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Importance of intermolecular $-C\equiv C-H\cdots X-C$ ($X = F, O, N$) and $-Y-H\cdots F-C$ ($Y = O, N$) hydrogen bonds in crystal structures

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Weak hydrogen bonds involving organic fluorine have been well demonstrated through structural, computational, and experimental charge density analyses in our previous studies. As the acetylenic hydrogen ($pK_a > 25$) is more acidic than aromatic hydrogen ($pK_a > 30$), it is expected to act as a better hydrogen bond donor than aromatic hydrogen. In this study, we intend to explore the potential of weak hydrogen bonds involving $-C\equiv C-H$ group as donors. A detailed study on the $-C\equiv C-H\cdots X-C$ ($X = F, O, N$) and $-Y-H\cdots F-C$ ($Y = O, N$) hydrogen bonds in small organic molecules has been conducted using Cambridge structure database analysis, estimation of the stabilization energy using Gaussian 16, and topological properties of these interactions using Bader's Atoms in Molecule (AIM) theory using AIM 2000. Our study provides novel insights into the role of the $-C\equiv C-H$ group as a donor to form weak hydrogen bonds involving electronegative elements as an acceptor in crystal engineering.

Introduction

Intermolecular interactions play a significant role in building crystalline architecture.¹ Strong hydrogen bonds like $-O-H\cdots O$, $-O-H\cdots N$, $-N-H\cdots O$, $-N-H\cdots N$, *etc.*, that guide and alter crystal structures efficiently through the formation of various supramolecular motifs like dimers, trimers, tetramers, chains, ladders, *etc.*² Their pivotal role in crystal engineering has been well documented.³ While the stronger hydrogen bonds behave predictively,⁴ the weaker ones are significantly unpredictable.⁵ Several weak hydrogen bonds like $C-H\cdots O$, $C-H\cdots N$, $C-H\cdots S$, *etc.* have been documented in the literature.⁶ Many weak hydrogen bonds involving less electronegative donors like the $C-H$ group have been shown to alter the crystal packing of molecules,⁷ which also contain strong hydrogen bonds. Still, their dominance is inhibited by several weaker hydrogen bonds, thereby leading to a different crystal packing of a series of isomeric molecules. Weak hydrogen bonds involving the aromatic $-C-H$ group as donors with various electronegative acceptors (F, Cl, O, N , *etc.*) have been studied extensively.^{8–11} It has been demonstrated that aromatic $C-H$ groups ($pK_a > 30$) act as hydrogen bond donors and form various supramolecular motifs in crystal structures, thereby contributing to the stabilization of such structures.^{12,13} Although pK_a is measured in solution, as the crystals of organic compounds are mostly

grown from solutions of the compound, the acidity of hydrogens plays a significant role in the formation of various crystal lattices. Therefore, the interactions that are observed in the solid state as a result of predominant intermolecular interactions that prevail in solution, resulting in nucleation and growth of a crystalline architecture. We have been involved in the study of weak interactions involving "organic fluorine" for the last couple of decades and elucidated the significance of intermolecular $-C-H\cdots F-C$ hydrogen bonds and $-C-F\cdots F-C$ interactions, specifically the C atoms being part of an aromatic ring.^{14–20} It was demonstrated that intermolecular $-C-H\cdots F-C$ hydrogen bonds are capable of producing head-to-head and head-to-tail dimers, molecular chains and ribbons, *etc.*, just like strong hydrogen bonds offered by $-COOH$ and $-CHNH$ -groups. It was also elucidated that weak $-C-F\cdots F-C$ interactions can generate molecular chains and dimers.^{21,22} The acetylenic hydrogen ($pK_a \approx 25$), being more acidic than aromatic hydrogens, is expected to act as a better hydrogen bond donor and form stronger hydrogen bonds with highly electronegative elements like F, O , and N , bonded to C , compared to the aromatic hydrogens. Previously, Böese and co-workers reported molecular complexes of acetylene with various small organic molecules using *in situ* crystallization experiments.^{23–25} Acetylenic groups have been reported to act as weak π acceptors by many groups through both experimental and computational methods.^{26–28} Crystal structures of many metal complexes have been found to have weak $-C\equiv C-H\cdots O-C$ hydrogen bonds involving acetylene $C-H$ group as a donor and the O atom (H_2O , $-COO^-$, $M=O$, $C=O$, $P=O$ *etc.*) as acceptor in the Cambridge

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Table 1 CSD search results on C–H...F–C hydrogen bonds with special emphasis on $\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}$

Sl. No.	Type of interaction	Number of hits
Search 1	$\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}$	40
Search 2	$\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}(\text{Ar})$	32
Search 3	$\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}(\text{sp}^2)$	3
Search 4	$\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}\equiv\text{C}^*$	1
Search 5	$(\text{Ar})\text{C}-\text{H}\cdots\text{F}-\text{C}$	8291
Search 6	$(\text{sp}^2)\text{C}-\text{H}\cdots\text{F}-\text{C}$	1126
Search 7	$\text{C}-\text{H}\cdots\text{F}-\text{C}$	14620
Search 8	$\text{C}\equiv\text{C}-\text{H}\cdots\text{O}-\text{C}$	250
Search 9	$\text{C}\equiv\text{C}-\text{H}\cdots\text{N}-\text{C}$	37
Search 10	$\text{N}-\text{H}\cdots\text{F}-\text{C}$	509
Search 11	$\text{O}-\text{H}\cdots\text{F}-\text{C}$	330

Structural Database.^{29–34} It is noteworthy that the number of structures found to have hydrogen bonds of the type $\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}$ is significantly less in the database compared to $\text{C}(\text{sp}^2/\text{sp}^3)-\text{H}\cdots\text{F}-\text{C}$ hydrogen bonds (Table 1). Interestingly, one of the early reports demonstrated that a molecule preferred to have $\text{C}(\text{sp}^3)-\text{H}\cdots\text{F}-\text{C}$ hydrogen bonds with $\text{F}-\text{C}(\text{sp}^2)$ group, wherein a terminal $\text{C}\equiv\text{C}-\text{H}$ group was available to form a hydrogen bond with the $>\text{C}=\text{O}$ group and the $\text{F}-\text{C}(\text{sp}^2)$ groups present in the molecule.³⁵ This observation triggered this investigation to explore the capability of the $\text{C}\equiv\text{C}-\text{H}$ group as a hydrogen bond donor and its significance in crystal engineering. To understand the significance of $\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}$ hydrogen bonds in crystal packing, we studied the structures reported in the Cambridge Structural Database (CSD),²⁹ calculated the stabilization energy of the dimers formed by such interaction using Gaussian 16³⁶ and compared the same with the dimers formed by $\text{C}\equiv\text{C}-\text{H}\cdots\text{X}-\text{C}$ ($\text{X} = \text{O}, \text{N}$) and $-\text{Y}-\text{H}\cdots\text{F}-\text{C}$ ($\text{Y} = \text{O}, \text{N}$) hydrogen bonds. Further, we intended to compare the topological properties of these interacting molecular pairs using Bader's Atoms in Molecules (AIM)³⁷ approach using AIM2000³⁸ package. The salient features of our results are reported in this article.

Methodology

Cambridge structural database search

An extensive search was conducted using the structures reported in the 2024 edition of the Cambridge Structural Database, using the program Conquest version 2024.1.0 for C–H...F–C hydrogen bonds with a special emphasis on $\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}$ hydrogen bonds. The search was conducted using H...F distance ranging between 1 and 2.67 Å and the $\angle\text{C}-\text{H}\cdots\text{F}$ between 90° and 180°. The hits were restricted to structures with an R factor less than 5%, only organic molecules, no disordered molecules, and no powder structures were considered. The $\text{C}\equiv\text{C}-\text{H}\cdots\text{F}-\text{C}$ hydrogen bonds were classified into 4 different subgroups where the hybridization of the C atom of the F–C acceptor was specified (no restriction, aromatic, sp^2 , and sp). It was observed that the $\text{C}\equiv\text{C}-\text{F}$ group is reported only once (REFCODE NEDMIV) in CSD, and the molecule displayed the desired hydrogen bond ($d_{\text{H}\cdots\text{F}} = 2.668$ Å and $\angle\text{C}-\text{H}\cdots\text{F} = 132.7^\circ$). Details of these searches are listed in Table 1. To compare the occurrence and characteristics of $\text{X}-\text{H}\cdots\text{F}-\text{C}$ ($\text{Y} = \text{N}, \text{O}$) hydrogen bonds (where

the pK_a of N–H and O–H groups are >7 and 4–18, respectively) with our target hydrogen bond ($\text{C}\equiv\text{C}-\text{H}\cdots\text{X}-\text{C}$, $\text{X} = \text{F}, \text{O}$, and N), additional searches were conducted using the same conditions. These results are also listed in Table 1. It is observed that the number of molecules having an acetylenic group is much less in the CSD (total number 4950). Among them, only 379 molecules contain one or more F–C groups. Among these 379 molecules, the occurrence of the desired hydrogen bond falling within our search criteria is significantly less (Table 1). The pK_a of O–H and N–H groups are significantly less than that of aromatic and acetylenic C–H groups. Therefore, in principle, they (O–H and N–H groups) should act as better donors for a hydrogen bond. Hence, we also searched for hydrogen bonding interactions wherein the donor atom was O or N ($\text{N}-\text{H}\cdots\text{F}-\text{C}$ and $\text{O}-\text{H}\cdots\text{F}-\text{C}$). These results are listed in Table 1. Some of the molecules from their respective searches have been shown in Fig. S1–S5.

Computational study

Based on the results of the CSD search and analysis of the search results, the stabilization energy of the dimers formed by $\text{C}\equiv\text{C}-\text{H}\cdots\text{X}-\text{C}$ ($\text{X} = \text{F}, \text{N}, \text{O}$) (*i.e.* Searches 1, 2, 3, 4, 8, and 9), and $\text{Y}-\text{H}\cdots\text{F}-\text{C}$ ($\text{Y} = \text{N}, \text{O}$) (Searches 10, and 11) among selected molecules was calculated using Gaussian 16. Among the hits from the database search, the smallest molecules with a lower number of non-hydrogen atoms were (for computational ease) identified for computational study such that the pool of molecules represented the entire range of H...X distance ranging between 1 and 2.67 Å and the $\angle\text{C}-\text{H}\cdots\text{F}/\angle\text{Y}-\text{H}\cdots\text{F}$ between 90° and 180°. The energy of the monomer and the energy of the dimers were calculated using the density functional theory (DFT) implementing B3LYP functional and 6-31+g(d) basis set with the basis set superposition error (BSSE) correction for the dimers. It was also made sure that the selected molecules did not have any other intermolecular interactions between the pair of molecules that were linked by the desired hydrogen bond. The wavefunctions for the molecular pairs were also generated using Gaussian 16 for atoms in molecules (AIM) calculations. AIM2000 was used to obtain the topological parameters of the pair of molecules connected by the desired hydrogen bond. From AIM analysis, the electron density at the bond critical points ($\rho(r)_{\text{cp}}$, $\text{e}\text{Å}^{-3}$) of the desired interactions, the corresponding Laplacian ($\nabla^2\rho(r)_{\text{cp}}$, $\text{e}\text{Å}^{-3}$), and the length of the bond path (R_{bj} , Å) were extracted. The G_{cp} ($\text{kJ mol}^{-1}\text{Bohr}^{-3}$), V_{cp} ($\text{kJ mol}^{-1}\text{Bohr}^{-3}$), and H_{cp} ($\text{kJ mol}^{-1}\text{Bohr}^{-3}$) (Kinetic, potential, and total energy density respectively) were also calculated.

Results and discussion

The CSD search results indicate that the number of reported crystal structures of molecules having both $\text{C}\equiv\text{C}-\text{H}$ and C–F groups is very low in the database. Therefore, the number of hits having the desired hydrogen bond (Searches 1–4, and 8–11) is also low compared to the other related hydrogen bonds (Searches 5–7). This does not indicate that the $\text{C}\equiv\text{C}-\text{H}$ group acts as a poor donor towards the organic fluorine and other



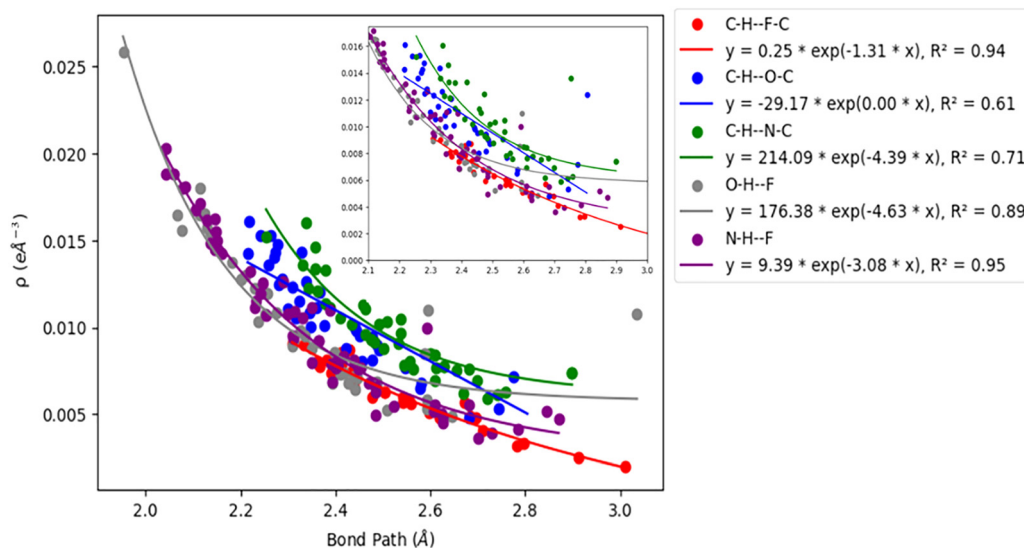


Fig. 1 Correlation plot of electron density (ρ (e Å⁻³)) at the BCP and bond path.

electronegative elements. The stabilization energy for these dimers is calculated using the formula:

$$E_{\text{Stabilization energy}} = E_{\text{Dimer}} - (E_{\text{Monomer 1}} + E_{\text{Monomer 2}})$$

Gaussian 16 was used to generate wavefunctions for the selected dimers, and AIM2000 was used to calculate the topological parameters of the pair of molecules interacting by the $\text{--C}\equiv\text{C--H}\cdots\text{X--C}$ (where X = F, N, O) and $\text{Y--H}\cdots\text{F--C}$ (where Y = N, O) hydrogen bonds. AIM analysis provided the electron density ($\rho(r)_{\text{cp}}$, e Å⁻³), and Laplacian ($\nabla^2\rho(r)_{\text{cp}}$, e Å⁻⁵) at the bond critical point (BCP) and the bond path (R_{ij} , Å). Additionally, the kinetic ($G(r_{\text{c,p}})$), potential ($V(r_{\text{c,p}})$), hydrogen bond energy (E_{HB}), and total energy densities ($E(r_{\text{c,p}})$) at the bond critical point were also calculated using the following

equations³⁷

$$G(r_{\text{c,p}}) = \frac{3}{10}(3\pi)^{\frac{2}{3}}\rho^{\frac{5}{3}} + \frac{1}{6}\nabla^2\rho$$

$$V(r_{\text{c,p}}) = \frac{1}{4}\nabla^2\rho - 2G(r_{\text{c,p}})$$

$$E(r_{\text{c,p}}) = G(r_{\text{c,p}}) + V(r_{\text{c,p}})$$

$$E_{\text{HB}} = -\frac{1}{2}V(r_{\text{c,p}})$$

Acetylenic hydrogen ($\text{p}K_{\text{a}} \approx 25$) is considered to be more acidic than aromatic hydrogens ($\text{p}K_{\text{a}} \approx 30$), thus making it a

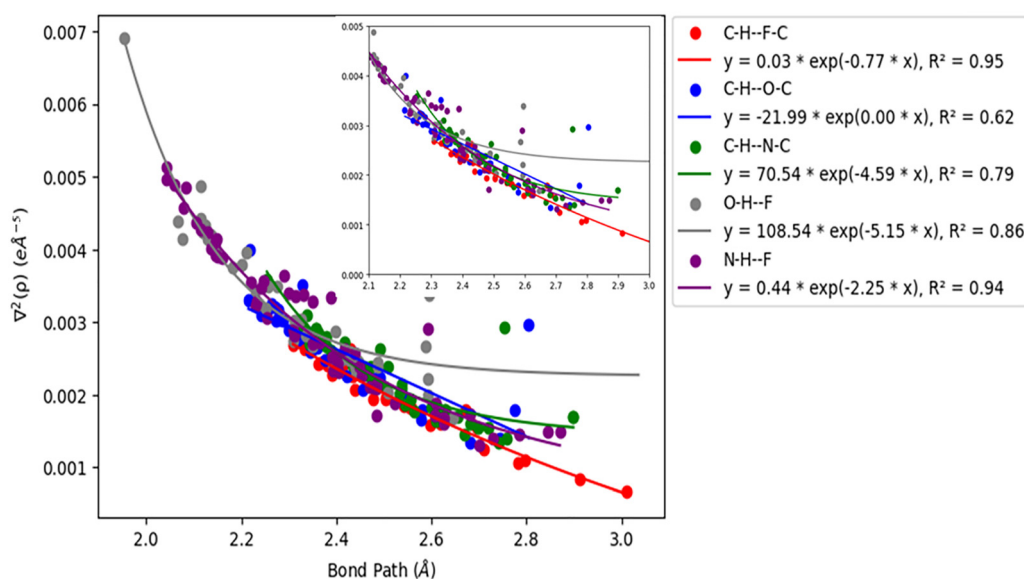


Fig. 2 Correlation plot of Laplacian of the electron density ($\nabla^2\rho$ (e Å⁻⁵)) and bond path.



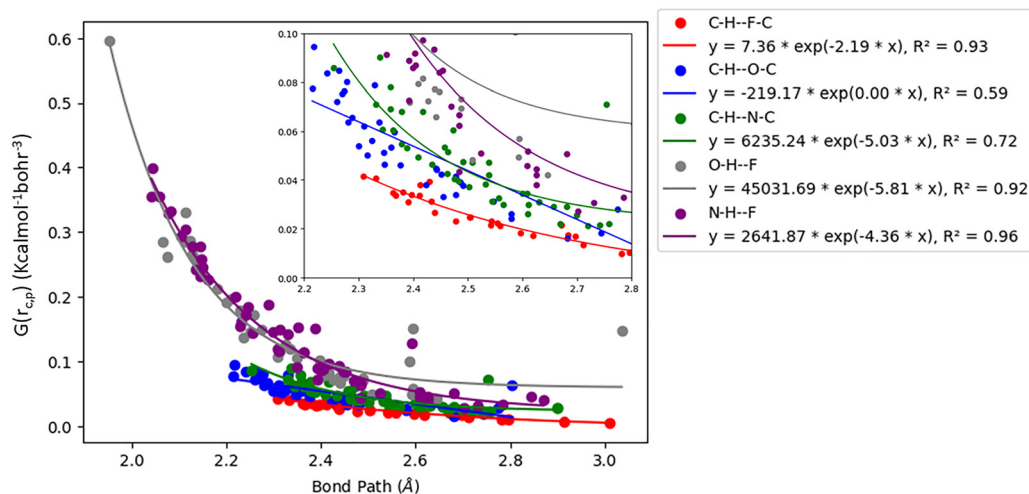


Fig. 3 Variation of kinetic energy density ($G(r_{c,p})$) with Bond Path for different interactions.

better hydrogen bond donor. Hence it is expected that $-C\equiv C-H$ group maybe capable of forming stronger hydrogen bonds with highly electronegative elements such as F, O, and N bonded to carbon compared to aromatic hydrogen atoms. Our AIM 2000 analysis reveals that the electron density and the Laplacian at the critical point (3, -1) are lowest in dimers formed *via* $-C\equiv C-H \cdots F-C$ hydrogen bonds. To comprehend the data reported in Tables S1–S5, we plotted (a) $\rho(e \text{ Å}^{-3})$ vs. $R_{ij}(\text{Å})$ (Fig. 1), (b) $\nabla^2\rho(e \text{ Å}^{-5})$ vs. $R_{ij}(\text{Å})$ (Fig. 2), (c) $G(r_{c,p})$ vs. (R_{ij}) (Fig. 3), (d) $V(r_{c,p})$ vs. (R_{ij}) (Fig. 4), (e) $E(r_{c,p})$ vs. (R_{ij}) (Fig. 5), and (f) E_{HB} vs. (R_{ij}) (Fig. 6) with appropriate color-coding for different types of interactions using the data reported in Tables S1–S5. Although the electron densities at the BCPs and the corresponding Laplacian for the dimers formed by $-C\equiv C-H \cdots X-C$ ($X = O, N$) and $-Y-H \cdots F-C$ ($Y = O, N$) hydrogen bonds are similar, dimers with $-C\equiv C-H \cdots F-C$ hydrogen bonds generally resulted in marginally lower values of electron density and Laplacian at the BCP for the studied dimers (Fig. 1 and 2).

The plots of $G(r_{c,p})$, against bond path (R_{ij}) show that the values for $-C\equiv C-H \cdots F-C$ interactions are consistently lower (less positive) compared to the other sets of interactions (Fig. 3). Similarly, the plots of $V(r_{c,p})$, $E(r_{c,p})$, and E_{HB} against R_{ij} demonstrate that the values for $-C\equiv C-H \cdots F-C$ interactions are consistently higher (less negative) than those for the other interactions (Fig. 4–6). Although the differences in the values of $G(r_{c,p})$, $V(r_{c,p})$, $E(r_{c,p})$, and E_{HB} are minimal and lie within a comparable range with the other interactions, the variations observed indicate that all the dimers are stable and highlight the importance of $-C\equiv C-H$ as a hydrogen bond donor and its futuristic applications in crystal engineering.

Conclusions

The pK_a value of the acetylenic hydrogen in the ethynyl group ($-C\equiv C-H$) indicates that it exhibits greater acidity than

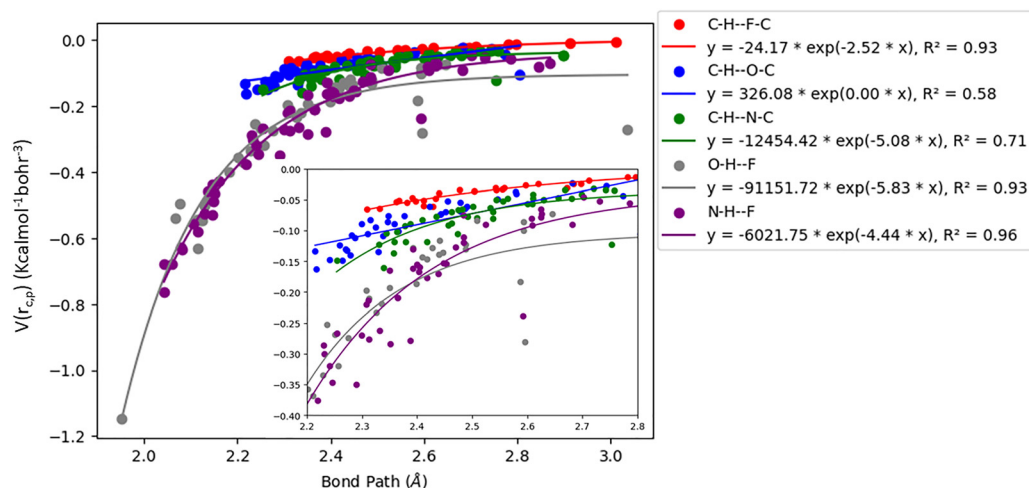


Fig. 4 Correlation plot of potential energy density ($V(r_{c,p})$) with bond path for different interactions.



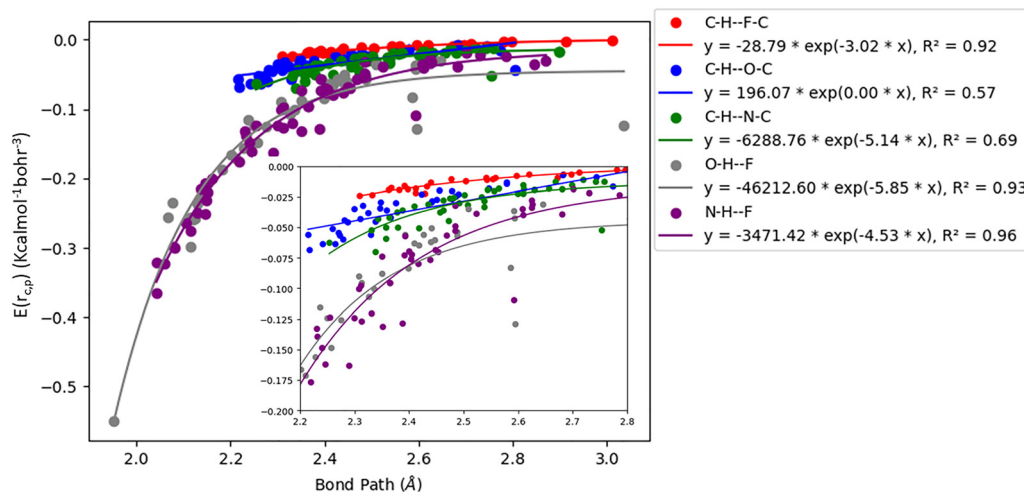


Fig. 5 Correlation plot of the total energy density ($E(r_{cp})$) with bond path for different interactions.

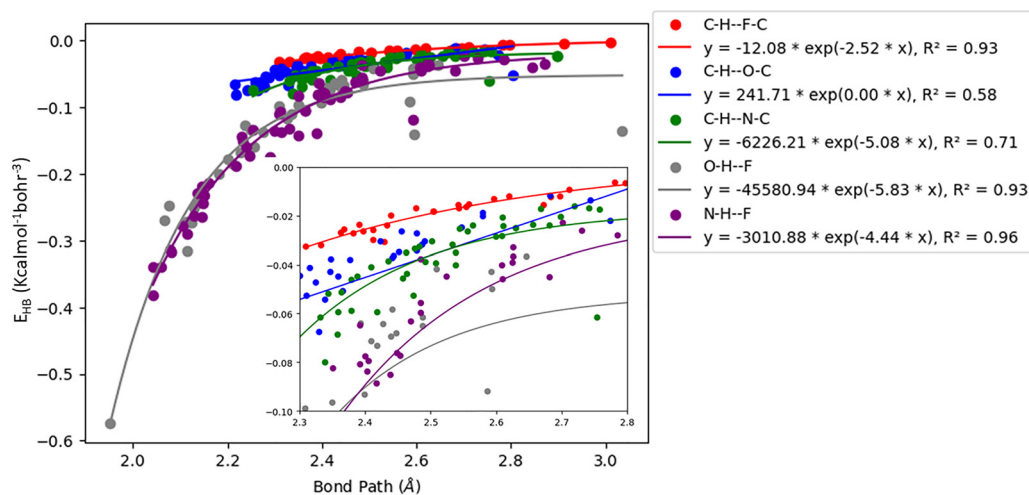


Fig. 6 Correlation plot of the hydrogen bond energy density (E_{HB}) with bond path for different interactions.

hydrogen atoms attached to aromatic carbons (sp-hybridized *versus* sp²-hybridized carbons). Our current comprehensive analysis of the crystal structures using computational methods reveals that the ethynyl group functions as a hydrogen bond donor, contributing to the stabilization of crystal structures. Furthermore, the pK_a values of hydroxyl (O-H) and amino (N-H) groups demonstrate that these functionalities possess an even greater acidic character than the acetylenic C-H bond. Computational energy assessments and topological parameter evaluations suggest that the acetylenic group acts as an equally effective donor as oxygen and nitrogen atoms in hydrogen bonding interactions. This again underlines the importance of the intermolecular hydrogen bonding interactions involving $-C\equiv C-H$ group in stabilizing the crystal structures. The study provides useful insights on $-C\equiv C-H\cdots F-C$ hydrogen bonds and their ability to act as a significant attractive interaction in the crystal lattice. It is noteworthy that the scarcity of $-C\equiv C-H\cdots F-C$ hydrogen bonds compared to the $-C-H\cdots F-C$

hydrogen bonds in CSD is solely due to the unavailability of crystal structures of molecules containing both $-C\equiv C-H$ and $F-C$ groups in the Cambridge Structural Database but their role in crystal packing cannot be refuted or ignored, rather can be explored in detail with more targeted synthesis of molecules for futuristic applications.

Author contributions

Agantuk Saha and Sakshi conducted the database search and analysis, computations, analysis of computational data, and drafted the manuscript and SI. Angshuman Roy Choudhury conceptualised the problem, supervised the computational study and associated data analysis, modified the draft manuscript, scrutinised the presented data, and finalised the manuscript.



Conflicts of interest

There are no conflicts to declare.

Data availability

All the data files, including the input and output files used for the computations reported in this manuscript, are available with us and will be produced if the reviewers or readers require the files for their analysis and understanding.

Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cp03886c>.

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