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Blue Shifting C−H···O Hydrogen Bonded Complexes between Chloroform and Small Cyclic Ketones: Ring-Size Effects on Stability and Spectral Shifts

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Blue-shifting C−H···O hydrogen bonded complexes between chloroform and three small cyclic ketones (cyclohexanone, cyclopentanone, and cyclobutanone) have been identified by use of FTIR spectroscopy in CCl_4 solution at room temperature. The shifts of the C−H stretching fundamental of chloroform (ν_{C-H}) in the said three complexes are +1, +2, and +5 cm^{-1}, respectively, and the complexation results in enhancement of the ν_{C-H} transition intensity in all three cases. The 1:1 stoichiometry of the complexes is suggested by identifying distinct isosbestic points between the carbonyl stretching ($\nu_{C=O}$) fundamentals of the monomers and corresponding complexes for spectra measured with different chloroform to ketone concentrations. The $\nu_{C=O}$ bands in the three complexes are red-shifted by 8, 19, and 6 cm^{-1}, and apparently have no correlation with the respective blue shifts of the ν_{C-H} bands. Spectral analysis reveals that the complex with cyclohexanone is most stable, and the stability decreases with the ring size of the cyclic ketones. A qualitative explanation of the relative stabilities of the complexes is presented by correlating the hydrogen bond acceptor abilities of the carbonyl groups with the ring size of the cyclic ketones. Quantum mechanical calculations at the DFT/B3LYP/6-311++G(d,p) and MP2/6-31+G(d) levels were performed for predictions of the shapes of the complexes, electronic structure parameters of C−H (donor) and C=O (acceptor) groups, intermolecular interaction energies, spectral shifts, and evolution of those properties when the hydrogen bond distance between the donor−acceptor moieties is scanned. The results show that the binding energies of the complexes are correlated with the dipole moments, proton affinity, and n(O) → σ*(C−H) hyperconjugative charge transfer abilities of the three ketones. NBO analysis reveals that the blue shifting of the ν_{C-H} transition in a complex is the net effect of hyperconjugation and repolarization/rehybridization of the bond under the influence of the electric field of carbonyl oxygen.

1. Introduction

Energetic and spectroscopic attributes of weak C−H···O hydrogen bonds (HBs)[1] have been widely discussed in recent literature.[2−5] A primary reason for the overwhelming interest to this subtle type of attractive molecular interaction is due to a notion that, collectively, such weak forces could be an important determining factor for stability of many important biomolecular structures.[6−15] One of the intriguing spectroscopic features of such HBs, although noted only in a handful of model 1:1 complexes of haloalkanes as HB donors and water, ethers and small carbonyl compounds as acceptors, is the spectral blue shifting of the stretching fundamental of the donor C−H group (ν_{C-H}) with concomitant diminution of its infrared absorption intensity.[16−21] Thus, the two universal spectroscopic features of classical HBs (X−H···Y type), red shifting and IR intensity enhancement of the donor X−H stretching vibration, are reversed in the former cases and the traits have also been predicted by electronic structure calculation.[16−38] However, the spectroscopic studies for demonstrations of such blue shifting HBs in small molecular complexes were performed in low-temperature environments, like inert gas liquids,[17,18,20] solid inert gas matrices[16] and supersonic jet expansion,[39] and under such cryogenic conditions the molecular complexes are stabilized mostly by London dispersion forces.[40] We demonstrate here, however, that the blue-shifting C−H···O hydrogen bonded (H-bonded) 1:1 complexes of chloroform with small cyclic ketones can easily be identified in CCl_4 solutions at the room temperature, and the spectral shifts and infrared transition intensities of the stretching fundamentals of the C−H bond of chloroform and C=O bonds of the cyclic ketones strikingly evolve with the ring size of the acceptors.

Even though no direct relationship has been laid down correlating the magnitude of the ν_{C-H} blue shifts with the binding interaction energies of C−H···O H-bonded complexes, many believe that there is no fundamental difference in the bonding characteristics between the blue and conventional red-shifting HBs.[33,34,37,38,41,42] The prevailing view for stability of the latter in a X−H···Y type complex, where X is an electronegative element such as O, N, or F, and Y contains a region of high electron density, is due to electrostatic attraction (dipole−dipole, dipole induced dipole, etc.) between H and Y, which elongates and weakens the X−H bond, resulting in red-shifting.[4,5,43] The second viewpoint is the hyperconjugative charge transfer from electron rich Y to σ*(X−H) orbital that results in energy lowering of the complex.[44,45] The weakening of X−H bond occurs due to increased population of the σ*(X−H) orbial, which results in bond length elongation and the consequent red-shifting of the X−H stretching frequency. However, Stone, Fowler, and Buckingham argued that it is somewhat deceptive

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to distinguish between the said two types of interactions, because, both result in the same effect.[46] Alternatively, for many of the C—H···Y type H-bonded complexes, electronic structure calculations reveal a correlation between blue shifting and shortening of C—H bonds,[17,18,20,25,27,30,32,47] and the behavior is consistent with the bond lengthening and red-shifting effects of classical HBs. To interpret the blue-shifting effects, a number of mechanisms have been proposed in recent years. Hobza and Havlas proposed a two-step mechanism in which the electron density is transferred first from the HB acceptor to a remote part of the donor followed by charge reorganization within the donor molecule.[30,32] The other mechanisms are as follows:(i) an interplay of repolarization/rehybridization of the carbon-centric orbital of the C—H bond by the electric field of the acceptor group and hyperconjugative Y → σ^*(C—H) charge transfer at a shorter intermolecular distance of donor−acceptor molecules;[27] (ii) contraction of the C—H bond by the electric field of Y;[31,48−57] and (iii) interplay of electrostatic interactions and short-range overlap repulsion.[29] Among these, the repolarization/rehybridization mechanism, which can be applied intuitively to a variety of C—H···Y-type H-bonded complexes, has been found to be quite useful to interpret the bond shortening and blue shifting effects.[27,58] Apparently, attempts to utilize this model designed for 2c,2e bonds directly toward hypervalent 3c,4e-bonds in rare gas F—He—H···N2 complexes were unsuccessful due to unique properties of such highly delocalized bonds.[59] However, Alabugin et al. have extended the model and proposed that bond shortening of the Rg—H bond following its repolarization in presence of N_2 occurs via increased contribution of ionic resonance form, $F^-[Rg—H]^+$, which parallels the rehybridization in case of classic 2c, 2e bonds.[60]

From spectroscopic viewpoints, the cyclic ketones used as HB acceptors in the present study are interesting, because the carbonyl stretching fundamental ($\nu_{C=O}$) frequencies of these molecules are different for four-, five-, and six-member systems.[61] The measured $\nu_{C=O}$ values of cyclobutanone (CBN), cyclopentanone (CPN), and cyclohexanone (CHN) are 1788, 1748, and 1717 cm^{-1}, respectively. The differences are attributed to different bonding parameters of the C═O group that arise because of angular strains at the sp^2 hybridized carbonyl carbon atom. We show here that those differences make the HB acceptor ability of the three cyclic ketones ring-size dependent. Thus, in the present work, we have used the three ketones to investigate the effects of tuning the HB acceptor ability on spectral shift and intensity change of the ν_{C-H} band of donor chloroform. The FTIR spectra of the complexes were measured in CCl_4 solutions at room temperature for ensuring that the complexes produced are thermally stable. The electronic structure calculations of monomers, as well as complexes, were performed for predictions of changes of the C—H and C═O bond parameters of the donor−acceptor molecules. The optimizations were performed also in scan mode for prediction of evolution of those parameters as a function of HB distance, and the results were used to interpret the observations.

2. Experimental Method

The cyclic ketones and chloroform were procured from Aldrich and used without further purification. The IR spectra were recorded using a Bruker IFS66S FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a KBr beam splitter. The cell used for measuring the spectra of the liquids consisted of a pair of KBr windows separated by a Teflon spacer of 0.5 mm thickness. An instrument resolution of 0.5 cm^{-1} was used throughout all of the measurements. The sample compartment and optics housing of the spectrometer were purged continuously with dry nitrogen at room temperature (22 °C) during the measurements.

3. Theoretical Calculation

The geometries of all of the molecular species, chloroform, three cyclic ketones, and their 1:1 complexes were optimized by MP2/6−31+G(d) and DFT/B3LYP/6-311++G(d,p) theoretical methods.[62,63] BSSE corrections of the binding energies were performed by the counterpoise method.[64] Relaxed scans with respect to HB distance ($R_{H\cdots O}$) were carried out, where all geometrical parameters of a complex for fixed $R_{H\cdots O}$ were allowed to be optimized. Normal mode vibrational frequencies of the monomers and three complexes were calculated at the MP2/6-31+G(d) level. To calculate the natural charges at the donor−acceptor sites of the bare molecules and complexes, hybridization characteristics of various bonding orbitals, and hyperconjugation interaction between the nonbonded lone-pair orbitals on carbonyl oxygen (n(O)) and σ^*(C—H) orbital of chloroform, we performed NBO analysis. The G03 package was used to perform all the calculations for the present study.[65]

4. Results and Discussion

4.1. Description of the Measured Spectra. The formation of H-bonded complexes between chloroform and cyclic ketones were probed by monitoring the evolution of ν_{C-H} band of the former and $\nu_{C=O}$ band of later molecules in the FTIR spectra measured with solutions containing various proportions of the donor−acceptor molecules in CCl_4. Figure 1 depicts the changes of the band shapes of the $\nu_{C=O}$ bands of three ketones for increasing the ketone to chloroform concentration in solutions. The concentration of cyclic ketone in each solution is 0.025 M, and ketone to chloroform concentration ratios in the four solutions are 1:1, 1:5, 1:10, and 1:15.

The top panel of the figure shows the complex formation effect on the $\nu_{C=O}$ band of cyclohexanone (CHN). The monomer band appears at 1717 cm^{-1}, and on addition of chloroform, a new band representing the formation of a 1:1 complex develops at 1709 cm^{-1}. The appearance of an isosbestic point (1715 cm^{-1}) between the band maxima of the monomer and the complex indicates the 1:1 stoichiometry of the complex (CHN···$CHCl_3$). A commercial curve fitting program (originpro7.5 PFM) was used to perform the spectral deconvolution. The deconvolution of the band corresponding to 1:10 mol ratio is shown in the right-hand side of the panel, where the fitted bands for the monomer and complex are denoted by blue and red curves, respectively. The similar changes of the $\nu_{C=O}$ bands of cyclopentanone (CPN) and cyclobutanone (CBN) are shown in the middle and lower panels, respectively. For the latter two systems, the red shifts of the bands are 19 and 6 cm^{-1}, respectively.

The same set of solutions was used to monitor the complex formation effects on the ν_{C-H} band of chloroform. In Figure 2, we have presented the appearance of this band corresponding to the three 1:1 complexes, and the band of bare chloroform is also presented to depict the complexation-induced changes. The ketone to chloroform mole ratio in the three cases was 1:10, and a solution of the same molar concentration of $CHCl_3$ in CCl_4 was used to record the background. The positive sign of the displayed bands (after background subtraction) of the complexes indicates that the intensity of the ν_{C-H} band is enhanced upon complex formation. The band maximum of bare $CHCl_3$ (dotted line) appears at 3018 cm^{-1}, and that of three complexes with CHN, CPN, and CBN appear at 3019, 3020,

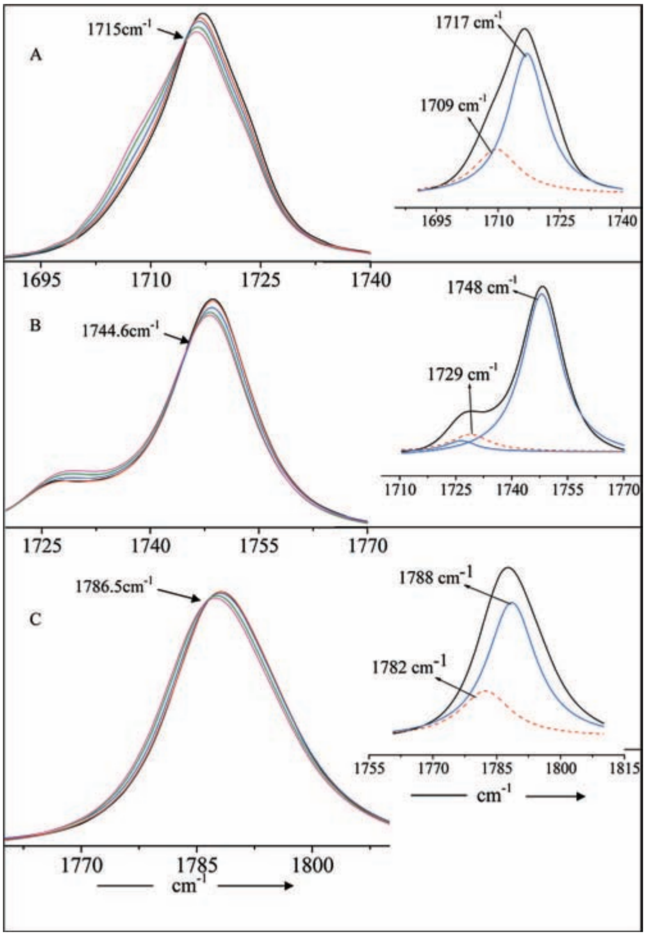

Figure 1. Carbonyl stretching fundamental ($\nu_{C=O}$) region of the FTIR spectra of the three cyclic ketones, (A) CHN, (B) CPN, and (C) CBN, measured in a 0.025 M solution of CCl_4 containing varying amounts of $CHCl_3$. The band shapes evolve owing to complex formation. In all three cases, appearances of distinct isosbestic points (denoted by arrows) indicate that the complexes have 1:1 stoichiometry. Red, blue, green, and magenta curves represent 1:1, 1:5, 1:10, and 1:15 ketone to chloroform mole ratios in CCl_4, respectively. On the right-hand side of each panel, the deconvoluted spectrum for a solution of 1:10 ketone to chloroform mole ratio is depicted. The blue curve denotes the $\nu_{C=O}$ band of a bare carbonyl group (monomer) and red dotted curve denotes the corresponding complex in the envelope. In case of CPN, the complex at 1729 cm^{-1} overlaps nearly with a monomer band at 1727 cm^{-1}.

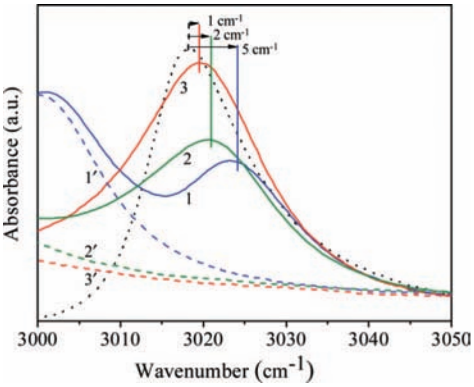

Figure 2. C−H stretching fundamentals of (black dotted curve) free chloroform and its 1:1 complexes with (red, 1) CHN, (green, 2) CPN, and CBN (blue, 3). The peak positions of the curves are marked by vertical lines. In the same spectral range, the higher frequency tails of the ring C−H bands of the free cyclic ketones (0.025 M) are also presented here (dashed curve, marked with X′) with the respective color codes for comparison.

TABLE 1: Spectral Shifts ($\Delta\nu$) of the Donor (C−H) and Acceptor (C═O) Groups and Free Energies of Formation ($\Delta G°_f$) of the Three CH···O HB Complexes of Chloroform and Cyclic Ketones[a]

complex	$\Delta\nu_{C-H}$ (cm^{-1})	$\Delta\nu_{C=O}$ (cm^{-1})	$\Delta G°$ (kcal/mol)	$\epsilon^{com}/\epsilon^{cl}$
CHN···$CHCl_3$	+1.0	−8.0	−0.60	5.0
CPN···$CHCl_3$	+2.0	−19.0	+0.09	10.5
CBN···$CHCl_3$	+5.0	−6.0	+0.47	11.7

[a] Complexation-induced enhancement of the ν_{C-H} transition intensity ($\epsilon^{com}/\epsilon^{cl}$) in the three complexes is presented in the right-most column.

and 3023 cm^{-1}, respectively. Thus, the blue shifts of the donor ν_{C-H} vary systematically with the ring size of the acceptor, and the shifts are 1, 2, and 5 cm^{-1} for complexations with CHN, CPN, and CBN, respectively. Apparently, the intensity enhancement is largest for complexation with CHN and least with CBN, and this enhancement sequence is opposite to the sequences of blue shifting. Since the observed intensities depend both on relative binding stability ($\Delta G°$) of the complexes and complexation-induced changes of molar extinction coefficient, i.e., $\epsilon^{com}/\epsilon^{cl}$ (ϵ = molar extinction coefficient), both parameters ($\Delta G°$ and $\epsilon^{com}/\epsilon^{cl}$) have been estimated separately (Table 1) by analyzing the intensities of the complex ν_{C-H} bands for several sets of solutions (see Supporting Information). The complex with CHN appears to be most stable ($-V_e\ \Delta G°$), and the order of stability follows the sequence CHN > CPN > CBN. The enhancements of ϵ of the ν_{C-H} band ($\epsilon^{com}/\epsilon^{cl}$) for complexations with the three ketones are estimated to be 5.0, 10.5, and 11.7 for CHN, CPN, and CBN, respectively, and the order follows the sequence of blue shifting.

In the following sections, we have explained the origin of different stability and spectral shifts of the three complexes. An intuitive explanation, correlating several relevant electronic structure parameters of the donor C−H and acceptor C═O bonds with the ring size of the cyclic ketones is given first followed by a detailed prediction of those parameters by quantum mechanical calculations performed at different levels of theory. Although the latter approach is rigorous and provides quantitative data, the former is found to be valuable to explain intuitively the manifested spectroscopic differences of the complexes in terms of simple rules of structural organic chemistry.

4.2. Intuitive Interpretation of Stability and Spectral Shifts of the Complexes. It has been shown in a number of recent studies that there is no fundamental difference between the blue-shifting (improper) and red-shifting (classical) HBs,[33,34,37,38,41,42] i.e., the same set of factors are responsible for stability of both types of HBs. In a C−H···O═C H-bonded complex, the primary stabilizing factors are (i) long-range electrostatic interactions between the weakly polar C−H and electron-rich O atom of the carbonyl group (dipole−dipole, dipole−induced dipole, etc.)[4,5,42,43] and (ii) hyperconjugative charge transfer from the filled nonbonded orbitals of O to σ^*_{C-H} orbital when the two molecular groups approach to each other sufficiently close that orbital overlap between them is effective.[27,44,45] We argue below that the stabilization energies in the three complexes are different, and which can be correlated with the geometric parameters of the cyclic ketones.

Since $\nu_{C=O}$ of CBN is nearly 70 cm^{-1} larger compared to that of CHN, the C═O bond of the former can be thought to be somewhat stronger than the latter. In other words, the bonding

TABLE 2: A Few Relevant Geometric Parameters, Dipole Moment, PA, and $\nu_{C=O}$ Frequencies of the Three Cyclic Ketones Predicted by MP2/6-31+G(d) and DFT/B3LYP/6-311++G(d,p) Theoretical Methods

	MP2/6-31+g(d)			DFT/B3LYP/6-311++g(d,p)		
monomer parameters	CHN	CPN	CBN	CHN	CPN	CBN
$\angle C_c{-}C_r{-}C_c$ (deg)	115.21	108.75	92.94	115.28	108.43	92.59
$R_{C=O}$ (Å)	1.2333	1.2268	1.2181	1.2127	1.2068	1.1983
dipole moment (Debye)	3.93	3.83	3.68	3.47	3.28	3.11
PA (kcal/mol)	199	195	165	208	204	194
$\nu_{C=O}$ (cm^{-1})	1744.6	1772.2	1814.2	1766.4	1794.5	1843.9
$\nu_{C=O}$ (cm^{-1}) (experimental)	1717	1748	1788			

TABLE 3: Natural Charges on Donor (H) and Acceptor (O) atoms and Hybridization of the Carbon Orbital in C═O of the Three Cyclic Ketones Obtained From NBO Analysis by MP2/6-31+G(d) and DFT/B3LYP/6-311++G(d,p) Methods

	MP2/6-31+G(d)			DFT/B3LYP/6-311++G(d,p)		
	CHN	CPN	CBN	CHN	CPN	CBN
q(O)	−0.6520	−0.6483	−0.6337	−0.5590	−0.5558	−0.5351
hybridization of the C_c in C═O bond	sp$^{2.19}$	sp$^{2.09}$	sp$^{1.99}$	sp$^{2.18}$	sp$^{2.09}$	sp$^{1.99}$
% s on C_c (C═O)	31.26	32.32	33.35	31.40	32.30	33.36
	$CHCl_3$			$CHCl_3$		
q(H)	0.2898			0.2069		

characteristics of the C═O group in the three molecules must be having some differences whose origin can be understood qualitatively in the following way. The $\angle C_r{-}C_c{-}C_r$ bond angle, where C_c is carbonyl carbon atom and C_r stands for two adjacent carbon atoms within the ring, of the three cyclic ketones are 92.9°, 108.8°, and 115.2° for CBN, CPN, and CHN, respectively (Table 2). These angles are much shorter compared to the ideal value of 120° for a sp^2 hybridized carbonyl carbon. Therefore, for $C_r{-}C_c$ bonds, the hybridization of C_c orbitals (sp^n) should be such that $n > 2$, and in the three cyclic ketones the value of n should follow the sequence CBN > CPN > CHN. Since total s of C_c is constant, the s character in the carbon-centric hybrid orbital of the C═O bond should be larger than that in an ideal sp^2 hybrid orbital. Therefore, for the C═O bond of the three cyclic ketones, the value of n should be smaller than 2, and is expected to be smallest in case of CBN. This implies that the bonding electrons are more tightly bound within the two atoms of the C═O bond of CBN compared to that of CHN. In effect, the carbonyl group of CBN should have less polar character than CHN, and the dipole moment and natural negative charge on the carbonyl oxygen atom (q(O)) of CHN should be larger compared to CBN. The ring-size of CPN being intermediate of the former two, those molecular parameters should have intermediate values. Therefore, it can be anticipated that the electrostatic stabilization energy of the HB complexes of chloroform with the said three cyclic ketones would follow the sequence CHN > CPN > CBN.

At a relatively shorter intermolecular separation, the H-bonded complexes are stabilized further via hyperconjugation. The interaction depends sensitively on relative orientation of the donor−acceptor groups for effective orbital overlap. According to the arguments presented above, CHN is a better electron donor than CBN because of greater accumulation of electron density at the carbonyl oxygen. Thus, from viewpoints of both stabilization mechanisms the CHN···$CHCl_3$ complex should be the most stable, and the stability is expected to follow the sequence CHN···$CHCl_3$ > CPN···$CHCl_3$ >CBN···$CHCl_3$. As mentioned before, the same sequence of stability has been inferred on the basis of estimated free energies of complex formation ($\Delta G°$).

The observed blue shifting of the C−H stretching fundamental of chloroform in the three complexes is the outcome of a subtle balance between hyperconjugation and repolarization of the C−H bond by the electric field of the carbonyl oxygen. Repolarization increases partial positive charge ($\delta+$) on the hydrogen atom, and this induces, according to Bent's rule,[66] rehybridization of the carbon orbitals, and the s character in the one directed toward H atom is increased. Such rehybridization causes strengthening of C−H bond with consequent increase of the bond stretching frequency. Using quantum mechanical calculations, it has recently been shown, by Alabugin et al., that the effect is quite general when the C−H group is the HB donor, and at shorter intermolecular separation this shortening effect is counterbalanced by hyperconjugation interaction.[27] Since the latter has been argued to be smallest in CBN···$CHCl_3$ complex, the blue-shifting effect should have largest manifestation in this system, and for the same reason the effect should be smallest in CHN···$CHCl_3$ complex.

4.3. Quantum Chemistry Predictions of Structure, Stability and Spectral Shifts. For quantitative predictions of structure and spectral properties of the three complexes, we performed quantum mechanical calculations at MP2/6-31+G(d) as well as DFT/B3LYP/6-311++G(d,p) levels. It is worth mentioning at the outset that one cannot expect complete agreement between the predictions of such gas phase calculations with the observed spectral changes for measurements performed in CCl_4 solutions. The calculations at the MP2 level consider not only the interactions between groups involved directly in H-bonding, but also take into account the dispersion interactions among the nonbonded groups of the donor−acceptor molecules as well. In the liquid phase, the latter interactions are likely to be less important to determine the complex geometry, because molecular moieties are individually solvated. Therefore, only direct interactions between the donor−acceptor groups (e.g., C−H and C═O in the present systems) should be important. Nevertheless, we show below that the predictions of gas-phase calculations are useful to understand some of the intrinsic differences of the three cyclic ketones, and how some components of the interaction energies and relevant electronic structure parameters of the donor group (C−H) evolve when $R_{H\cdots O}$between the donor−acceptor molecules is altered.

4.3a Structure and Vibrational Frequencies of Bare Molecules. Some calculated geometric and spectroscopic parameters of the three cyclic ketones are presented in Table 2. It is remarkable to note that the relative values of these parameters of the three ketones are exactly what was predicted intuitively based on the structure-bonding correlation (see section 4.2). Below, we summarize the correspondences between the two approaches.

(1) The values of $\nu_{C=O}$ of the three ketones predicted by the two theoretical methods, MP2/6-31+G(d) and DFT/B3LYP/6-311++G(d,p) display excellent agreement with the measured values. Second, the bond length of C═O group ($R_{C=O}$) and $\nu_{C=O}$ display excellent correlation, i.e., as the ring size of the cyclic ketones becomes smaller, $\nu_{C=O}$ increases and $R_{C=O}$ decreases.

(2) The sequence of calculated dipole moments, according to both theoretical methods, is CHN > CPN > CBN, and this has also been predicted intuitively. The same sequence is also reflected in the calculated proton affinities (PA) of the three ketones. The sequence of this parameter denotes the inherent tendency of the three cyclic ketones for H-bonding with the partially charged hydrogen atom of chloroform, and the electrostatic ion-dipole interaction between the proton and carbonyl groups of the cyclic ketones appears to concur with the sequence of PAs. The second important factor that contributes to PA is the charge transfer type interaction between carbonyl oxygen and proton, and this depends on donor ability of the carbonyl oxygen. This point has been discussed further in this section (see below).

(3) The origin of the sequence of the dipole moments of the three cyclic ketones can be understood analyzing the nature of the carbon hybrid orbital of the C═O bond. The NBO analyses (Table 3) by both theoretical methods show that the hybridizations of the carbonyl carbon atom orbital in the C═O bond are $sp^{1.99}$, $sp^{2.09}$, and $sp^{2.19}$ for CBN, CPN, and CHN, respectively. This sequence of hybridization explains the relative values of dipole moments of the three ketones and also the natural charges (q(O)) on carbonyl oxygen atoms (shown in the Table 3), because, the electron in a bonding orbital with larger s character is more tightly bound. The $n(O) \rightarrow \sigma^*(C-H)$ hyperconjugative charge transfer interaction was proposed to be a dominant stabilization mechanism for HBs, and it depends on availability of the charge to be donated from nonbonding orbital of oxygen, this should also be largest in the case of the CHN···$CHCl_3$ complex. Thus, from the viewpoints of electrostatics as well as hyperconjugation interaction mechanisms, the sequence of overall stability is expected to be CHN···$CHCl_3$ > CPN···$CHCl_3$ > CBN···$CHCl_3$. We show below that the same is also predicted by calculations.

It is noteworthy, however, that although the calculated sequence of *s* percentages agree with that has been inferred intuitively, but the actual values, i.e., *n* of sp^n hybridization, differ. It has been suggested intuitively that the value of *n* should be smaller than 2 for all three cyclic ketones, but the calculated numbers are 2.19, 2.09, and 1.99 for CHN, CPN, and CBN, respectively. These discrepancies can be understood in the framework of the Bent's rule.[66] According to this rule, the extent of s character of the carbon hybrid orbital of the C−X bond depends on electropositive/ negative character of the substituent X. The percentage of *s* character in the hybrid orbital is increased when X is electropositive in nature, and *s* character decreases when X is electronegative. Since electronegativity of oxygen (3.44) is larger than carbon (2.55) according to Pauling scale, the *s* character in the carbon hybrid orbital should be smaller in the C═O bond compared to that in a C═C bond of, say, ethylene. It was shown earlier that the carbon orbital of C−F bond can best be described as sp^4 hybridized in alkanes, sp^3 hybridized in alkenes and sp^2 in alkynes.[67] Therefore, the present systems also illustrate the generality of the rehybridization effect. In ref 67, Alabugin and Manoharan presented an extensive discussion on the effect performing computational studies on variety of complexes and chemical reactions.

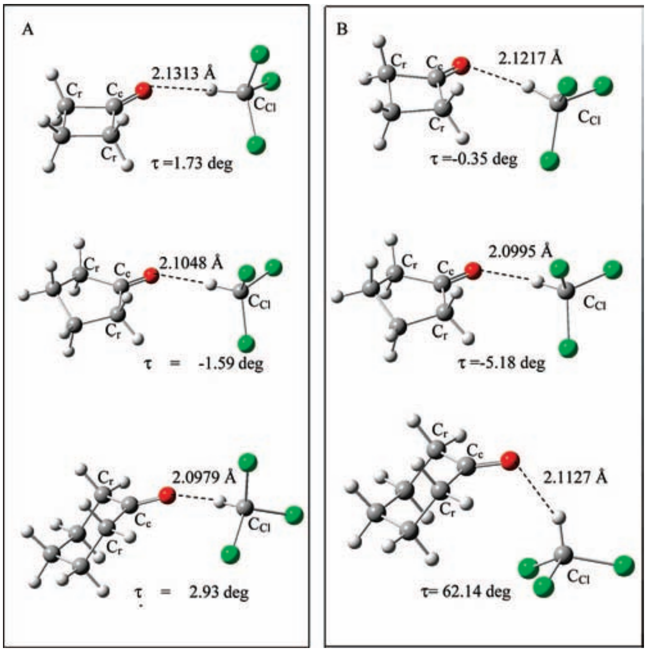

Figure 3. Optimized structures of the 1:1 complexes of chloroform with the three cyclic ketones. Parts A and B represent the calculated set of structures by DFT/B3LYP/6-311++G(d,p) and MP2/6-31+G(d) levels of theory, respectively. $R_{H\cdots O}$ is denoted by dashed lines.

4.3b Structure and Stability of the Complexes. The optimized structures of the complexes for calculations at DFT/B3LYP/6-311++G(d,p) and MP2/6-31+G(d) levels of theory are shown in Figure 3, and some relevant geometric parameters of these structures, in addition to those shown with the figures, are presented in Table 4. The key features of the predictions are the following:

(1) In the optimized structures of all three complexes predicted by DFT method the donor C−H group of chloroform has similar orientation about the acceptor C═O group. Thus, the dihedral angle τ ($\tau = \angle C_r-C_c-O\cdots H$) in complexes with CBN, CPN, and CHN are 1.7°, −1.6°, and 2.9°, respectively. However, in the structures predicted by MP2 method, the said dihedral angles are −0.3° and −5.2° for CBN···$CHCl_3$ and CPN···$CHCl_3$, respectively, but for CHN···$CHCl_3$ the angle is much different, 62°. We show below that such geometry differences have significant impact on interaction energies that require overlap between two orbitals on donor and acceptor groups.

(2) The similarities in DFT optimized structures of the three complexes indicate that the local interactions between the donor and acceptor groups are the dominant factors in determining the binding energies of the complexes by this method. The sequence of the predicted binding energies (Table 5) is consistent with the expectation considering donor abilities (hyperconjugation interaction) and dipole moments (electrostatic interaction) of the cyclic ketones. Furthermore, these energies are correlated with the $R_{H\cdots O}$ in the complexes. However, the dissimilarities in optimized geometries by MP2 method indicate that in addition to local interaction between the donor−acceptor groups, the interactions among the non-bonded groups (dispersion) are also taken into account by this method, the effect of the latter is quite apparent in case of CHN···$CHCl_3$ complex, because, the molecular shape of CHN is largely different from the other two. Because of such structural dissimilarity, the sequence of the

TABLE 4: Some Significant Geometric Parameters of the Three CH···O H-Bonded Complexes and Changes of the Bond Lengths of the Donor (C—H) and Acceptor (C=O) Groups Owing to Complex Formation[a]

	MP2/6-31+g(d)			DFT/B3LYP/6-311++g(d,p)		
	CHN··· CHCl$_3$	CPN··· CHCl$_3$	CBN··· CHCl$_3$	CHN··· CHCl$_3$	CPN··· CHCl$_3$	CBN··· CHCl$_3$
R_{C-H} (Å)	1.0866	1.0876	1.0872	1.0849	1.0849	1.0842
$R_{H\cdots O}$″	2.1127	2.0995	2.1217	2.0979	2.1048	2.1313
R_{C-C}″	3.7147	3.8671	3.7924	4.1648	4.1068	4.1546
$R_{C=O}$″	1.2362	1.2303	1.222	1.2167	1.2111	1.2022
Δr_{C-H}″	−0.0002	+0.0008	+0.0003	+0.0149	+0.0149	+0.0142
$\Delta r_{C=O}$″	+0.0024	+ 0.0036	+0.0039	+0.0040	+ 0.0043	+0.0040
∠C=O···H (deg)	123.56	123.76	119.64	140.50	135.99	137.74
∠ C$_r$—C$_c$—O···H (deg)	62.14	−5.18	−0.35	2.93	−1.59	1.73

[a] τ = The dihedral angle, ∠ C$_r$—C$_c$—O···H.

TABLE 5: Binding Energy and Hyperconjugation Interaction Energy between Donor-Acceptor Groups As Obtained from NBO Analysis of the Three CH···O H-Bonded Complexes[a]

	column I			column II			column III			column IV		
energy (kcal/mol)	DFT/B3LYP/6-311++g(d,p)			MP2/6-31+g(d)			MP2/6-31+g(d)			MP2/6-311++g(d,p)		
	CHN CHCl$_3$	CPN CHCl$_3$	CBN CHCl$_3$	CHN CHCl$_3$	CPN CHCl$_3$	CBN CHCl$_3$	CHN CHCl$_3$	CPN CHCl$_3$	CBN CHCl$_3$	CHN CHCl$_3$	CPN CHCl$_3$	CBN CHCl$_3$
ΔE	4.39	3.95	3.64	4.47	4.54	4.38	4.67	4.61	4.15	4.35	4.24	3.77
n(O) → σ*(C—H)	5.06	4.98	4.50	5.85	10.30	9.39	10.23	10.11	9.17	4.81	4.80	4.27

[a] Columns I and II display those energies calculated by DFT/B3LYP/6-311++G(d,p) and MP2/6-31+G(d) methods for full optimizations, and columns III and IV display the single-point energies calculated by MP2/6-31+G(d) and MP2/6-311++G(d,p) methods on DFT/B3LYP/6-311++G(d,p) optimized geometries.

TABLE 6: Natural Charges on H and O Atoms of HB Donor—Acceptor Groups, and the s Character in the Carbon Hybrid Orbitals of the C=O Bonds of the Three Complexes, As Obtained from NBO Analysis by MP2/6-31+G(d) and DFT/B3LYP/6-311++G(d,p) Theoretical Methods

	MP2/6-31+G(d)			DFT/B3LYP/6-311++G(d,p)		
	CHN··· CHCl$_3$	CPN··· CHCl$_3$	CBN··· CHCl$_3$	CHN··· CHCl$_3$	CPN··· CHCl$_3$	CBN··· CHCl$_3$
q(H)	0.3253	0.3278	0.3253	0.2498	0.2505	0.2445
Δq(H)	(0.0355)	(0.038)	(0.0355)	(0.0429)	(0.0436)	(0.0376)
q(O)	−0.6915	−0.6847	−0.6634	−0.5910	−0.5876	−0.5616
Δq(O)	(0.0395)	(0.0364)	(0.0297)	(0.032)	(0.0318)	(0.0265)
hybridization of the C$_c$ in C=O bond	$sp^{2.22}$	$sp^{2.12}$	$sp^{2.03}$	$sp^{2.21}$	$sp^{2.12}$	$sp^{2.02}$
%s on C$_c$ (C=O)	30.98	31.99	32.95	31.06	31.98	33.09

donor abilities of the cyclic ketones, which is important for stabilization via hyperconjugation mechanism, is not reflected in the predicted binding energies of the three complexes (column II, Table 5). For occurrence of n(O) → σ*(C—H) hypercojugative charge transfer, efficient overlap between the two orbitals is essential. This interaction energy, as revealed by NBO analysis, is relatively smaller in CHN···CHCl$_3$ compared to the other two complexes, and this happens because of a very different value of τ in the former complex. To verify this, we have performed single-point energy calculation by MP2/6-31+G(d) and MP2/6-311++G(d,p) methods on the DFT optimized geometries, and the results are presented in columns III and IV of Table 5. It is seen that the total energy and hyperconjugational energy follow the expected sequence for the three complexes. This confirms also that the hyperconjugation interaction contributes significantly to the experimentally measured sequence of stabilities of the three complexes.

(3) In Figure 4, we have shown the dependence of hyperconjugation energy on $R_{H\cdots O}$ (HB distance) taking the CBN···CHCl$_3$ complex as a representative example, and similar behavior has been noted for the other two systems. It is seen that for an increase of only 0.3 Å distance from the optimized value of $R_{H\cdots O}$, there is nearly a 50% drop of the hyperconjugation energy. The behavior is significant, because, in a CCl$_4$ solution the molecules are surrounded by solvent shell and that limits the closest possible approach the two H-bonding moieties. As a result, the intermolecular distances between the donor—acceptor molecules in the solution phase are likely to be larger compared to that of the gas-phase optimized structures. We show below that such difference could have profound effects on complexation-induced spectral shifts of C—H stretching vibrations in a solution phase study compared to the predictions of gas phase calculations.

(4) NBO analysis (Table 6) predicts that the natural charges at the binding sites (H and O atom) are increased on complex formation (induced dipole moments) in all three complexes, and this happens as a result of electrostatic induction as well as hyperconjugative charge transfer at a relatively shorter intermolecular separation. According to the Bent's rule, the increased positive charge on the H atom (decrease in effective electronegativity) of the H—C bond of chloroform (repolarization) affects rehybridization of the carbon bonding orbitals leading to an increased *s* character of the orbital directed toward the H atom. Such rehybridization can give rise to shortening of the C—H bond length.

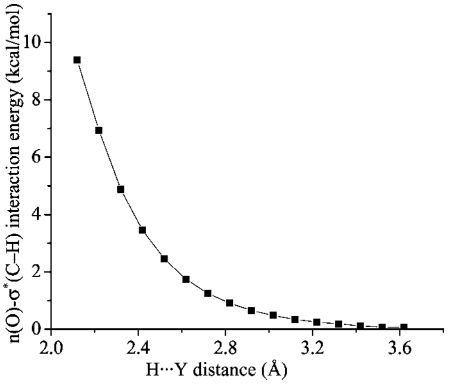

Figure 4. $n(O) \rightarrow \sigma^*(C-H)$ hyperconjugation interaction energy as a function of $R_{H\cdots O}$ of $CBN\cdots CHCl_3$ complex obtained from NBO analysis in a relaxed scan performed at MP2/6-31+G(d) level of calculation.

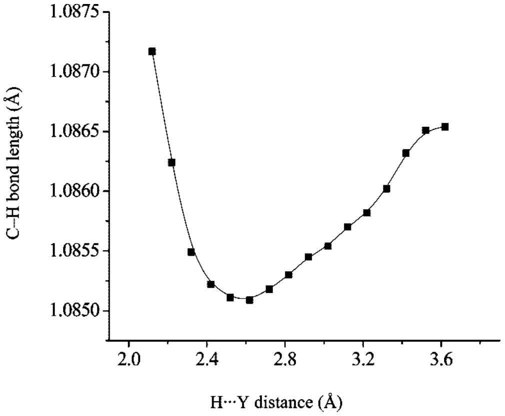

Figure 5. Variation of C—H bond length with $R_{H\cdots O}$ of $CBN\cdots CHCl_3$ complex in a relaxed scan at MP2/6-31+G(d) level.

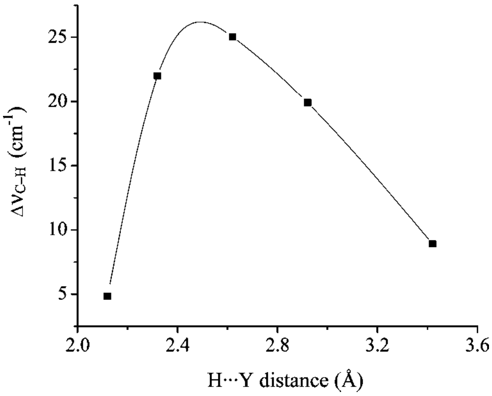

Figure 6. Variation of the predicted ν_{C-H} of chloroform with the $R_{H\cdots O}$ in case of $CBN\cdots CHCl_3$ complex.

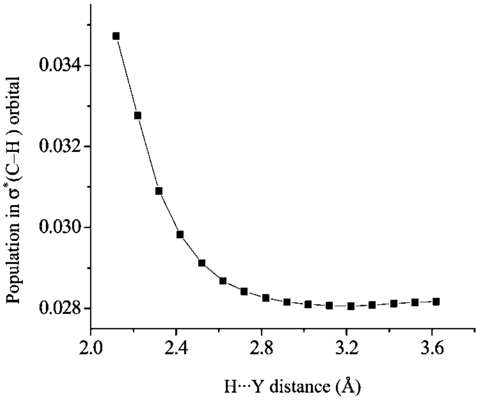

Figure 7. Changes in population of $\sigma^*(C-H)$ orbital of chloroform in the $CBN\cdots CHCl_3$ complex in a relaxed scan of $R_{H\cdots O}$ performed at MP2/6-31+G(d) level.

4.3c Structure and Spectral Shifts of the Complexes. To correlate the measured spectral shifts, $\Delta\nu_{C-H}$ and $\Delta\nu_{C=O}$, with the distortions of the electronic and geometric parameters of the donor−acceptor molecules on complex formation, and to rationalize the spectral changes with effects arising due to ring size of the cyclic ketones, we calculated the vibrational frequencies of all molecular species by MP2/6−31+G(d) method. It is worth mentioning that in most of the recent reports on blue-shifting H-bonded complexes, calculations at similar levels of theory were performed for predictions of spectral properties. For example, in case of deuterated acetone and deuterated oxirane complexes with a series of chlorofluorohaloforms, Delanoye et al. showed that the agreement between the measured blue shifts of the ν_{C-H} bands of the donor groups of haloforms display good correlations with those predicted by MP2/6−31G(d) theoretical method.[17,18] Very recently, Joseph and Jemmis studied a variety of H-bonded complexes by MP2/6-31+G(d) method.[3] In the present work, we also have performed frequency calculation by the MP2/6−31+G(d) method. Therefore, the predictions of spectral properties of the H-bonded complexes studied here can be compared with those of earlier studies. We summarize our analysis under the following headings:

(1) Corresponding to the optimized geometries, the predicted shifts of ν_{C-H} (chloroform) in complexes with CBN, CPN, and CHN are +5, −2, and +14 cm^{-1}, respectively. Thus, although there is partial agreement, but the sequence certainly does not follow the respective measured shifts of +5, +2, and +1 cm^{-1}. It is notable that the largest deviation between the observed and predicted shifts occurs in case of CHN complex. We believe that this deviation is due to the distorted optimized geometry of the $CHN\cdots CHCl_3$ complex predicted by the same method compared to the other two systems. NBO analysis shows that the hyperconjugation energy corresponding to the optimized complex geometry is much smaller, therefore, rehybridization effect (bond shortening) supersedes the hyperconjugation effect (bond lengthening) resulting in net large blue shift (+14 cm^{-1}).

(2) The electronic structure calculations performed till the date on C—H···O H-bonded systems conclude that the blue- or red-shifting of ν_{C-H} frequencies are correlated with shortening or lengthening of the C—H bond.[17,18,20,25,27,30,32,47] In the case of $CBN\cdots CHCl_3$ complex studied here, the correlation between the C—H bond length and blue shifts of ν_{C-H} are displayed in Figures 5 and 6, respectively. The maximum bond length shortening occurs for the $R_{H\cdots O}$ value of ~2.6 Å, and blue-shifting is also largest at this intermolecular separation. At lower values of $R_{O\cdots H}$, the bond elongates due to dominance of the hyperconjugation interaction. The $R_{H\cdots O}$ dependence of the hyperconjugation energy is shown in Figure 4, and in Figure 7, we have shown how the population of σ^* (C—H) orbital changes with $R_{H\cdots O}$. Since the expected sequence of the $R_{H\cdots O}$ values in the three complexes considering the donor abilities of the cyclic ketones is $CBN\cdots CHCl_3$ > $CPN\cdots CHCl_3$ > $CHN\cdots CHCl_3$, and the same sequence is also predicted by calculation (Figure 3A), the blue shifting of the ν_{C-H} band of chloroform in the complexes should also follow the above sequence.

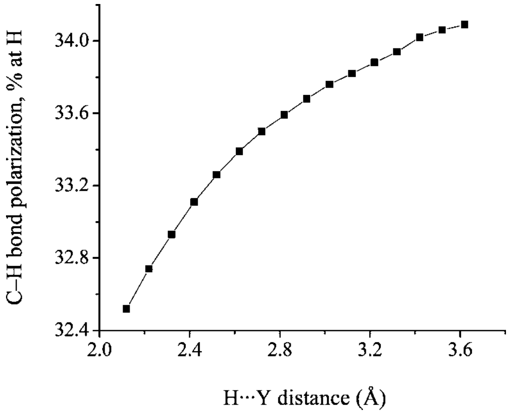

Figure 8. Variation of σ(C—H) polarization (% of electron density at H) of chloroform in CBN···$CHCl_3$ complex in a relaxed scan of $R_{H\cdots O}$ performed at the MP2/6-31+G(d) level of theory.

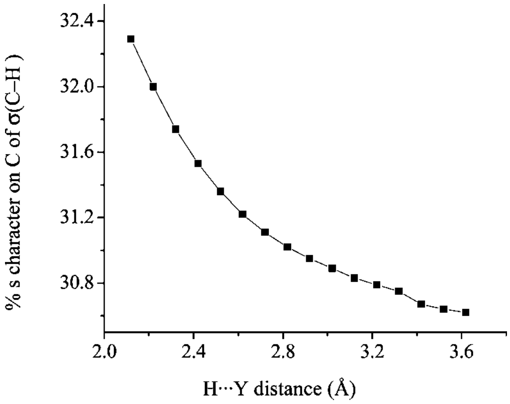

Figure 9. Variation of "*s*" character (%) in the carbon hybrid orbital of the C—H bond of chloroform in CBN···$CHCl_3$ complex with $R_{H\cdots O}$ obtained in a relaxed scan performed at the MP2/6-31+G(d) level of theory.

(3) In Figures 8 and 9, we have shown the changes in C—H bond polarization and percentage of *s* character of the carbon hybrid orbital of the bond upon decrease of $R_{H\cdots O}$ from a large intermolecular separation. It shows that the *s* character (%) of the carbon hybrid orbital of C—H bond is increased (rehybridization), and it causes strengthening of the bond (shortening effect). Alabugin et al. explained, in the framework of the Bent's rule, that this rehybridization effect is the outcome of repolarization of the bond by the electric field of carbonyl oxygen.[27] Similar changes have also been predicted in the complexes with other two cyclic ketones.

(4) At the HB acceptor site, calculation predicts a reduction of the carbonyl stretching fundamental frequency ($\nu_{C=O}$) in all three complexes. From an energetic viewpoint, the smaller shift observed for CHN compared to CPN is an anomalous behavior, because the binding energy with $CHCl_3$ of the former is larger than that of the latter. The observation contrasts with the common perception that spectral shift of a group involved in H-bonding is a measure of the binding energy.[68] We offer the following tentative explanation for this spectral behavior. Calculation shows that the normal mode corresponding to the C═O stretching vibration of the cyclic ketones is not localized only at this bond, but the mode has contributions also from other internal coordinates as well. In Figure 10a, we have shown the displacement vectors corresponding to this mode of CPN calculated by the MP2/6-31+G(d) method. It was shown earlier by analyzing potential energy distribution of the normal modes that in case of CPN the contribution of C═O stretching internal coordinate to this mode is ~78% and in case of CHN the contribution is ~75%.[69,70] In part b of the figure the normal mode of the CPN···$CHCl_3$ complex is depicted, and it shows that the mode has small contribution of the C—H bending vibration of chloroform moiety as well. In fact, the C—H bending occurs in phase with C═O stretching, and this happens because the two modes are nearly at resonance. This prediction indicates that complexation with chloroform induces small changes in the potential energy distributions of the cyclic ketones, and this could be the origin of the apparent anomaly in sequence of spectral shifts of this mode in the three complexes. We mention again that the intermolecular interaction between the donor—acceptor molecules is somewhat affected by solvation process in a CCl_4 solution. Consequently, the actual changes of the potential energy distribution are likely to be different from the predictions of the gas-phase calculation. However, the same does not happen in case of C—H stretching vibration of chloroform, because the mode is practically localized at the C—H bond.

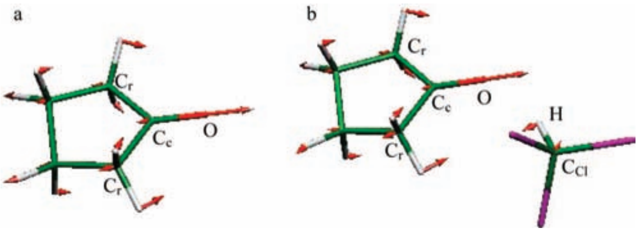

Figure 10. Normal modes corresponding to C═O stretching vibrations of (a) bare CPN and (b) CPN···$CHCl_3$ complex.

(5) Finally, as pointed out earlier in all three complexes, the blue shifting of C—H stretching fundamental occur with enhancement of IR absorption intensity. The behavior is similar to the chloroform complexes with acetone and oxirane, noted earlier by van der Veken and co-workers.[18] In the case of the CBN···$CHCl_3$ complex, the ratio of the molar extinction coefficients of complex to monomer ($\epsilon^{com}/\epsilon^{cl}$) of the ν_{C-H} band estimated from the measured spectra is ~11, and the ratio predicted by theoretical calculation (MP2/6-31G+(d)) is 110. Since the IR absorption intensity depends approximately on the dipole moment gradient, $\partial\mu/\partial r_{C-H}$,[17] the observed intensity enhancement indicates that this gradient of chloroform C—H bond is increased in all three complexes. In an earlier report, the value of this gradient for free chloroform was calculated to be 0.131 DÅ^{-1}, and modeling the H-bonded acceptor, (dimethyl ether), as a source of the electric field, the enhanced value of the gradient in the chloroform-dimethyl ether complex was predicted to be 0.621 DÅ^{-1}.[17] In the present work, although we have not performed such model calculation, the data of the NBO analysis on this system (Table-6) show an increase in the C—H bond dipole moment due to repolarization of the bond by the acceptor cyclic ketones (more natural charges on both C and H atoms). Such changes augment the dipole gradient and the IR intensity of the ν_{C-H} band on complex formation.

Conclusions

In the present work, we have demonstrated that the CH···O═C type H-bonded complexes between chloroform and three small cyclic ketones are quite stable in a CCl_4 solution at room temperature. The FTIR spectroscopy reveals that the C—H stretching fundamental transition (ν_{C-H}) of the donor molecule (chloroform) exhibits blue-shifting with enhancement in transition intensity. The spectral blue shifts and stability of the complexes ($\Delta G°_f$) depend on the ring size of the cyclic ketones. The shifts for complexes with CBN, CPN, and CHN are +5, +2 and +1 cm^{-1}, respectively, and the corresponding estimated values of $\Delta G°_f$ are 0.47, 0.09, and −0.60 kcal/mol. Thus, the blue-shifts and binding stability display a kind of reverse relationship, i.e., the most stable complex exhibits least amount of blue-shift. The observations imply that although the HB acceptor sites of the three ketones are functionally the same, but the acceptor ability is different and it depends on the detailed geometric parameters of the molecule. Furthermore the red-shifts of the acceptor carbonyl group of the three ketones are different, and these show no correlation with the binding energies of the complexes. This behavior is contrary to the common perception that red-shift is a measure of hydrogen bond energy. Using the simple concepts of structure-bonding relationships, we have explained how the polarity of the carbonyl groups of the three cyclic ketones, which stabilizes the H-bonded complexes by electrostatic and hyperconjugation interactions, could be correlated with the ring size of the cyclic ketones. These arguments are further extended by providing quantitative electronic structure parameters of the donor (C−H) and acceptor (C=O) groups predicted by quantum chemistry calculations at MP2/6-31+G(d) and DFT/B3LYP/6-311++G(d,p) levels. It has been shown that as the donor and acceptor moieties are made to approach each other from a large separation, the C−H bond undergoes repolarization and rehybridization that results in shortening of the bond length and increases the value of ν_{C-H}. At sufficiently smaller intermolecular separation, the $n(O) \rightarrow \sigma^*(C-H)$ hyperconjugation interaction between two molecules dominates and it lowers the value of ν_{C-H}. The optimized C−H bond length is the net effect of two opposing factors. In a CCl_4 solution at room temperature, the average intermolecular separation between donor−acceptor molecules is likely to be different compared to the prediction of a gas-phase quantum chemistry calculation. Therefore, the predicted spectral shifts are liable to be different from the observed values. The reverse correlation observed between the ν_{C-H} blue shifting and stability of the three complexes has been interpreted as the outcome of a balance between hyperconjugation and repolarization/rehybridization effects.

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Supporting Information Available: Principle of estimation of $\Delta G°$ and $\epsilon^{com}/\epsilon^{cl}$ for complex formation from measured spectra. Complete citation for Gaussian 03 (ref 65). This information is available free of charge via the Internet at http://pubs.acs.org.

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