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Non-covalent C–Cl…π interaction in acetylene-carbon tetrachloride adducts: Matrix isolation infrared and *ab initio* computational studies

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ABSTRACT

Non-covalent halogen-bonding interactions between π cloud of acetylene (C_2H_2) and chlorine atom of carbon tetrachloride (CCl_4) have been investigated using matrix isolation infrared spectroscopy and quantum chemical computations. The structure and the energies of the 1:1 C_2H_2–CCl_4 adducts were computed at the B3LYP, MP2 and M05-2X levels of theory using 6–311++G(d,p) basis set. The computations indicated two minima for the 1:1 C_2H_2–CCl_4 adducts; with the C–Cl…π adduct being the global minimum, where π cloud of C_2H_2 is the electron donor. The second minimum corresponded to a C–H…Cl adduct, in which C_2H_2 is the proton donor. The interaction energies for the adducts A and B were found to be nearly identical. Experimentally, both C–Cl…π and C–H…Cl adducts were generated in Ar and N_2 matrixes and characterized using infrared spectroscopy. This is the first report on halogen bonded adduct, stabilized through C–Cl…π interaction being identified at low temperatures using matrix isolation infrared spectroscopy. Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) analyses were performed to support the experimental results. The structures of 2:1 ($(C_2H_2)_2$–CCl_4) and 1:2 (C_2H_2–$(CCl_4)_2$) multimers and their identification in the low temperature matrixes were also discussed.

1. Introduction

Non-covalent intermolecular interactions play an important role in chemistry and biology [1,2]. Understanding the nature of these weak intermolecular interactions involved in molecular recognition is rapidly growing. During the last century, the hydrogen bond (H-Bond) has played the centrestage among weak interactions. Extremely weak interactions such as C–H…π interactions have received much attention, due to their importance in crystal packing, molecular conformations and molecular recognition [3].

The concept of weak interactions has gone beyond the H-Bond with the recognition of weak interactions involving other elements [4]. The most developed among these is the halogen bond (Hn-Bond), X–Hn…Y where Hn is a halogen atom, which has attracted a large number of experimental and theoretical investigations [5–20]. The crucial role of the Hn-Bond in the field of drug design, supramolecular chemistry, crystal engineering and physical organic chemistry has been the main driver for these major advances [5–17]. While the H- and Hn-Bonds appear similar in many respects, there are some striking differences. The variations in the polarity of the X–H bond are very high, as in C–H *vs.* F–H, but there is only one orbital and one electron that hydrogen brings in. However, in terms of number of electrons and orbitals available, the Hn-Bond brings in several additional considerations [17–20]. There are three lone pairs which can affect the nature of the Hn bond and hence the Hn…Y interaction. In general, the Hn-Bonds can be expected to have greater contributions from dispersion interactions, in comparison to the H-Bond. In view of the generality and importance of the Hn-Bond, a formal definition of the Hn-Bond has been formulated under the auspices of the IUPAC [21].

In the recent past, Hn-Bonding was interpreted in a different dimension through a 'σ-hole' concept and subsequently, it has become the subject matter for theoretical chemists to examine the nature of electronegative halogen atom with the lone pair of electrons as an electron acceptor [22–27]. Politzer et al. reported for the first time that the region of positive electrostatic potential on the outer region is responsible for a halogen atom to behave like a hydrogen atom [28]. Since, potential electron donors such as halogens can be thought of electron acceptors, the concept was further extended to the π-cloud and was endorsed theoretically [22,29–31].

Non-covalent interactions of halogens with π-electron clouds are extremely important in crystal engineering [17–20] and in biological processes as these are the key intermediates in the electrophilic halogenations of alkenes, alkynes, allenes and aromatic systems [32–34]. Furthermore, these interactions were observed in many inclusion compounds and in aromatic compounds with

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halogens [35–39].The operational part of the IUPAC definition is still broad to include the interaction of a chlorine atom of a C–Cl bond with a π-system.

Interest is growing among the scientific community to explore the interactions involving π cloud, with the acceptor being the halogen atom, instead of the formal hydrogen atom. There have been numerous theoretical studies on C–Hn…π interactions. Tomura has performed *ab initio* computations on non-covalent interactions between the triple bonds and chlorine atoms (C–Cl…π) in the adducts of acetylene with chloromethanes using HF and MP2 methods with Dunning's correlation consistent basis sets and concluded that the intermolecular potentials are flat near the minimum and the main contributions to the binding energies are long-range dispersion interaction [40]. Lu et al. performed *ab initio* computation on a series of adducts formed between C–Hn and 'π' framework of aromatics and other systems [41]. These authors reported that the interaction energies of C–Hn…π is comparable with C–H…π bonds. It was also observed that the dispersion interaction is the main contributor for the stabilization of the C–Hn…π adducts. Li and co-workers studied the Hn-Bonds between $C_2H_{4\text{-}n}F_n$ (n = 0–2) double bonds and chlorine monofluoride [42]. Recently, Shishkin et al. reported the C–Cl…π interaction inside supramolecular nanotubes of hexaethynylhexamethoxy-6-pericyclyne and it was deduced that the C–Cl…π interaction arises due to σ-hole direction through DFT computations [43].

A few experimental works on the Hn…π interaction is reported. Bloemink et al. characterized the T-shaped structure of C_2H_2-Cl_2 adduct and the geometry of the C_2H_4-ClF adduct using pulsed nozzle microwave spectroscopy [44,45]. Legon has reported the experimental characterization of varieties of Hn-Bonded adducts in the gas phase by supersonic expansion using microwave spectroscopy [32]. Recently, Matter et al. reported the experimental evidence for the C–Cl…π and C-Br…π interaction in the orally bioavailable molecule AVE-3247 using X-ray crystal structures, binding energies, 3D database searches and *ab initio* calculations [46].

Herrebout and co-workers have found evidences for the Hn…π interaction in low temperature inert matrix liquids. Using FTIR and Raman spectroscopy, the formation of Hn-Bonded C-X…π 1:1 complexes of the trifluorohalomethanes (CF_3Cl, CF_3Br and CF_3I) with ethene and propene have been evaluated by Hauchecorne et al. in liquid Ar [47]. Nagels et al. studied the Hn-Bonded interaction between CF_3X (X = Cl, Br and I) with benzene and toluene in liquid Kr [48]. Quite recently, Nagels and Herrebout probed the triple bonded acetylinc π cloud as a possible electron donor to CF_3X (X = Cl, Br and I) in liquid Kr using infrared and Raman spectroscopy [49].

Matrix isolation infrared spectroscopy is a versatile technique to study these weak interactions [50–52]. We have earlier explored the C–H…π interactions, a class of weak H-Bonding interactions in the adducts formed by $CHCl_3$, C_2H_4, and C_6H_6 with C_2H_2 [53–55]. Likewise, we have studied the Hn-Bonded interaction of trimethyl phosphate (TMP) and CCl_4 using matrix isolation infrared spectroscopy and *ab initio* computations [56]. By combining the *ab initio* computations with experiments, the existence of Cl…O interaction in adducts of TMP and CCl_4 in nitrogen matrix was confirmed. An examination of electron density topology in the adducts clearly revealed the existence of a weak Cl…O interaction.

In spite of the existence of diverse studies on the weak Hn-Bonding interactions, to the best of our knowledge until date, there is no report on experimental confirmation of the adducts stabilized through C–Hn…π interaction using low temperature matrix isolation technique. We report here the first experimental observation of an Hn-Bond involving the chlorine of carbon tetrachloride (CCl_4) and the π cloud of acetylene (C_2H_2) using matrix isolation infrared spectroscopy. We also explored this interaction computationally to support our experimental observations and to provide insights into the nature of the Cl…π interaction.

2. Experimental Section

Matrix isolation experiments were performed using a RDK-408D2 (Sumitomo Heavy Industries Ltd.) closed cycle helium compressor cooled cryostat. The cryostat was housed in a vacuum chamber where the base pressure was $<1 \times 10^{-6}$ mbar. C_2H_2 (Commercial Grade, Asiatic Oxygen Limited, India) and CCl_4 (GR grade, Merck) were used as such, without further purification. All the samples were subjected to several freeze-thaw cycles before use. N_2 and Ar (Inox, purity of 99.9995%) were used as matrix gases. C_2H_2 and CCl_4 were premixed with the matrix gases to obtain the desired matrix-to-sample ratios. The C_2H_2/CCl_4/matrix gas mixture was then deposited onto a KBr substrate maintained at 12 K. Typical matrix-to-sample ratios ranging from 1000:0.25 to 1000:0.5 for C_2H_2 and 1000:0.5 to 1000:2 for CCl_4 were used in the experiments. The matrix was deposited at a typical rate of ~3 mmol/h and a deposition typically lasted for about ~80 min.

Infrared spectra of the matrix isolated samples were recorded over the range 4000 to 400 cm^{-1}, using a BOMEM MB 100 FTIR spectrometer, operated at a resolution of 1 cm^{-1}. The matrix was then slowly heated to 35 K (Ar) and 30 K (N_2), which was maintained at this temperature for about 15 min and then re-cooled to 12 K. Spectra of the annealed matrix, were again recorded. All the spectra shown here were those recorded after annealing the matrix.

3. Computational Details

The C_2H_2–CCl_4 adducts were calculated using the GAUSSIAN 03 suite of programs [57]. Geometry optimizations were performed both at *ab initio* (Moller-Plesset second order perturbation (MP2) theory) and DFT (B3LYP, and M05-2X levels of theory) methods using a 6–311++G(d,p) basis set. Geometries of the monomers were first optimized and starting from the optimized monomer geometries, the structural optimization of the 1:1 and higher multimeric adducts was accomplished without imposing any geometrical constraints. Vibrational wavenumber calculations performed on the optimized geometries enabled us to characterize the nature of the stationary points and to assign the observed wavenumbers in our matrix isolation experiments. The computed wavenumbers for the different modes were scaled on a mode-by-mode basis for assigning the experimental features. Stabilization energies, computed for the adducts were also corrected separately for both zero point energies and basis set superposition errors (BSSE).

Atoms in Molecules (AIM) analysis [58,59] was performed on the optimized geometries of C_2H_2, CCl_4 and C_2H_2–CCl_4 adducts computed at B3LYP/6–311++G(d,p) level of theory using the AIMPAC package. To understand the nature of hyperconjugative charge-transfer interactions in determining the stability of the adducts, Natural Bond Orbital (NBO, version 3.1) analysis was performed, invoked through Gaussian G03W [60]. Energy decomposition analysis was performed at B3LYP/6–311++G(d,p) level of theory using ADF package [61–64].

4. Results and discussion

4.1. Experimental details

Fig. 1 shows the infrared spectra of C_2H_2 with varying concentrations of CCl_4 in N_2 and Ar matrixes, covering the region 3295–3265 cm^{-1} (grid A) and 3310–3250 cm^{-1} (grid B), respectively. The spectra shown in the figure were recorded after the sample was annealed at 30 K (N_2) and 35 K (Ar), respectively. In an Ar matrix, C_2H_2 shows two strong absorptions at 3288.9 and 3302.8 cm^{-1} (Fig. 1, grid B, trace 'a') which have been assigned to components of a Fermi diad involving the ν_3 mode and a combination band ($\nu_2 + \nu_4 + \nu_5$) [65]. The corresponding feature for C_2H_2 in the N_2 appears as a strong feature at 3282.8 cm^{-1} (Fig. 1, grid A, trace 'a'). The features observed at 3285.0 and 3263.3 cm^{-1} are due to C_2H_2 dimer in an Ar matrix. The corresponding feature for the C_2H_2 dimer in N_2 matrix was observed at