymmetry created by the presence of the Lewis acid in the matrix. In our experiments, the Cp modes did not prove to be sensitive to the presence of base in the matrix, and experiments involving Cp and BrCp with the oxygen base dimethyl ether yield no perturbation of the parent 808 cm^{-1} band and no evidence of complex formation. Second, the fact that our absorption increases in intensity and shifts more to the blue as we move from NH_3 to $(CH_3)_3N$ (a stronger base) suggests the perturbation is caused by something more specific than the mere presence of base in the matrix. Our concentration and annealing studies also support this conclusion. We therefore assign the parent band at 808.5 cm^{-1} to the CH(Br) out-of-plane bend.

The experimental results suggest that our product is a hydrogen bonded complex in which the nitrogen of the base is hydrogen bonded to the proton adjacent to the Br substituent. All of the spectral changes are consistent with those that are known to occur as a result of hydrogen bond formation (as opposed to the formation of van der Waals complexes). In addition, the spectral features we observe are consistent with what others have observed for hydrogen bonds involving the C−H group of a hydrocarbon. Specifically, Ault and coworkers[10] observed for alkenes with nitrogen bases product absorptions that fell into four groups: (1) those occurring near and to the red of the parent alkenic C−H stretching mode; (2) those occurring near and to the blue of the parent CH_2 or CHX bending modes; (3) those occurring near and to the red of one or more of the parent C−X stretching modes; (4) those occurring, for some systems, quite near vibrational modes of the base. The new absorptions in our product spectra fall into Ault's second category. In particular, Ault reports shifts to higher energy of the hydrocarbon bending modes, with shifts that are smaller than the alkenic C−H stretch (υ_s). The magnitudes of these shifts are less than those observed for alkynic hydrogen-bonded complexes,[6−9] indicating that the alkene−base hydrogen-bonding interaction is weaker than the corresponding alkyne−base interaction. The changes we observe in the bending modes of BrCp are in general much smaller than what Ault reports for alkynes and alkenes. In comparison to alkynes, this is not surprising, since the C−H···N hydrogen bond is expected to be relatively strong for a proton with 50% s character. Compared to alkenes, however, this is somewhat surprising, since cyclopropane often behaves more like an alkene than an alkane. The pK_a/% s character of ethylene is 36.5/33 compared to cyclopropane, which is 39/30.[14] Although these are similar, there is obviously a large difference in behavior between ethylene and cyclopropane, as evidenced by the fact that cyclopropane does not form hydrogen-bonded complexes with the bases NH_3, $(CH_3)_3N$, or $(CH_3)_2O$ in an argon matrix. It is well-known that putting an electron-withdrawing substituent on a hydrocarbon increases its acidity.[47−49] Ault found that, for a given base, the greater number of halogens on the ethylene, the greater the shifts. Our ab initio results show that when a Br substituent is added to the cyclopropane ring, the proton adjacent to the substituent becomes the most electropositive site in the molecule. In addition, the calculated hydrogen-bond strength for BrCp−NH_3 is 2.35 kcal/mol, which is twice as strong as that calculated for Cp−NH_3. Also, the CH···N distance is 2.301 Å for BrCp−NH_3, which is 0.579 Å shorter than that of Cp−NH_3 (see Figures 3 and 4). Finally, the calculated pK_a (which we emphasize is a gas-phase value) for BrCp is almost 9 units lower than that of Cp. All of these computational results demonstrate that the addition of the Br substituent to the Cp ring activates the C−H group so that it becomes the most favorable site for hydrogen-bond formation.

The theoretical frequencies summarized in Table 1 strongly support our experimental results. As can be seen, the largest shifts in the BrCp fundamental frequencies upon complexation with NH_3 are calculated for both of the CH(Br) bending modes. Since only the relative frequency shifts are of interest, unscaled frequencies are reported. It is well-known that absolute frequencies are systematically higher than experimental values at our level of calculation. It was nonetheless straightforward to correlate theoretical and experimental frequencies. Both of the CH(Br) bending modes are predicted to be blue-shifted, which is what we observe experimentally. The relative magnitudes of the shifts in the in-plane and out-of-plane bending modes also agree nicely with our experimental results, in fact, the shifts we observe in these modes (12.3 and 6.2 cm^{-1}, respectively) are approximately one-half of the magnitude of the predicted shifts (21.4 and 14.0 cm^{-1}). These computational results support our assignment of product bands, which, as stated above, argues in favor of a hydrogen-bonded structure with the proton adjacent to the Br hydrogen bonded to the N atom of the base. It is reasonable to assume, however, that since our observed shifts in bending modes are smaller than those reported for alkynes, alkenes, and highly substituted alkanes, that this hydrogen bond is weaker than those reported thus far.

Perhaps the most important spectral feature that Ault reports for alkenes is the shift in frequency of the alkenic C−H stretching mode υ_s (category 1). This shift in C−H stretch, $\Delta\upsilon_s$, is often taken as a measure of the strength of the hydrogen-bonding interaction. For alkynes and alkenes, Ault reports red shifts in the range 30−300 and 10−150 cm^{-1}, respectively.[10] We do not observe such a shift in our product spectra. The C−H(Br) stretch for BrCp is reported to be at about 3065 cm^{-1} (solid phase).[28] In this region of the parent spectrum we see several weak and broad overlapping bands, together which are about 110 cm^{-1} wide. Immediately to the red of these bands is a strong absorption (parent CH_2 stretches) which returns to the baseline at 3000 cm^{-1}. It is very likely that the shift in this mode for us falls underneath these parent absorptions. (We note that working with a nitrogen matrix did not help in this region).

Our frequency calculations predict a blue shift of 6.9 cm^{-1} for the CH(Br) stretch (ν_s). Although the direction of this shift is not what is expected, the magnitude is small and argues strongly that this band would in fact be very likely to be lost in the background of parent BrCp absorptions. The unexpected direction of this shift (i.e., blue, when clearly a red shift is anticipated) can be understood as follows. The calculated (MP2/6-311+G-(d, p)) C−H(Br) distance is very slightly elongated (0.002 Å) in the complex, relative to the parent, indicating that this C−H bond is weakened by its interaction with NH_3, implying a red shift upon complexation. The frequency calculations (HF/6-311+G(d,p)), however, predict a slight blue shift (6.9 cm^{-1}) for the CH(Br) stretch. Notably, these results indicated stronger CH stretch couplings in the complex, compared to BrCp, as the source of the shift. On the basis of the contribution of atomic displacements to the normal mode, the CH(Br) stretch was nearly a local mode, of composition 87% local CH(Br) stretch, 13% remaining CH groups. In comparison, the composition of the CH(Br) stretch normal mode for the NH_3 complex was 60% local CH(Br), 40% CH. We also note that there are no $(CH_3)_3N$ parent bands until about 2978 cm^{-1}, and again, it is very unlikely that the C−H shift would fall underneath these bands, since this would imply a shift of about 70 cm^{-1}, which is about what is observed for ethylene with $(CH_3)_3N$. This is larger than what we would expect for BrCp based on our frequency calculations and given that our other observed shifts are much smaller than those reported for alkenes. It is interesting to note that the CF_3H-H_2O complex formed in an argon matrix[21] showed shifts to the blue of the C−H bending mode but showed no perturbation of the C−H stretch $\nu_{s.}$ This complex is known to be a hydrogen-bonded complex in which the oxygen of the water interacts with the proton of the CF_3H. The corresponding CCl_3H complex, however, does show a shift in the C−H stretch upon complexation with H_2O. Both complexes show a C−H stretch shift with NH_3. Finally, we do not observe shifts in our parent C−X stretching mode at 551 cm^{-1} or in any vibrational modes of the bases (Ault's category 3 and 4). For many of the complexes Ault studied, either a distinct absorption or a shoulder appeared on the low energy side of one of the C−X stretching modes, but the shifts observed were on the order of 3−10 cm^{-1}. Considering that all of our shifts are smaller than those reported for alkynes and alkenes, it is not surprising that we are not seeing a shift in our C−X modes. Furthermore, our frequency calculations predict a red shift of 6.6 cm^{-1} for the C−Br stretch at 551 cm^{-1}. This value is what is expected in terms of direction. This shift is about equal to that of the CH(Br) stretch discussed above. Again, the small magnitude of this shift supports our lack of observation of any change in this mode upon complexation. We note, too, that changes in C−X stretches were not observed in several complexes studied by Ault[10] and also not observed in the case of CX_3H (where X = F, Cl) with the bases H_2O and NH_3.[21] Finally, the C−Br in-plane bend and out-of-plane bend are also predicted to blue shift (see Table 1), but both of these shifts are quite small (0.6 and 2.3 cm^{-1}, respectively), and we did not study this region of the spectrum.

In this study, three bases were employed. The $(CH_3)_2O$ was not a strong enough base to form a complex with the BrCp, whereas the nitrogen bases NH_3 and $(CH_3)_3N$ were. This makes sense, since nitrogen bases are stronger than oxygen bases.[50] In the case of the out-of-plane bend, the shift is larger with the stronger base. For both bends, however, the difference in shift with the two bases is only about 0.5 cm^{-1}, which is quite small. Ault also observes a systematic trend for a given hydrocarbon through a range of bases, with shifts being larger the stronger the base. Again, the smaller differences we see as we move from NH_3 to $(CH_3)_3N$ further supports the conclusion that this C−H···N hydrogen-bond is weaker than those formed between alkynes and alkenes with nitrogen bases.

Conclusions

This work represents the first detailed matrix isolation study of Cp and BrCp with strong bases (with the exception of Cp with NH_3). There is no evidence of complex formation with Cp and the nitrogen bases employed, and no evidence of complex formation between either Cp or BrCp with the oxygen base employed. Evidence of complex formation between BrCp and the nitrogen bases comes from changes in the CH(Br) bending modes. These modes have been shown to provide strong evidence of complex formation even in the absence of changes in C−H or C−X modes of the carbon acid. In addition, our calculations predict the largest shifts for the two CH(Br) bending modes and thus support our experimental findings. This work serves, in a comparative way, to elucidate the conditions necessary for hydrogen bond formation to occur. We have shown that the Br substituent is necessary to activate the C−H group to form a C−H··· N hydrogen bond. This hydrogen bond is one of the weakest formed in a matrix to date and represents the first complex in which a cyclopropane is shown to donate a proton in hydrogen bond formation.

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