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Probing C-H···N interaction in acetylene-benzonitrile complex using matrix isolation infrared spectroscopy and *DFT* computations

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ABSTRACT

Hydrogen-bonded complexes of acetylene (C_2H_2) and the benzonitrile (C_6H_5CN) have been investigated using matrix isolation infrared spectroscopy and *DFT* computations. The structure of the complexes and the energies were computed at B3LYP and B3LYP+D3 levels of theory using 6–311++G (d, p) and aug-cc-pVDZ basis sets. *DFT* computations indicated two minima corresponding to the C-H···N (global) and C-H···π interactions (local) of 1:1 C_2H_2-C_6H_5CN complexes, where C_2H_2 is the proton donor in both complexes. Experimentally, the 1:1 C-H···N complex identified from the shifts in the C-H and C≡N stretching modes corresponding to the C_2H_2 and C_6H_5CN sub-molecules in N_2 and Ar matrices. Atoms in Molecules and Natural Bond Orbital analyses were performed to understand the nature of interaction and to unravel the reasons for red-shifting of the C-H stretching frequency in these complexes. Energy decomposition analysis was carried out to discern the various stabilizing and destabilizing components as a result of hydrogen bonding in the C_2H_2-C_6H_5CN complexes.

1. Introduction

There has been an emphasis on the study of intermolecular interactions and in particular weak hydrogen bonds involving C-H···O, C-H···N, C-H···X (X-halogens) and C-H···π interactions, as these serve as a driving force for many molecular phenomena and processes in chemistry, biology and material science [1–3]. Spectroscopic studies of weak complexes isolated at low temperatures have provided a wealth of information on the structures and dynamics, which paved way to understand the macroscopic phenomena.

Benzonitrile (C_6H_5CN) is a prototypical system for an aromatic molecule with a cyano group, which forms a key element in many bio-molecular systems [4,5]. Benzonitrile has a high dielectric constant (ε = 26.0), and it is miscible with a range of ionic and polar solvents [6]. Acetylene and benzonitrile are used as starting material for the preparation of pyrimidines and pyridines [7]. Furthermore, this binary system is used as a catalyst in photochemical reactions [8–11].

Green and Harrison studied the infrared and Raman spectra of benzonitrile in the vapor phase and assigned the vibrational features of the benzonitrile molecule [12,13]. Jakobsen reported the infrared and Raman spectra of isotopically substituted liquid benzonitrile-d_5 and subsequently assigned the vibrational features of benzonitrile [14].

Bernstein et al. studied the infrared spectra of 16 solid state nitriles, isonitriles and related compounds isolated in Ar and H_2O matrices. They observed that the C≡N stretching bands of the majority of nitriles fall in the region 2200–2080 cm^{-1}. The CN bands were found to be considerably broader in H_2O matrix. The spectra observed for different nitriles were used as a database to interpret the infrared features observed in the CN region and these data are being obtained by Infrared Space Observatory (ISO) [15].

Pacansky and Coufal studied the infrared spectra of benzonitrile-HCN and the acetonitrile dimer by selectively photolyzing the mono-phenyl-tetrazine and 1,4-dimethyltetrazine. The tetrazine precursors were isolated in low-temperature matrices and irradiated with UV light to produce nitrile-HCN and nitrile dimer adducts [16].

Hoops and Ault studied the photochemical reactions of chlorobenzene, α,α,α-trifluorotoluene, benzonitrile and nitrobenzene with $CrCl_2O_2$. The matrix isolation infrared technique and theoretical calculations were used to identify the photoproducts. Photoirradiation resulted in oxygen atom transfer, the formation of complexes between the corresponding cyclic ketone derivatives and $CrCl_2O_2$. In benzonitrile, on irradiation, the C-H group gets

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activated and insertion of oxygen atom into the C-H group resulted in the formation of cyanophenol and the interaction of the cyanophenol with $CrCl_2O_2$ was observed [17].

Several groups have studied the C-H···N interactions both by experimental and theoretical methods [18–22]. Our interest in the weak hydrogen-bonded systems led to earlier studies on complexes of CHF_3, $CHCl_3$, C_2H_4, C_6H_6, C_6H_5OH, CH_3CN, C_5H_5N, and CH_3-OH with C_2H_2 using matrix isolation infrared spectroscopy [23–30].

In the C_2H_2-C_5H_5N system, complex stabilized by a C-H···N interaction was experimentally observed in an Ar matrix. *Ab initio* computations performed on the C_2H_2-C_5H_5N complex at HF and B3LYP levels of theory using a 6–311++G (d, p) basis set supported the experimental observation [29].

Recently, we have reported the hydrogen-bonded interactions of acetylene with acetonitrile. The complex stabilized by the C-H···N interaction was trapped in both Ar and N_2 matrices. The structure and the energies of the complex were computed at the B3LYP and MP2 levels of theory using a 6–311++G (d, p) and aug-cc-pVDZ basis sets. Computations indicated one minimum corresponding to the 1:1 C_2H_2-CH_3CN complex, with CH···N interaction, where C_2H_2 is the proton donor [28].

Earlier we have studied C_2H_2-C_2H_4 [25] and C_2H_2-C_6H_5OH [27] systems and observed experimentally both type of complexes, one where C_2H_2 was the proton donor and another, where it played the role of a proton acceptor. In the matrix isolation experiment, the rigid inert gas matrix in combination with the low temperature makes it possible to trap both complexes.

In this work, we have studied the interaction of C_2H_2 and C_6H_5CN. Benzonitrile has three electron rich sites, nitrogen, C≡N triple bond and π-cloud of the benzene ring, which can form either an σ or π type hydrogen bond or both. C_2H_2 acts as a proton donor as the hydrogen attached to the 'sp' carbon atom is acidic. Alternatively, C_2H_2 can also play the role of a proton acceptor through its π-cloud. It is interesting to study the interaction between the C_2H_2 and C_6H_5CN to see whether any or all complexes could be trapped and studied in the experiment performed at low temperatures.

2. Experimental section

Matrix isolation experiments were performed using an RDK-408D2 (Sumitomo Heavy Industries Ltd.) closed cycle helium compressor cooled cryostat, and it is housed in a vacuum chamber where the base pressure was better than 1×10^{-6} mbar. C_2H_2 (Commercial Grade, Asiatic Oxygen Limited, India) and benzonitrile, C_6H_5CN (Merck, HPLC grade 99.8%) were used as such, without further purification. However, the samples were subjected to several freeze-pump-thaw cycles before its use. Ultra high pure N_2 (INOX, 99.995%) and Ar (INOX, 99.9995%) were used as matrix gasses, in which C_2H_2 gas was premixed to obtain the desired matrix-to-sample ratio. The C_2H_2/matrix gas mixture and C_6H_5CN were then deposited using double jet nozzle onto a KBr substrate maintained at 12 K and the deposition lasted for about 60 min at a typical rate of ~3 mmol/h. We used typical matrix-to-sample ratios ranging from 1000:0.1 to 1000:0.25 for C_2H_2 and 1000:0.2 to 1000:0.8 for C_6H_5CN.

Infrared spectra of the matrix isolated samples were recorded in the range 4000 to 400 cm^{-1}, using a vertex 70 Bruker FTIR spectrometer, operated at a resolution of 0.5 cm^{-1}. The matrix was then slowly warmed to 30 K (N_2) and 35 K (Ar) for about 15 min and then re-cooled to 12 K. Spectra of the matrix, thus annealed, were again recorded.

3. Computational details

All the calculations were performed using Gaussian 09 suite of programs [31]. Geometry optimizations were performed for the complexes at *DFT* hybrid exchange-correlation functional (B3LYP) and dispersion corrected (B3LYP empirical dispersion = GD3) methods [32] using 6–311++G (d, p) and aug-cc-pVDZ basis sets. Starting from the optimized monomer geometries, the geometry of the 1:1 complexes was optimized without imposing any structural constraints. Vibrational wavenumber calculations were performed for the optimized geometries to enable us to characterize the nature of the stationary points and also to assign the observed wavenumbers in our matrix isolation experiments. Stabilization energies, computed for the complexes were corrected separately for both zero-point energies and basis sets superposition errors (BSSE) [33].

Atoms in Molecules (AIM) analysis [34,35] was performed on the optimized geometries of C_2H_2, C_6H_5CN and C_2H_2-C_6H_5CN complexes computed at B3LYP/6–311++G (d, p) level of theory using the AIMPAC package [36].To understand the nature of hyper conjugative charge-transfer interactions in determining the stability of the adducts, Natural Bond Orbital (NBO; version 3.1) analysis was performed, invoked through Gaussian 09 [37]. Energy decomposition analysis was performed for the 1:1 C_2H_2-C_6H_5CN complexes at the B3LYP+D3/TZ2P level of theory using ADF-2016 package [38–40].

4. Results and discussion

4.1. Experimental details

Fig. 1 (block A and B) shows the matrix isolated infrared spectra of C-H asymmetric ν_3 stretching mode of C_2H_2 in N_2 and Ar matrices. The spectra shown in the figure were obtained after annealing at 30 K and 35 K in N_2 and Ar matrices, respectively. The ν_3 mode of C_2H_2 is observed at 3282.8 and 3288.8 cm^{-1} in N_2 (Fig. 1a block A) and Ar matrix (Fig. 1a block B), respectively. The features due to C_2H_2 dimer were observed at 3279.5 and 3257.4 cm^{-1} in N_2 and 3285.6, 3270.2 and 3263.2 cm^{-1} in Ar matrix. A strong absorption peak at 3240.0 cm^{-1} is due to C_2H_2-H_2O complex in Ar matrix [41]. When C_2H_2 and C_6H_5CN were co-deposited and annealed, a new feature was observed at 3238.8 (Fig. 1b–c, block A) and 3238.6 cm^{-1} (Fig. 1b–c, block B) in N_2 and Ar matrices, respectively.

Fig. 2 block A and B (2260–2230 cm^{-1}) shows the infrared spectra of ν_2 symmetric CN stretching mode of C_6H_5CN isolated in N_2 and Ar matrices. The features observed as site split features at 2242.6, 2238.1, 2235.9 cm^{-1} (Fig. 2a block A) in N_2 and 2245.3, 2241.7 and 2237.6 cm^{-1} in Ar matrix (Fig. 2a block B) are due to ν_2 symmetric CN stretching mode of C_6H_5CN, which agrees well with the reported value. The multiple features arise due to the benzonitrile molecule occupying several different sites, each with different geometry, in Ar and N_2 matrices [15]. The feature observed at 2251.3, and 2247.9 cm^{-1} in N_2 and Ar matrices is due to C_6H_5CN-H_2O complex [42]. When the precursors were co-deposited and annealed new product absorption peaks appeared in the CN stretching region of C_6H_5CN at 2245.8 and 2246.0 cm^{-1} in N_2 and Ar matrices.

The new features were observed only when both C_2H_2 and C_6H_5CN were co-deposited and gained in intensity as the concentration of either of the precursors was increased indicating that the feature is only due to C_2H_2 and C_6H_5CN complex.

4.2. Computations on the 1:1 C_2H_2-C_6H_5CN complexes

DFT computations on the 1:1 C_2H_2-C_6H_5CN complexes at the B3LYP and B3LYP+D3 level of theory using 6–311++G (d, p) and aug-cc-pVDZ basis sets yielded two minima with the global minimum being the structure stabilized through C-H···N interaction.