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REVIEW ARTICLE

Hydrogen Bonds with Chalcogens: Looking Beyond the Second Row of the Periodic Table

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Abstract | Compared to conventional hydrogen bonds like (O–H···N, N–H···O, O–H···O, N–H···N), hydrogen bonds involving heavier chalcogens like sulfur, selenium, and tellurium have been considered weaker owing to less electronegativity of these elements. However, various instances exist to prove that these hydrogen bonds (H bonds) are of similar strength of conventional hydrogen bonds, although the nature of hydrogen bonding could be different depending on a combination of electronegativity, polarizability, and dispersion effects. We have presented a plethora of such H bonds that have been investigated over past several decades through high-resolution laser spectroscopy, microwave spectroscopy, and quantum chemical calculations. These H bonds not only play important roles in biological systems, but are increasingly being tuned in nature and strength to construct artificial models that can aid our mechanistic understanding of non-covalent interactions and also help in modulation of activity, detection, and combat of diseases. We have discussed how these interactions could be exploited for applications in crystal engineering, superconductivity, gas capture, and field-effect transistor studies.

1 Introduction

The hydrogen bond (H bond) has always been the most venerated amongst non-covalent interactions as it can control and be responsible for three-dimensional arrangements of biomolecular structures and packing in crystals.[1–6] The fact that this concomitantly occurs with modulation of solute–solvent interactions opens up new avenues for influencing its strength with variation of the surrounding environment. The new definition of the hydrogen bond as given by IUPAC[7] states that "The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation." The emphasis on the electronegativity difference between the donor and acceptor atoms leads to natural choice of elements like N, O, and F from the second row to have been extensively explored with regard to their hydrogen-bonding preferences in crystal engineering and three-dimensional arrangements of proteins. Moving down to the heavier members of the chalcogen group, the electronegativity values for sulfur (2.58) and selenium (2.55) become smaller than that of oxygen (3.4) and become similar to that of carbon (2.55), that has been widely regarded as a weak H-bond acceptor[5, 8] and, hence, were initially clubbed together in a similar category as regards their hydrogen-bonding preferences.

The importance of H bonds involving sulfur in biological systems like ferredoxins, cytochrome P-450, metalloproteins, as well as supramolecular arrangements in organic crystals has been widely studied.[9–14] Considering that cysteine and methionine residues contain sulfur, further probes into the databases of protein structures reveal that the presence of sulfur-centered

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hydrogen bonds (SCHBs) can heavily influence protein structure and function.[15–19] However, such hydrogen bonds were belittled as “weak” interactions and were long overlooked with regard to the nature and strength of these contacts. For instance, in a study by Zhou et al.[20] from 500 protein structures, several observations regarding the nature of SCHBs were made. Their study mostly pointed out that SCHBs were longer in length with smaller bond angles and that while in cysteine residues, mostly weak S–H···π interactions were dominant, the methionine sulfur was a weak hydrogen-bond acceptor.[20] Even a crystal structure database search by Allen[21] and Steiner[22] led to the proposition that biologically, sulfur-centered hydrogen bonds may not be significant as they are poorer hydrogen-bond acceptors compared to oxygen, with the exception of certain thioethers.

However, strong N–H···S hydrogen bond in the crystals of $(\text{triazocyclononane})_2Fe_2S_6$ were found in a computational study by Francois et al.[23] and it was seen that the hydrogen-bond strengths for N–H···S and N–H···O interactions were found to be dependent on hydrogen-bond angle. In a computational study by Kaur et al.[24] from natural-bond orbital (NBO) analysis and symmetry-adapted perturbation theory (SAPT) analysis, adducts of dimethyl sulfide and dimethyl ether were considered with a variety of molecules to compare the H-bond acceptor capacity of sulfur and oxygen. The stabilization energies of the adducts were found to be comparable in spite of the S···H–Y H bonds being more deviant from linearity than that of O···H–Y hydrogen bonds. The electrostatic component played an important role in comparable stabilization of both these adducts and for the $(CH_3)_2O$ adducts, the repulsive E_{exc} component of the energy was higher due to the monomeric units being closer in $(CH_3)_2O$ adducts. Considering the neglected area of SCHBs, our group carried out extensive explorations of these interactions through model complexes as well as exhaustive sifting through data from PDB structures and have demonstrated that hydrogen-bonding interactions involving sulfur could be at par with the conventional N–H···O and O–H···O hydrogen bonds.[25–33]

From biological point of view, the study of selenium-centered hydrogen bonds (SeCHBs) becomes essential when we consider various prokaryotic and eukaryotic selenoproteins occurring in nature, with selenocysteine (the 21st amino acid) residues playing vital catalytic roles in redox reactions involving these proteins.[34–37] Furthermore, glutathione peroxidases, thioredoxin reductases, iodothyronine deiodinase, as well as selenophosphate synthetase 2 have been identified as selenoproteins crucial for enzymatic activity and biosynthesis.[36, 38] The replacement of oxygen in nucleotides by heavier chalcogens has opened up the pathway for new nucleic acid derivatives.[39, 40] It has been demonstrated that Se derivatization of nucleobases can aid X-ray studies of nucleic acids through multiwavelength anomalous dispersion (MAD) phasing.[41–44] It has been proposed that upon substituting the carbonyl oxygen atoms of DNA/RNA nucleobases with heavier chalcogens, the triplet state dynamics becomes slower which can have important implications for their use in photodynamic therapy.[45] It is observed that substitution with sulfur as well as selenium maintains high fidelity of base pairing along with efficient incorporation into DNA duplexes.[46]

The nature of hydrogen bonding involving selenium has been rapidly gaining attention in recent times.[35, 47–57] Various organoselenium compounds have been investigated in which peculiarities of the Se···H contacts have been observed, relative to the conventional N–H···O or O–H···O hydrogen bonds.[58] It includes electrostatic repulsions between Se and H atoms, higher degree of covalency of Se···H interactions as well as dominance of charge transfer influencing hydrogen-bond stability. It was seen from a recent study on *para*-substituted pyridine complexes of the form H_2Y···pyridine (where Y=O, S, Se) that similar charge transfer from nitrogen lone pair to $\sigma^*_{Y\text{–}H}$ orbitals was observed, with comparable redshift of the S–H and Se–H stretches in their respective complexes.[59]

The rare chalcogen, tellurium, has abundant applications as a ligand in coordination chemistry and as supramolecular synthon in organic crystals.[60, 61] Organotellurium compounds hold great promise in modulating redox potentials and catalysis in biological systems.[62] Tellurium has also been incorporated into amino acids[63–66] and enzymes (telluroenzymes)[65, 67] as well as in peptide bond mimics.[68] Hydrogen bonding in HTeXH (where X=O, S, Se, Te) monomers as well as its homochiral and heterochiral dimers was explored by Sanchez-Sanz et al.[69] through atoms-in-molecules (AIM), natural-bond orbital analysis as well as density functional theory-symmetry-adapted perturbation theory (DFT-SAFT) methodology. Stabilization orbital energy for hydrogen bonds of the form X1···HX2 were calculated at B3LYP/aug-ccPVTZ/LANL2DZ level that were around 48.12 kJ/mol for O···HO H bonds and subsequently decreased as heavier chalcogens were used, with the least stabilization energy value of 7.61 kJ/mol for Te···HTe hydrogen bonds. Intramolecular H bonds have been investigated by Sanz et al.[70] in a series of β-chalcogenovinylaldehydes, of the form HC(=X)–CH=CH–CYH (where X=O, S; Y=Se, Te), using ab initio G2(MP2) and B3LYP/6-311+G(3df,2p) DFT calculations. It was found that for both '*X*' being oxygen or sulfur, X–H···Se and X···H–Se hydrogen bonds were different in strength, but for the selenothiovinylaldehydes, the hydrogen bonds were weaker and relatively closer in strength; a fact that was mirrored in similar hydrogen bonds involving tellurium. An interesting revelation from the study was the considerable competition of X–H···Se and X···H–Se hydrogen bonds with chalcogen···chalcogen contacts in contrast to the interactions involving tellurium where the chalcogen–chalcogen interactions were dominant.

The multi-faceted aspects of chalcogen-centered hydrogen bonds (for sulfur, selenium, and tellurium) have been unraveled over the years by a combination of high-resolution gas-phase laser spectroscopy, microwave spectroscopy, and quantum chemical calculations. For this purpose, various simpler model compounds have been chosen, which, along with their clusters, can be prepared in the supersonic-jet cooled condition followed by recording their UV and IR spectra in this cooled condition.[30, 71] This technique is advantageous over conventional methods as it offers a cooled and solvent-free environment that can not only restrict the overall mobility of species (below the freezing point) with simultaneous reduction in the spread of the velocity distribution, but also can produce clusters (albeit weakly stabilized) that may not be detected at room temperature.[33, 72, 73] This, in combination with time of flight (TOF) mass-spectrometry can allow us to select and study the systems of interest in isolated conditions. There are many double resonance spectroscopic methods that have been employed for probing sulfur- and selenium-centered hydrogen bonds[56, 74] along with facilitating to probe those H bonds in peptides and nucleobases.[75, 76] A popular combination of techniques like laser-induced fluorescence (LIF), fluorescence dip infrared spectroscopy (FDIR), and two-color resonant two-photon ionization (2cR2PI) has been recently used by Wategaonkar's group[77] in probing the enigmatic nature of the N–H···S hydrogen bond.

Microwave spectroscopic techniques such as pulsed nozzle/molecular beam Fourier transform microwave (FTMW) spectroscopy have also been extensively used to study molecular structure of SCHB complexes in detail.[78–87] In particular, hydrogen-bonded dimers with H_2S, viz., C_2H_4···H_2S and C_6H_5CCH···H_2S have been investigated by Arunan et al.[79, 80] in supersonic-jet conditions through microwave experiments. Intramolecular hydrogen bonding in selenols (with selenol hydrogens interacting with π electrons of double bond) has been ascertained through both Stark and Fourier Transform microwave spectroscopy in different spectral ranges.[88] Very recently, the conformational equilibrium and internal motions of methyl 3-mercaptopropionate in a supersonic-jet expansion, with respect to effects of sulfur hydrogen bonding, were probed by Silva et al.[86] through microwave spectroscopy. Similarly, they have also calculated the rotational spectra of 3-mercaptopropionic acid recently and have ascertained the presence of S–H···O=C intramolecular hydrogen bond by comparison of rotational and centrifugal distortion constants with the existing experimental data.[87] The results of these kinds of investigations have been discussed at length in the subsequent sections.

These experimental findings are often corroborated with high-level quantum chemical calculations. Initial investigations are carried out by geometry optimization, electronic energy, frequency calculation, and dissociation/binding energies using GAUSSIAN[89] or TURBOMOLE[90] packages. This can be followed by a large number of available post ab initio quantum mechanical calculations. This includes the quantum theory of atoms-in-molecules (QTAIM)[91] that provides the bond critical points and Laplacian along with electron density distribution in the hydrogen-bonded complexes with AIM2000[92] software. The information regarding interacting bonding and antibonding orbitals involved in the H bonds is generally obtained by carrying out natural-bond orbital (NBO) analysis[93–95] with NBO 6.0 and NBOView 1. The interaction/binding energies of the hydrogen-bonded complexes are usually partitioned into electrostatic, dispersive, polarization, exchange and charge transfer components through energy decomposition analysis (EDA) programs like NEDA (natural energy decomposition analysis, included in GAMESS package)[96, 97]

In spite of the growing interest in this arena, the nature, strength, and directionality of hydrogen bonding in chalcogen-based systems still evinces contrasting views. In this review, we aim to capture the advances in aspects of H bonds involving heavier chalcogens like sulfur, selenium,

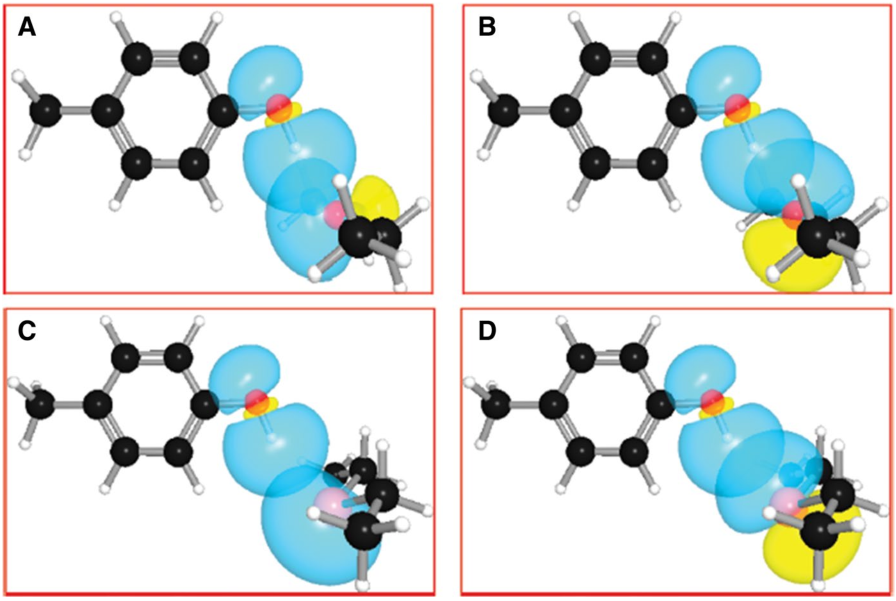

Figure 1: Donor–acceptor-interacting natural-bond orbitals for the p-CR.DEE (trans–trans or TT) conformer: **a** donor–acceptor-interacting NBO ($sp^2 \rightarrow \sigma^*$O–H), **b** donor–acceptor-interacting NBO ($p \rightarrow \sigma^*$O–H) and for *p*-CR.DES (TT) complex, **c** donor–acceptor-interacting NBO ($s \rightarrow \sigma^*$O–H), and **d** donor–acceptor-interacting NBO ($p \rightarrow \sigma^*$O–H) Adapted with permission from Ref.[99] Copyright 2010 American Chemical Society.

and tellurium, covering diverse assessments made through experimental and theoretical methods.

1.1 Nature of Hydrogen Bonding in Heavier Chalcogens: Comparisons with Conventional Hydrogen Bonds

Admittedly, sulfur and selenium are less electronegative and have diffused electron density than oxygen. However, in various studies, it has been noticed that the strength of hydrogen bonds involving heavier chalcogens like sulfur and selenium, as well as redshifts in N–H/O–H-stretching frequencies are comparable to those of oxygen-centered hydrogen bonds.

A comparative analysis of the characteristics of O–H···O and O–H···S hydrogen bonds as well as O–H-stretching frequencies were carefully carried out by our group by studying a series of diverse systems.[28, 29, 33, 98, 99] It was interesting to note how different experimental and theoretical computations on complexes of *para*-cresol (*p*-CR) with diethyl ether (DEE) and diethyl sulfide (DES) yielded seemingly paradoxical results. From NBO analysis, it was seen that the unequal nature of non-bonding lone-pair orbitals in *p*-CR.DEE (pure *p*- and sp^2 hybrid orbital) and *p*-CR.DES complexes (pure *p*- and pure *s*-orbital) led to structural difference in these complexes. However, the extent of overlap of the lone-pair orbitals with the antibonding orbital of O–H bond ($\sigma^*_{\mathrm{O-H}}$) in both the complexes (shown in Fig. 1) was similar which was also noticed from second-order perturbation energies. This could explain the comparable redshifts in O–H-stretching frequencies in both *p*-CR.DEE and *p*-CR.DES complexes, seeing the dependence on electron density transfer to antibonding O–H orbital which is similar for these complexes.

However, from AIM analysis, computed binding energies, and interaction energies, the weak hydrogen-bonding accepting nature of sulfur relative to oxygen was apparent, that contradicted the notion that redshift of the O–H-stretching frequency should necessarily be correlated with the hydrogen-bond strength. Natural energy decomposition analysis (NEDA) revealed that dispersive interaction energy was a major component of the *p*-CR.DES complex, but comparing these components with those of *p*-CR.H_2S complex, it appeared that alkyl substitution enhanced the hydrogen-bond accepting ability of sulfur.

We evaluated the nature of N–H···S H bonds through several experimental [resonant two-photon ionization (R2PI), resonant ion dip infrared spectroscopy (RIDIRS), and fluorescence dip infrared spectroscopy (FDIRS)] coupled with ab initio electronic structure calculations.[74] It was observed that the N–H···S H bonds in the indole-dimethylsulfide complex were unique owing to both electrostatic and dispersive contributions to the interaction energy. Where they resembled the C–H···Φ/N–H···Φ type of hydrogen bonds (i.e., where the hydrogen-bond acceptor is the π-electron density of an aromatic moiety, Φ is used to differentiate aromatic π-electrons from double- and triple-bond π-electrons) due to dispersive nature, the comparable binding energies of N–H···S and N–H···O hydrogen-bonded complexes along with greater N–H redshift in sulfur complex indicated stronger N–H···S interactions relative to N–H···O interactions.

Though stabilized by dispersion interactions, hydrogen-bond donation by sulfur (in S–H···Y hydrogen bonds) behaves in a similar fashion to that of polar O–H or N–H donors in conforming to acid–base formalism. It was observed from work of Wategaonkar et al.[100] that redshifts in S–H-stretching frequency (for S–H···S or S–H···O hydrogen bonds) were linearly correlated with the proton affinity of the acceptor with correlation coefficients of 0.8886. This also held true for the binding energies of H_2S clusters (extrapolated) that similarly increased with proton affinities with linear correlation coefficient of 0.9738.

Recently, Mishra et al.[56] have carefully tried to rationalize the inherent nature of selenium-centered hydrogen bonds through combined gas-phase spectroscopy and theoretical methods by investigating the stability of the indole···dimethyl selenide and phenol···dimethyl selenide complexes. They have highlighted how S/Se complexes can have multiple possible conformations having slightly different hydrogen-bond strengths as well as more chances of secondary interactions (Fig. 2).

It was observed from interaction energy decomposition analysis [through symmetry-adapted perturbation theory method and absolutely localized molecular energy decomposition analysis (ALMO-EDA)] that the comparable or higher N–H/O–H redshift in stretching frequency in the complexes with sulfur/selenium as acceptor (relative to that of oxygen as acceptor) was not as influenced by electrostatic or polarization effects as much as by relatively efficient charge transfer in selenium/sulfur-centered hydrogen-bonded complexes. This was also seen from an earlier study by Madzhidov et al.[58] in electronic structures of several organoselenium compounds and has been attributed to the greater polarizability and diffused electron density of S/Se complexes.

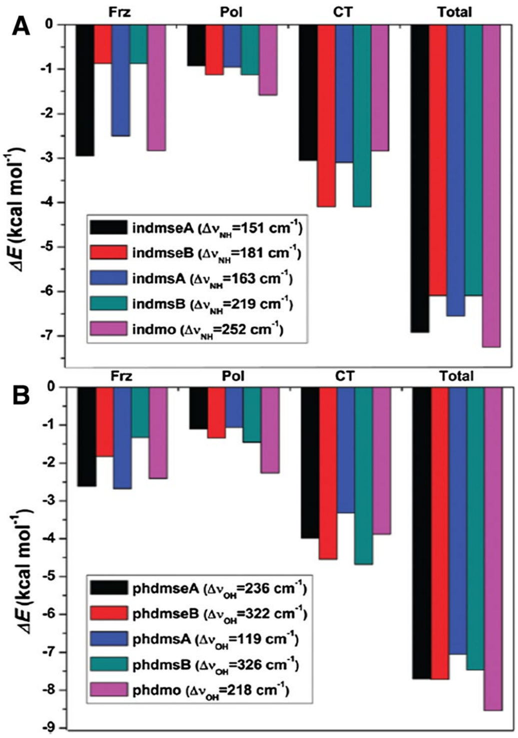

Figure 2: Decomposition of the interaction energies [into frozen density interaction (Frz), Polarization (Pol), and Charge Transfer (CT) components] of the different conformers of the complexes of **a** indole(ind) and **b** phenol(ph) with dimethylselenide (dmse), dimethyl sulfur (dms), and dimethyl ether (dmo) obtained at the B97-D/6-31+G(d,p) level of theory using the ALMO-EDA method. The redshift in the N–H/O–H-stretching frequency of the complexes has been provided in the box in the figure. Reproduced from Ref.[56] with permission from Royal Society of Chemistry via Copyright Clearance Centre.

It is also seen that the CT component follows an increasing systemic trend with respect to increase in N–H/O–H frequencies, which is not observed in case of corresponding oxygen containing complexes. Furthermore, it was also noted that relative to oxygen-centered hydrogen bonding, in case of S/Se-centered hydrogen bonding, greater variations in the NBO occupancies for *s*- and *p*-type lone pairs ($\Delta\eta_s$ and $\Delta\eta_p$) as well as N–H/O–H antibonding orbitals ($\Delta\eta_{\sigma*}$) were observed.

Overall, these kinds of studies have provided an idea about the complex nature of the hydrogen bonding of these heavier chalcogens, that depend on a combination of energetic, structural, and orbital overlap factors, and in subsequent sections, we have described many of such systems in depth.

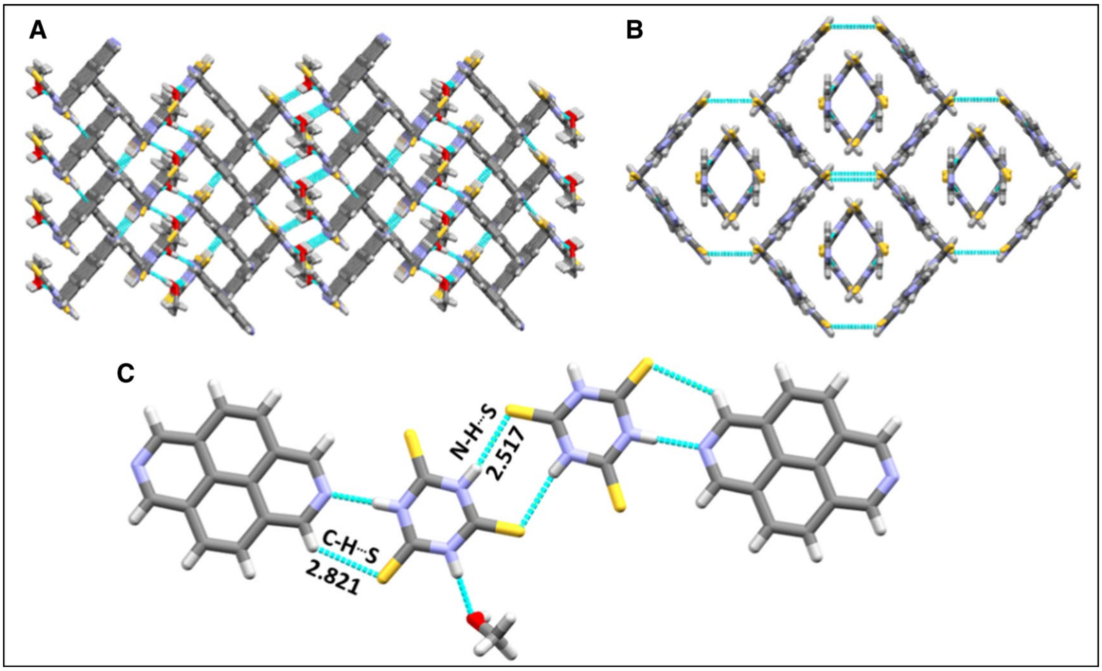

Figure 3: The two-dimensional arrangement in cocrystal of **a** trithiocyanuric acid with DABCO and **b** trithiocyanuric acid with 2,7 diazapyrene, whereas **c** shows the N–H···S and C–H···S hydrogen bonds sustaining individual chains in the packing of **a**.

1.2 Heavier Chalcogens as Hydrogen-Bond Acceptors

Having established the physical basis of the hydrogen bonds formed by heavier chalcogens, it is necessary to see how their directionality, strength, and presence alongside the conventional hydrogen bonds have been manipulated in structural chemistry. In particular, there exists a plethora of hydrogen bonds with sulfur and selenium as hydrogen-bond acceptors, while tellurium-centered hydrogen bonds are beginning to gain prominence rapidly.

Various crystal structures have been stabilized by N–H···S, C–H···S hydrogen bonds giving rise to two dimensional interpenetrated networks, channel, and tubular supramolecular structures.[101–107] For instance in a recent study by Argent et al.[108], trithiocyanuric acid formed five co-crystals with triazine, pyrazine, 2,7-diazapyrene, DABCO, and 1,2-di(4-pyridyl)ethylene with strong N–H···N H bonds supported by N–H···S, C–H···S hydrogen bonds as presented in Fig. 3. The directionality of these H bonds is vital to forming a variety of stacking and interpenetrated structures.

We have presented some interesting examples of X–H···Y (X=N, O, C and Y=S, Se, Te) H bonds in Table 1, that have been detected in biological systems and crystal structures.

In the previous section, we have described how the hydrogen-bond acceptor characteristics of sulfur and selenium were recently explored by Mishra et al.[56] A surprising result from computational methods was that the oxygen-centered hydrogen bonds showed one strongly hydrogen-bonded conformer, while the S/Se-centered hydrogen-bonded complex had minimum two conformations that were nearly isoenergetic; one conformation stabilized with strong N–H···Se/S, O–H···S/Se H bonds and another with weaker strength of these afore-mentioned H bonds compensated with better dispersion effects. This year, our group even explored for the first time, the possibility of using sulfur and selenium as acceptors for hydrogen bonding with neutral metal carbonyl hydrides.[123] The nature of the M–H···Y (*M*=Fe, Co, Mn, and Y=O, S, Se) hydrogen bonding was found to be dispersive in nature with the strength varying from ~ 5 to 30 kJ/mol.

Rotational spectra parameters like rotational constants, centrifugal distortion constants, and the nuclear spin–nuclear spin-coupling constants have been calculated by Lopez et al. for a series of isotopic tetrahydrothiophene···HCl/HF complexes, where the deviation from collinearity of the S···H–F/Cl hydrogen bond is just ~ 10–14°.[124, 125] Various axial and equatorial hydrogen-bond complexes of trimethylenesulfide···HCl and

Table 1: Some representative examples of systems (biological/supramolecular) in which heavier chalcogens accept hydrogen bonds.

N–H⋯S	Bacteriochlorophyll (PDB: 1BCL), Galactose oxidase (PDB : 1GOF)[31] Model complexes of Rubredoxin[16, 109] Ferredoxins[16, 110, 111] Cytochrome P-450[9, 11] *N*-acetyl-L-methioninyl-L-phenylalanine-amide[32]
N–H⋯Se	Phosphoethanolamine *N*-methyltransferase (PDB: 4KRG)[54] Human inositol 1,4,5-trisphosphate 3-kinase (PDB: 1W2F)[54] Angiotensin-I converting enzyme in complex with a selenium analog of captopril (PDB :2YDM)[54] Phenylamino(diphenyl)phosphine selenide, In(en)$_2$Se$_2$·2I[112]In(teta)$_2$Se$_2$·2I[112] Mo(IV) areneselenolates[113]seledinostannates[114]
N–H⋯Te	GaTe$_2$(en)$_2^-$[115]In$_4$Te$_9$(en)$^{6-}$[116]
O–H⋯S	Creatine kinase (PDB :1QH4), Aspartate aminotransferase (PDB: 1AJS)[31] Catalase, human erythrocyte (PDB: 1DGF)
O–H⋯Se	LayeredBa$_2$(OH)$_2$(H$_2$O$_{10}$Se$_4$[117] peri-substituted naphthalenes[118]
C–H⋯S	22π and 26π core-modified(S) sapphyrins and rubyrins[119, 120] polymorphs of Fe^{II}L^{Me}(NCS)$_2$[121]
C–H⋯Se	22π and 26π core-modified (Se) sapphyrins and rubyrins[119, 120] Aldols of chiral *N*-acyl selones[122]
C–H⋯Te	(η^4-Me$_8$taa)GeTe[48]

pentamethylenesulfide (PMS)⋯HF/HCl have also been investigated by their group using MB-FTMW spectroscopy.[126, 127] While the equatorial hydrogen bonds may be regarded as the primary hydrogen-bonding interactions, based on hydrogen-bond length, the secondary interactions (between methylene group hydrogens and $^{\delta-}$F/Cl) may sometimes be responsible for the nonlinearity of these bonds, making the axial hydrogen bonds more prominent experimentally.

There are not too many instances of hydrogen bonding involving tellurium and we see more examples of its direct contact with chalcogen/halogen. Still, H⋯Te hydrogen bonding keeps emerging unexpectedly in various crystal structures and supramolecular arrangements like that in the case of Ph$_3$PTe(Fu)I[128] and [In$_4$Te$_9$(en)]$^{6-}$ clusters. We have extensively discussed the various systems having this type of interactions in the following sections.

1.2.1 N–H⋯X Hydrogen Bonds (X=S, Se, Te)

N–H⋯O, N–H⋯S, and N–H⋯Se H bonds in urea, thiourea, and selenourea have been reviewed by Mak and Li[129], and have been found to be pivotal in directing various cage and channel-type enclosures for formation of host–guest structures. Indeed, N–H⋯S hydrogen bonds have been known to play vital structural roles in organic crystals of sulfur-substituted 2-aminopyridines[130] and intramolecular N–H⋯S and N–H⋯Se H bonds have also been found in crystal structures of molybdenum(IV)arenethiolates and areneselenolates.[113]

The importance of the N–H⋯S hydrogen bond on catalytic oxidation in a porphyrin–alkanethiolate complex has been emphasized by Suzuki et al.[131], and from crystal structure analysis, X-ray absorption fine structure (EXAFS), and cyclic voltammetry, it was found that the intramolecular N–H⋯S H bond made the metal-S bond length shorter, particularly for antibonding metal-S involvement in the HOMO. Only the hydrogen-bonded form of the complex (relative to those that had a lack of it) showed a positive shift of redox couple (~0.1 V for Fe^{III}/FE^{II} couple) in cyclic voltammograms, that was indicative of the N–H⋯S hydrogen-bond contribution to catalytic efficiency and eventual stability of the Fe(III) porphyrin–alkanethiolate structure. In diverse studies by Okamura et al., the N–H⋯S H bonds have been found to attenuate ligand-to-metal charge transfer/redox potential shift in benzene–thiolate complexes of Hg(II),[132] Fe(II), and Co(II)[133], as well as influence the O-Atom-Transfer Oxidation[134] in amide group containing molybdenum dithiolene compounds. Both single and double N–H⋯S H bonds were found to be present in model complexes of cytochrome P-450[11] as well as rubredoxin.[109]

In particular, ^{77}Se-^{1}H correlated NMR spectroscopy has been found to be a great tool in identification of the N–H⋯Se contacts and it has been seen that these hydrogen bonds have a stabilizing influence on the Mo–Se bonds in the complex. Intermolecular weak N–H⋯Se interactions have been known to stabilize the crystal structure of phenylamino (diphenyl)phosphine selenide[135] as well as primary arylselenoamides[136] of the form ArC(Se)NH$_2$. These N–H⋯Se hydrogen bonds have also been observed by ^{1}H–^{77}Se [Heteronuclear Multiple Quantum Coherence (HMQC)] NMR experiments by Wu et al.[137] in adducts obtained through a one-pot coupling process (mediated by triphosgene) of various amines to a chiral selone derivatizing agent. These weak N–H⋯Se hydrogen

Table 2: Computed binding energy (***D_0*** in kJ/mol) at CCSD(T)/aug-cc-pVDZ, redshift of N–H-stretching frequency (Δν in cm^{-1}), and donor–acceptor interaction energies EDA in kJ/mol) for N–H•••Y (Y=O, S, Se, and Te) complexes Reproduced from Ref.[54]with permission from Copyright 2017 American Chemical Society

	NPAA-X (trans-amide)			2PY-X (cis-amide)			NMFA-X (trans-amide)		
H-bond type	D_0	Δν (NH)	E_{DA}	D_0	Δν (NH)	E_{DA}	D_0	Δν (NH)	E_{DA}
N–H···O (X=DME)	39.2	− 99	46.1	44.9	− 250	75.9	27.2	− 97	46.1
N–H···S (X=DMS)	40.6	− 96	45.0	49.0	− 291	90.0	28.0	− 132	54.3
N–H···Se (X=DMSe)	41.2	− 91	42.1	50.4	− 262	83.0	29.5	− 120	51.4
N–H···Te (X=DMTe)	41.7	− 80	35.8	46.1	− 241	72.4	25.8	− 114	49.1

bonds (H···Se = 2.63 Å and < N–H···Se = 158(4)°) were also found to stabilize the crystal structure of phenylamino(diphenyl)phosphine selenide, where infinite chains parallel to c axis [with graph set motif *C*(4)] were generated.[135]

Apart from these instances, N–H···Se hydrogen bonds have been found to stabilize several crystal structures like that of *N*-selenocarbamoyl benzamidine $4\text{-MeC}_6H_4N(H)C(Ph)=NC(Se)NEt_2$,[138] $PhP(Se)(NHC_6H_4NH\text{-}1,2)$[139] and *N*-phenyl-*N′*-benzoylselenourea.[140] Recently, we modeled various model complexes based on methionine and selenomethionine residue interactions[54] and compared various N–H···S/Se interactions in these systems with binding energies and redshifts of N–H-stretching frequencies (scaled harmonic frequencies, indicated here) that are presented in Table 2.

To represent the cis and trans conformations of the amide groups of peptides and nucleobases, *N*-phenylacetamide (NPAA) and 2-pyridone (2PY) were chosen along with dimethylselenide (DMSe) and dimethylsufide (DMS) as hydrogen-bond acceptors that could mimic side chains of selenomethionine and methionine. Although dimethyltelluride could not be available for carrying out experiments, the corresponding values were estimated from fitting the available data on other amide N–H-stretching frequencies (experimental and computational). The NH···Te hydrogen bonds have been observed by Warren et al.[115] to hold together one-dimensional $GaTe_2(en)_2^-$ chains in the electrochemically synthesized gallium telluride complex $[(C_6H_5)_4P]GaTe_2(en)_2$. Furthermore, in a telluridoindate $[In(en)_3][In_5Te_9(en)_2]$, NH···Te hydrogen bonds have been known to stabilize one of the components, i.e., the acentric $[In_4Te_9(en)]^{6-}$ clusters.[116]

1.2.2 O–H···X Hydrogen Bonds (X=S, Se, Te)

The first experimental observation of O–H···S H bond in supercooled jet conditions, was reported by Wategaonkar's group[33], in various model complexes that could mimic the side-chain interactions of tyrosine with methionine residues. In the complexes, phenol, *p*-cresol, and 2-naphthol were taken as H-bond donor, while dimethylsulfide was chosen as H-bond acceptor. The experimental as well as computational results revealed that though the O–H···S interaction energy was more governed by contributions from charge transfer as well as dispersion energy, the similar nature of redshift of the O–H in both complexes with Me_2S and Me_2O revealed the comparable hydrogen-bond acceptor characteristics of sulfur and oxygen. They further delved into the comparison of the O–H···O and O–H···S hydrogen bonds in diverse complexes of *p*-cresol with diethylether and diethylsulfide as well as its complexes with methanol, ethanol, methanethiol, and ethanethiol, by employing IR/UV double resonance techniques.[29, 98, 99] The general consensus, as also mentioned in an earlier section, was that the redshifts in the O–H-stretching frequency were quite comparable for both O–H···O and O–H···S hydrogen bonds and the strength of these hydrogen bonds was augmented with increasing alkyl length chain of the hydrogen-bond acceptor. It was noted that the proton affinities of the hydrogen-bond acceptors did not necessarily follow the same trends as the redshifts of the O–H-stretching frequency as was the norm in the conventional hydrogen bonds.

Hydrogen bonding at C=O, S and Se sites in their respective urea, amide, and ketone derivatives has been extensively studied to evaluate the different nature of the interactions. The electronegativity of sulfur atom (2.58) being close to that of carbon gives rise to less effective hydrogen-bonding acceptance at thiocarbonyl sites owing to neutrality of S atom in R1, R2—C=S systems. However, resonance-assisted hydrogen bonding in thiourea and thioamides elevates these hydrogen bonds at C=S sites to that of significant strength, as quantified in a study by Wood et al.[141] where interaction energies for hydrogen bonds to thiourea were calculated to be − 20.6 kJ/mol, by intermolecular perturbation theory. In a study by Bibelayi et al.[53], the interaction energies for hydrogen bonding of the compounds, $NH(CH_3)_2C{=}X$, with that of a water molecule were calculated at B3LYP/6-311+G(3df,2p) level of theory to be − 28.5, − 21.5, and − 21.3 kJ/mol for X=O, S, and Se, respectively. An interesting observation from their studies came up in regard to the angle, φ, that is defined by the approach angle of the hydrogen atom towards the C=X moiety where the smaller angles for sulfur (($\varphi = 110(1)$–$112(3)°$)[21] and selenium ($\varphi = 95(4)°$) relative to that of oxygen (123.2–136.9°) were seen with oxygen atoms as donors. This was indicative of distinct directionality associated with S and Se atoms, that was proposed to have important implications for packing effects in crystal engineering. Further, in a combined vibrational spectroscopy and density functional theory study by Harada et al.[142], it was proposed that not only intramolecular O–H···Se hydrogen bonds played a vital role in conformational stabilization of 2-(methylseleno)ethanol, but also matched up in strength to the analogous O–H···O and O–H···S bonds in 2-methoxyethanol and 2-(methylthio) ethanol respectively.

Divalent selenium compounds in complex with methanol, such that selenium acts as H-bond acceptor, have been subjected to quantum chemical calculations with HF, MP2, and DFT methods to probe the electronic structure distribution in comparison to classical H bonds, according to Koch–Popelier criteria[58]. From topological features, the non-covalent nature of the Se···H interaction is clearly determined, with C–H···O interactions being proved weaker than Se···H–O hydrogen bonds with lower absolute values of Laplacian and electron density. Recently, through FTIR spectroscopy, comparable Gibbs energies at room temperature, for alcohol complexes of dimethylsulfide (O–H···S) and dimethylselenide (O–H···Se) were noticed, while stronger binding was noticed for the corresponding dimethylether complexes(having O–H···O hydrogen bonds).[143] The Se···H–O hydrogen bonds were also found to stabilize complexes of the form F_2CSe–HOX (X=F, Cl, Br, and I), that also co-exist with Se···X and X···F interactions, where the energy decomposition analysis predicted that the Se···H–O hydrogen bonds were responsible for the electrostatic energy of the complex.[144]

1.2.3 C–H···X Hydrogen Bonds (X=S, Se, Te)

The weak C–H···O hydrogen bond has been regarded as an important driving force in structural chemistry owing to its directional characteristics.[5, 8] However, the C–H···S interactions have also been proposed to be as vital in many complexes. In a cryo-spectroscopic experimental study by Michielson et al.[145], the C–H-stretching frequency was found to be redshifted by 43 cm^{-1} in the dimethyl sulfide(-d6) complex of the halothane $CHBrClCF_3$, with a complexation enthalpy of − 10.7 kJ/mol, that gave evidence of C–H···S hydrogen bonding, which was also supported by computational results. In an investigation of the aggregation of 2,3-thienyl- and phenyl- or 2,3-dithienyl-substituted propenoic acid, Csankó et al.[146] found that while O–H···O interactions sustained the short range in solution, upon going to the solid state, the (aromatic)C–H···S and (olefinic)C–H···S hydrogen bonds became the primary organizing force for larger aggregates by encouraging formation of two-dimensional sheets.

A contrary view emerged from ab initio and DFT calculations by Domagala and Grabowski[147], where in systems like $CH_4\cdots SH_2$, $C_2H_4\cdots SH_2$, the C–H···S contacts were proposed to be classified as van der Waals interactions rather than hydrogen bonds. However, there has been evidence that protons of benzoyl groups of certain arenethiolate moieties indulge in aromatic C–H···S hydrogen bonding, with the sulfur atom of the [4Fe–4S] cluster in certain ferredoxin model complexes.[110] Moreover, CH···S H bonds have been regarded as important crystal engineering tools for stabilizing packing in various crystals (for example, by promoting inter-sheet interactions) like organic conducting crystals of the tetrathiofulvene family[148] as well as crystals containing (1,3)-thiazolidine ring.[149]

The C–H···Se hydrogen bond was first observed in diselenocin by Iwaoka et al.[52], the presence of which was detected by solid-phase IR spectroscopy and later confirmed by ^1H NMR spectroscopy by evaluation of spin–spin-coupling constant between selenium and the benzylic hydrogen in its neighborhood. It was suggested from molecular orbital calculations as well as natural-bond orbital (NBO) analysis that the interaction of orbitals of the C–H bond with the lone pair of selenium may influence nature of C–H···Se hydrogen bonds.[150] The nature of C–H···Se hydrogen bond has been recently investigated by Chopra and Chakraborty[49] in a series of complexes Q_3C–$H\cdots SeH_2$ (Q=Cl, F, and H) and it is interesting to note the C–H bond

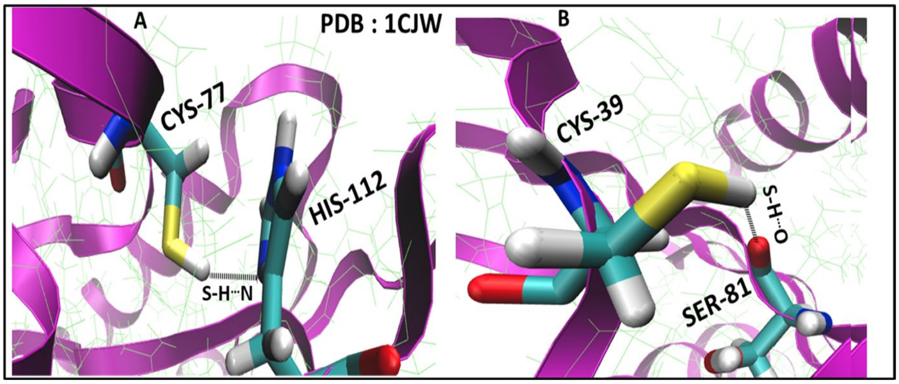

Figure 4: **a** S–H···N and **b** S–H···O hydrogen bonds in Serotonin *N*-acyltransferase.

redshift in chloroform complexes with blue shift in non-linear fluoroform complexes. This has been demonstrated to be dependent on the extent of electron density transfer to the σ*C–H orbital and a combination of rehybridization and hyperconjugative effects.

The first reported instance of C–H···Te hydrogen bonding was in a study by Steiner[48] where donation of hydrogen bonds by chloroform to sulfur, selenium, and tellurium was investigated. The compounds selected for the purpose were terminal chalcogenido complexes of the form (η^4-Me$_8$taa)GeE(where $E{=}$S, Se and Te) with chloroform solvent molecules incorporated into the crystal lattice. The hydrogen-bond lengths for C–H···Te ranged from 2.67 to 2.90 Å, while those of C–H···S and CH···Se hydrogen-bond lengths were reported to be in the range 2.38–2.51 Å to 2.47–2.62 Å.

1.3 Heavier Chalcogens as Hydrogen-Bond Donors

Heavier chalcogens can either donate hydrogen bonds to acceptors like O, N S, Se, and also to the π-electron density of an aromatic acceptor (denoted as X–H···Φ type of hydrogen bonds here). Sulfur as a hydrogen-bond donor for phenols and acids like 2,2,2′ trifluoroethanol in CCl$_4$ and hexane solution has been examined in the early studies using calorimetric data coupled with correlation of the enthalpy with frequency shifts.[151–153] The hydrogen-bond donating capacities of chalcogens like sulfur and selenium have also been noted in various biological systems. For example, in Fig. 4, we have presented both S–H···N (between Cys-77 and His-112) and S–H···O H bonds (between Cys-39 and Ser-81 residues) in serotonin *N*-acetyltransferase (in complex with a bisubstrate analog).

In organoselenium compounds like 3-aminopropenoselenal, selenium has been known to behave as both hydrogen-bond donor and acceptor in intramolecular interactions with nitrogen sites.[154] It is interesting to note that in complexes with CO$_2$ as proton acceptor, the υ(C–H)-stretching frequency is usually blue-shifted upon C–H···O hydrogen bonding and hence amongst 100 proton donors evaluated in a study by Szostak,[155] S/Se–H···O=C hydrogen bonds have also been explored.

Various examples of hydrogen-bond donation by sulfur and selenium have been highlighted in Table 3, followed by extensive explanation in the successive sections.

1.3.1 X–H···Y (Y=O, N) σ-Type Hydrogen Bond

Comparison between S–H···N and O–H···N hydrogen bonds was carried out by Grzechnik et al.[163] through infrared matrix isolation spectroscopy and ab initio calculations of the complexes of CH$_3$OH and CH$_3$SH with ammonia. The intensity of the S–H-stretching frequency was found to grow by 300 times after complexation, as compared to that of the O–H stretch that increased in intensity by just about 20 times. This was attributed to the unusual behavior of the dipole moment function of S–H as a proton donor. S–H···O hydrogen bonds have been observed by Scheiner[164] in neutral and cationic (CH$_3$)$_2$SH species along with their fluoro-substituted derivatives where significant binding energy of 34 kcal/mol was observed for these hydrogen bonds in spite of competition from C–H···O hydrogen bonds as well as chalcogen and tetrel bonds. Recently, intramolecular S–H···O=C hydrogen bonds were characterized in 3-mercaptopropionic acid from Fourier transform microwave (FTMW) spectroscopic methods along

Table 3: Some representative examples of systems (biological/supramolecular) in which heavier chalcogens donate hydrogen bonds

S–H···O	Human tetrahydrofolate dehydrogenase/cyclohydrolase (PDB: 1A4I), Flavin reductase P from Vibrio harveyi (PDB: 1BKJ), Galactose oxidase (PDB: 1GOF), chondroitinase B from Flavobacterium heparinum (PDB: 1DBG) purine nucleoside phosphorylase (PDB :1B8O), Bence-Jones protein (PDB: 1BFD), deubiquitinating enzyme (human UCH-L3) (PDB: 1UCH)
Se–H···O	3-Selenoxo-propionaldehyde[156]Selenoacetic acid[157]
S–H···N	*E. coli* DNA repair enzyme endonuclease IV (PDB :1QTW), Human methionine aminopeptidase-2 (PDB: 1B6A), regulator of chromosome condensation (RCC1) in human (PDB: 1A12), pyrrolidone carboxyl peptidase (PDB: 1A2Z)
Se–H···N	3-Imino-propeneselenol[154]
S–H···π	Formate dehydrogenase (PDB : 2NAC), [benzene]-H_2S clusters[158]
Se–H···π	H_2Se-monosubstituted benzene dimers[159]
S–H···S	Bacteriophage T4 endonuclease V (PDB: 2END), Human kinesin motor domain (PDB :1BG2), Azotobactervinelandii ferredoxin (PDB: 7FD1), Rat pancreatic lipase related protein 2 (PDB:1BU8), Horse Liver Alcohol Dehydrogenase (PDB: 3BTO), Human glutathione reductase (PDB: 3GR1)
Se–H···Se	Selenophenol[160]propanediselenal[161]$S_{0.3}Se_0{\cdot}6H_3$ superconductor[162]Selenoacetic acid[157]
Se–H···S	3-Selenoxo-propanethial[156]$S_{0.3}Se_0{\cdot}6H_3$ superconductor[162]

with theoretical calculations.[87] In another study, Wategaonkar et al.[100] prepared complexes of H_2S with diethyl ether (Et_2O), dibutyl ether (Bu_2O), and 1,4-dioxane (DO) in supersonic-jet condition, and observed redshifts of the S–H-stretching frequency by magnitude of 46, 63, and 49 cm^{-1}, respectively, by carrying out infrared predissociation spectroscopy and vacuum ultraviolet (VUV) spectroscopic techniques. The study confirmed the presence of S–H···O interactions stabilized by dispersion forces in these complexes.

A comparison of hydrogen-bond strengths between N–H···Se and Se–H···N intramolecular hydrogen bonds was carried out for various conformations of 3-amino-propeneselenal (APS), belonging to primarily three tautomer classes, viz., 3-APS, 3-imino-propeneselenol (IPS) and 3-imino-propaneselenal (IP). DFT calculations (B3LYP) and MP2 methods (6-311++G** basis set, G2MP2 level of theory) were employed by Raissi et al.[154] to demonstrate that in a variant of the IPS conformer (IPS-1), the Se–H···N hydrogen bonds were stronger than that of N–H···Se hydrogen bonds in the proton-transferred tautomer of IPS-1, i.e., a variant of the PS system (PS-1). Furthermore, the redshifting of the Se–H-stretching frequency in IPS-1 with respect to a rotamer IPS-2 was more (345.39 cm^{-1})than that of the corresponding redshift of the N–H stretch (320.40 cm^{-1}) in the PS-1 system, showing stronger Se–H···N hydrogen-bonding tendency, It was also seen that in the first singlet excited state (S_1), the hydrogen bonding in IPS-1, of the form Se–H···N=C, was significantly strengthened, in comparison to that of N–H···Se=C type of hydrogen bonds(in PS-1). This year, Se–H···N interactions in p-substituted pyridine SeH_2 complexes were elucidated by Jaju et al.[59] with calculations at the MP2/aug-cc-pVTZ level, where tuning of the Se–H hydrogen-bond donating ability was observed with the electron-donating and withdrawing substituent. The stabilization energy of the Se–H···N–H hydrogen bond was found to be in the range of 10–15 kJ/mol and better interactions were ensured with electron-donating substituents that favored election transfer from the nitrogen lone pair to the σ^*_{Se-H} orbitals.

1.3.2 X–H···*Φ* π-Type Hydrogen Bond (Where *Φ* Represents the Aromatic Ring π-Electrons)

A special class of hydrogen bonds arises when S–H or Se–H involves in H bonds with the aromatic ring electron density.[165] It has been established already that C–H···π, N–H···π, O–H···π interactions, though weaker than classical hydrogen bonds, play vital roles in biological and chemical recognition and can also influence protein–water and protein–drug interactions through a combination of direct electrostatic and dispersive contacts as well as polarization effects.[166–169] It was surprising to note, in a study by Boxer et al.[170] with thiophenol and benzene-based aromatic solvents, that S–H···π H bonds are electrostatic in nature.

From laser spectroscopy and ab initio calculations of complexes of H_2S with indole and 3-methyl indole, it was shown that S–H···π H bonds were stronger than other X–H···π (X) C, N, and O) H bonds.[26] Additionally, the S–H··· π interaction was found to be stronger than the N–H⋯S H bond in these complexes, while the opposite trend was noticed for O–H⋯π and N–H⋯O H bonds. Using reduced variational space self-consistent field (RVS) analysis, the different components of interaction energy revealed that, as seen in Fig. 5, for IND-H_2S(π) complexes, all terms (electrostatic, exchange repulsion, and dispersion stabilization) were greater than that of the IND–H_2O(π) complex.

From a combination of microwave spectroscopy and theoretical methods, Goswami and Arunan[79] have also noticed a difference in donor characteristics of H_2S with regard to benzene and phenylacetylene. While in both the compounds, it is expected that geometrically, H_2S would be oriented over the aromatic electron cloud enabling S–H⋯π interactions, for the $C_6H_5CCH\cdots H_2S$ complex, the H_2S hydrogens have a tendency to shift from the aromatic ring plane towards the acetylenic plane.

Recently, Senćanski et al.[159] have considered a model system of H_2Se-monosubstituted benzene dimer, where the Se–H⋯π interactions were studied by varying the substituents on the benzene ring. It was seen that the high polarizability of Se caused the dispersion effects to contribute more to the interaction energy terms, that were seen to be higher in the presence of a non-polar substituent, particular for $SiMe_3$ (for which interaction energy was the highest at − 3.29 kJ/mol relative to the unsubstituted benzene), thus providing energy stabilization of these complexes. In this context, it is pertinent to mention that these interactions in various substituted aromatic rings have been explored by Nakanishi et al.[171] where ^{77}Se NMR chemical shifts have been found to be affected by aryl orientation effects as well as ring substitution.

1.3.3 X–H⋯Y (where *X*, Y=S, Se, Te) Hydrogen Bonds

The first unambiguous experimental evidence of S–H⋯S (with $d_{H\cdots S}$ ~ 2.778 Å and ∡S–H⋯S ~ 175°) hydrogen bonds, in an anisotropic structured H_2S dimer, has been given recently by microwave spectroscopy.[83] In a thiolate salt, $[PPh_4]$ $[SCH_2CH_2SCH_2CH_2SH]$, Boormann et al.[172] observed strong S–H⋯S interactions (with S⋯S distance ~ 3.454 Å and ∡S–H⋯S ~ 176°), that linked centrosymmetric dimers of the anions in head-to-tail fashion. Such evidences were also found from absorption spectra and optical density experiments by Mukherjee et al.[173] where sulfur site of ethylene trithiocarbonate was found to accept hydrogen bonds from a variety of thiophenols.

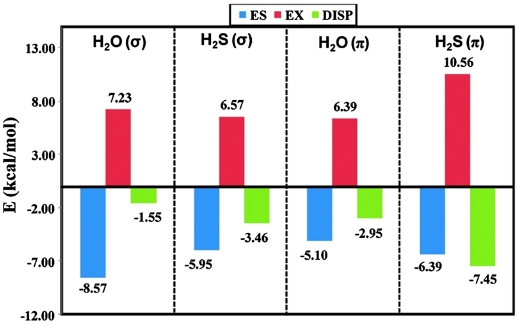

Figure 5: The electrostatic attraction (ES), exchange repulsion (EX), and dispersion energy (DISP) contributions obtained using RVS decomposition analysis for IND·H_2O (σ), IND·H_2O (π), IND·H_2S (σ), and IND·H_2S (π) complexes. Reprinted with permission from ref [26] Copyright 2009 American Chemical Society.

Unusual S–H⋯S and Se–H⋯Se hydrogen bonds (with interaction energies of −2.3 and −3.2 kJ mol^{-1}, respectively) have been found by Thomas et al. [160] in organic alloys of thiophenol and selenophenol synthesized through cryo-crystallography and were further confirmed by electron density topological analysis. It is intriguing that attempts to synthesize the alloys with phenol-thiophenol/selenophenol failed due to "incompatibility" of the shorter O–H⋯O hydrogen bonds with these weaker interactions. Recently, Rafat and Nowroozi[156, 174] investigated resonance-assisted hydrogen bonding in the various tautomeric forms (enol, thiol, and selenol) forms of 2-selenoformyl-3-thioxo-propionaldehyde (STP) as well as 3-mercapto propeneselenal that revealed a wide variety of possible hydrogen bonds that also included Se–H⋯S and S–H⋯Se hydrogen bonds.

1.4 S-, Se-, and Te-Mediated Hydrogen Bonds in Biological Systems: Occurrence and Applications

Hydrogen bonds between thiolate sulfur ligands and the polypeptide backbone have been instrumental in determining stability of various iron–sulfur proteins like ferredoxins, and this has been detected by Mino et al. in a resonance Raman spectroscopy study.[175] Furthermore, extensive analysis of four kinds of N–H⋯S hydrogen bonds involving inorganic sulfur as well as cysteinyl sulfur has been carried out by Adman et al.[16] in ferredoxins, where it has been proposed that change in environment of the Fe–S center could affect the N–H•••S-bonding pattern. An exciting observation from the study by Kolling et al.[176] reveals that in Rieske clusters, hydrogen bonds between tyrosine (Tyr-156), and cluster ligand Cys-129 residues along with Se hydrogen bonding to atom S1 of the cluster could modulate the redox potential of Rieske [2Fe–2S] iron–sulfur protein of cytochrome bc_1. In [4Fe–4S] ferredoxin model arenethiolate complexes studied by Ueno et al.[110] using an array of techniques like cyclic voltammetry, solution NMR, as well as IR spectroscopy, the regulation of redox potential has been demonstrated to be achieved by a cooperative effect between N–H···S and C–H···S hydrogen bonds. Furthermore, in bacterial [4Fe–4S]-type ferredoxins, the S–H···S hydrogen bonds were not only involved in stability of the polar backbone but also in fixing the structural orientation of cysteine residues relative to the clusters. The presence of these cysteine residues could control the electron flow in electron transport chain by modulation of the reduction potential.[111]

An evaluation of various interactions (C–H···S, S–H···π) indulged in by sulfur containing residues in membrane proteins was carried out by Gómez Tamayo et al.[177], where it was seen that compared to aromatic–aromatic interactions, Met–Met, Met–Phe, and Cys–Phe interactions were predominant, whereas these interactions coupled with Cys-aliphatic and Met-aliphatic interactions took precedence over aliphatic–aliphatic interactions. This is proposed to have implications for the functional specificity of the proteins keeping in mind the strong interactions as well as flexibility and adaptability of these residues.

In glutathione peroxidase, the selenol group of the selenocysteine residues has been found to be stabilized and activated by hydrogen bonding with the nearby tryptophan and glutamine residues.[34, 178] Recently, efforts were made by Mishra et al.[179] in mimicking the side-chain interactions between the amino acids tryptophan and selenomethionine, by considering indole and dimethylselenide as model systems and also by statistical analysis of PDB structures containing selenomethionine and its hydrogen-bonding patterns. The analysis initially revealed that not only the number of interactions where a single water molecule facilitated hydrogen bonding involving selenomethionine residues was twice that of direct Se hydrogen-bonding interactions, but also that the probability of such occurrences was maximum when $d_{D/A\cdots Se} = 5–5.5$ Å and $\measuredangle D/A\cdots O\cdots Se = 80–90°$. Out of the various complexes probed through gas-phase spectroscopy as well as computational methods, the Ind···H_2O···Me_2Se complex was the most representative of single water-mediated selenium hydrogen-bonding interactions amongst amino acid residues.

Now, it is established that selenomethionine is routinely introduced into biomolecules for assisting in X-ray crystal determination of proteins. Luo[180] tried to introduce selenourea molecules by soaking biomolecules like thaumatin, trypsin, lysozyme, and B-DNA in selenourea solution for 10 min, and the binding of selenourea through penetration into the biomolecular solvent network was observed. For lysozyme protein (as demonstrated in Fig. 6), nine binding sites of selenourea were noted with N–H···Se interactions with different sites of the protein.

Our group has critically evaluated the N–H···S interactions between the methionine/cysteine and backbone amides through gas-phase vibrational spectroscopy, coupled cluster [CCSD(T)], and dispersion-corrected density functional (B97-D3) methods by considering various model hydrogen-bonded complexes.[32] Our results strongly supported the fact that N–H···S hydrogen bonds were as strong as the N–H···O and N–H···O=C hydrogen bonds and much higher strength wise than the weak N–H···π H bonds, as was conventionally thought to be. We also further employed similar arsenal of techniques along with extensive exploration of PDB structures to explore the N–H···Se hydrogen bonds in selenomethionine residues[54] and the strength was again found to be comparable with the afore-mentioned conventional hydrogen bonds. These observations were also computationally extended to N–H···Te hydrogen bonds and it was concluded that the strength of N–H···X interactions (X=S, Se, Te) does not only depend on the electronegativity of these chalcogens but rather on its interplay with the atomic charge, polarizability of these hydrogen-bond acceptor sites.

Furthermore, we also explored the folding behavior of the methionine side chain in proteins by considering two Met-containing capped dipeptides, namely, *N*-acetyl-L-phenylalaninyl-L-methionine-amide (FM) and *N*-acetyl-L-methioninyl-L-phenylalanine-amide (MF) in a high-resolution gas-phase spectroscopy study coupled with DFT-D calculations[25] that revealed strong $NH_{backbone}\cdots S_{Met}$ bonds to be responsible for this kind of folding; a propensity that was echoed in 24% of the protein structures (that we

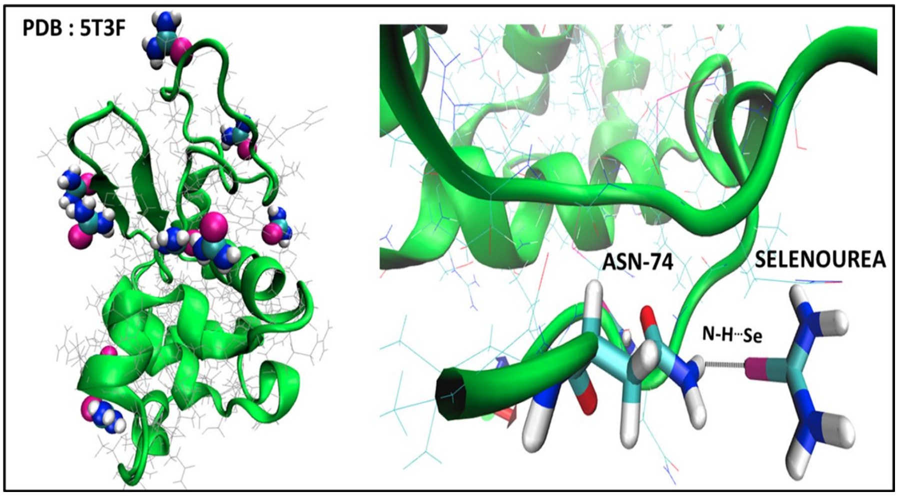

Figure 6: Binding of selenourea to lysozyme protein through N–H···Se H bonds.

considered for comparison purposes) that folded through this pathway.

Substitution of oxygen by sulfur and selenium into nucleobases enhances their tumor-targeting capabilities and efficiency as drug molecules. Duplex DNA constructed by incorporation of thioguanine was probed by Somerville et al.[181], as presented in Fig. 7, and it was found that base pairing of cytosine with thioguanine caused an opening of around ~ 10° towards the major groove and also decreased the base pairing lifetime by 80 times relative to that of normal DNA. Furthermore, from crystal structure studies of Se-incorporated DNA, it was found that the base pairing between ^{Se}guanine–cytosine was of similar pattern as that of guanine–cytosine with the difference being the longer base pairing length by 0.3 Å.[43]

Hydrogen-bonding preferences and molecular structure of modified nucleobases should be explored imperatively when we consider the hydrated nature of DNA and the possible implications for the biological activity. Keeping this in mind, tautomeric preferences of 6-selenoguanine have been studied by Karthika et al.[182] using AIM and NBO analyses. Hydrogen bonding of N–H···O, O–H···N, O–H···Se, and Se–H···O types has been observed in the hydrated complexes and useful information about the nature of selenium hydrogen bonding has been gained from this study. While the Se–H···O hydrogen-bond distances lie in the range of 2.118–2.163 Å, (with H-bond angles more than 143°) in the monomer and hydrated forms, the Se···H–O distances are within the range of 2.367–2.63 Å (with H-bond angles ~ 152.3–173.6°), indicating stronger preference of selenium for hydrogen-bond donation. They also concluded that the although the O–H···Se and Se–H···O hydrogen bonds were longer than the conventional hydrogen bonds, there was comparable charge transfer contributing to stabilization of the various complexes in solution. Se-mediated hydrogen bonds (Se···H–N) have been found in synthesized 4-Se-thymidine 5′-triphosphate (visible yellow in color) and its incorporation into DNA yields colored DNA, which is not only useful for crystal structure determination (through MAD phasing) but also for DNA-based detection of diseases and pathogens.[183]

1.5 Other Potential Areas of Application

The hydrogen bonds formed by heavier chalcogens are not only exploited for mimicking biological systems but are also exploited in crystal engineering for synthesis of novel materials and tuning of supramolecular architecture.[112, 116, 135] A few of these application areas have been highlighted in Fig. 8. For instance, π-conjugated thiophenes and their selenium analogs that are packed in their crystal structures with hydrogen bonds including Se···H and S···H interactions exhibit useful optoelectronic properties and may be used in field-effect transistor devices.[184]

We have already discussed the synthesis of organic alloys from room-temperature liquids, thiophenol and selenophenol, with X–H···Y (X, Y=S, Se) hydrogen bonds in the system.[160] Superconducting mixed sulfur and selenium hydrides of the composition $S_xSe_{1-x}H_3$ are held together by Se–H···Se and Se–H···S hydrogen bonds in their crystal lattices.[162] Similarly, Se–H···Se hydrogen bonds have been found in the packing arrangements of superconducting selenium

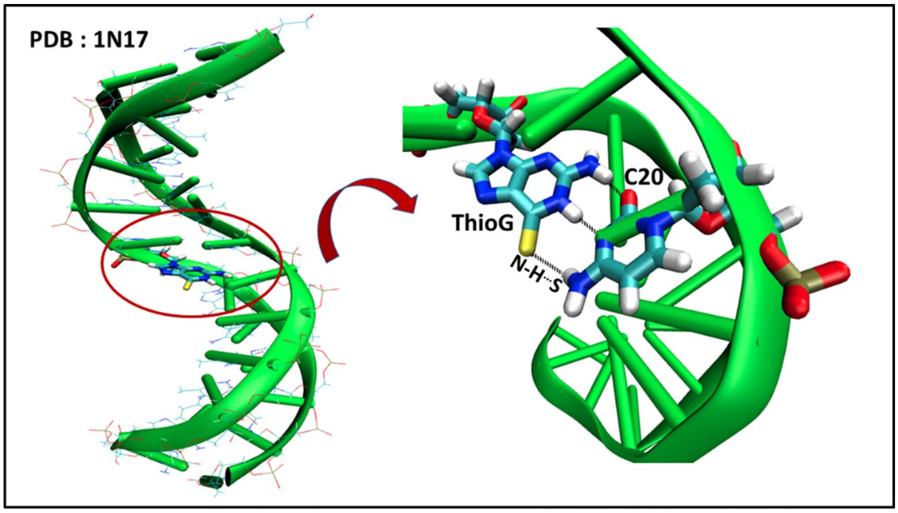

Figure 7: N–H···S hydrogen bonds along with N–H···N and N–H···O hydrogen bonds play an important role in stabilization of thioguanine-incorporated duplex DNA (PDB: 1N17).

hydrides.[185] Polymorphs of telluridoindate that are stabilized by N–H···Te interactions have been known to exhibit photocatalytic properties.[116] The structure of a rare ditelluroether $(C_{10}H_7)Te(CH_2)_4Te(C_{10}H_7)$ has been analyzed where Te···H hydrogen bonds direct the three-dimensional frameworks.[186] Our group has exploited sulfur-centered hydrogen bonds along with chalcogen–chalcogen interactions to facilitate efficient absorption of sulfur dioxide, particularly for the anion [4-amino salicylate]$^-$ or PAS, that is bound to SO_2 molecules through C–H···S hydrogen bonds. [187]

Finally, our group has also tried to design organic materials exhibiting piezoelectric response by exploiting uncommon properties of sulfur/selenium-centered H bonds. It was not only found that piezo-coefficients were closely correlated to dipole moment/polarizability, but also that sulfur-centered hydrogen-bonded complexes achieved the maximum piezo-response. The piezo-coefficient of thiophenol-nitrobenzene (SPH-NBz) dimer is 14 pm/V, which is higher than that of 2-methyl-4-nitroaniline (10.9 pm/V), the organic crystal with the largest known piezoelectric response.[188]

2 Conclusions

In this review, we have presented a detailed account of the occurrence, nature, and strength of various kinds of hydrogen bonds involving heavier chalcogens, where they participate as hydrogen-bond donor, acceptor, or both. The experimental determinations involving combinations of gas-phase laser spectroscopic methods mostly involve preparation of the species under supercooled jet conditions that have an edge over conventional spectroscopic methods owing to reduced complexity of spectra. The communion of these techniques with high-level ab initio quantum chemical calculations has enabled us to study the electron density distribution, components of interaction energies, as well as interaction of natural-bond orbitals in various hydrogen-bonded complexes. We have included various recent examples of X–H···Y (where X=O, N, C, S, Se, Te and Y=S, Se, Te, or vice versa) from crystal structures and biological systems to give an idea about the ubiquitous existence of such kind of hydrogen bonds. From experimental as well as computational studies, we could conclude that the hydrogen bonds involving heavier chalcogens cannot be dubbed as “weaker” than their conventional counterparts, but rather governed by a conglomeration of factors like polarizability, electronegativity, as well as directionality that are unique to each system. Moreover, a general trend shows up that most of the contribution to the binding energy of the hydrogen-bonded complexes (with S, Se, and Te) comes from dispersive effects rather than electrostatic components, as common in O–H···O, N–H···O, O–H···N hydrogen bonds. It is truly surprising to note how the directionality of even weaker C–H···X (X=S/Se/Te) hydrogen bonds can govern packing effects in many supramolecular assemblies and this fact effectively negates some of the earlier suggestions of these kinds of interactions being just weak van der Waals forces.

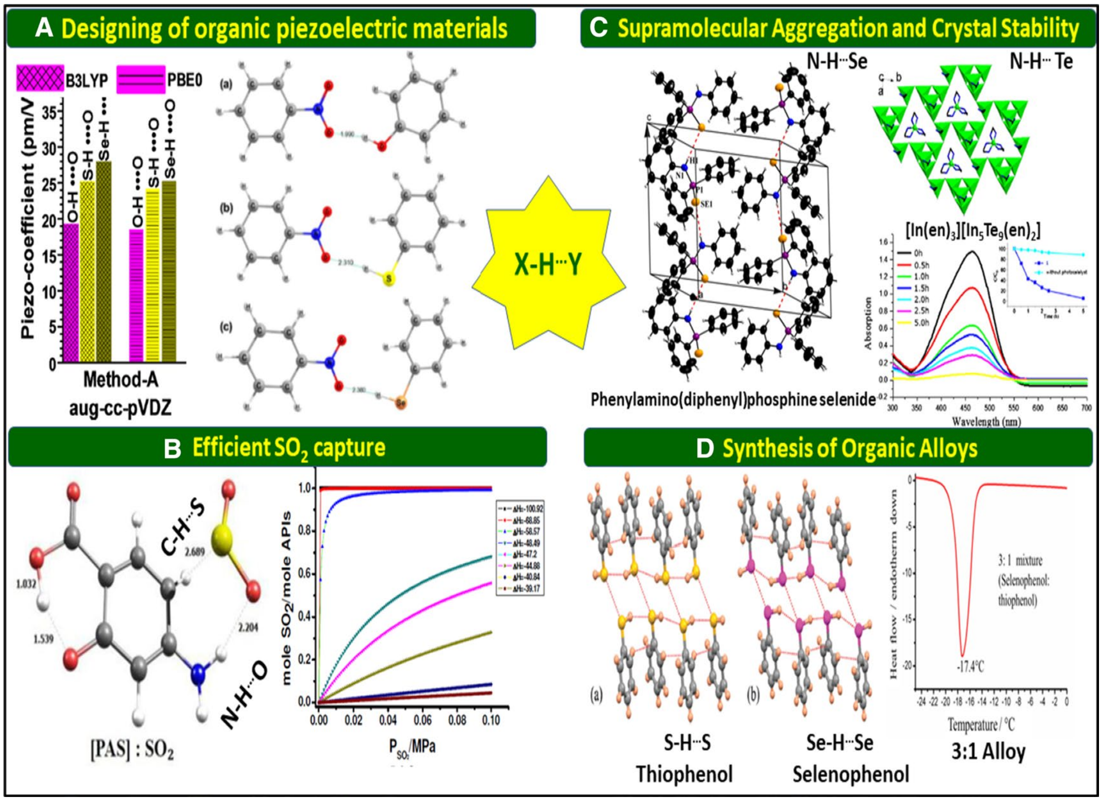

Figure 8: Employing hydrogen bonds involving heavier chalcogens (S, Se, Te) in various applications like **a** designing of organic piezoelectric materials (Reprinted from Ref.[188] with permission from Wiley Publishers), **b** facilitating SO_2 capture through combination of C–H···S and N–H···O hydrogen bonds in [4-amino-salicyate(PAS) that can absorb 4.69 mol of SO_2/mole (Reprinted with permission from Ref.[187] with permission from Wiley Publishers), **c** influencing supramolecular aggregation via N–H···Se hydrogen bonds in phenylamino(diphenyl)phosphine) selenide as well as through N–H···Te in $[In_4Te_9(en)^{6-}$ component cluster in a telluridoindate (Reprinted from Ref.[116, 135] the former being covered under (https://creativecommons.org/licenses/by-nc/3.0/legalcode) Creative Commons Attribution-NonCommercial 3.0 License and published under ARKIVOC, and the latter, with permission from Elsevier Publishing, respectively), and **d** devising organic alloys of various proportions of room-temperature liquids of selenophenol and thiophenol (9:1, 3:1, etc.), taking advantage of their isostructural supramolecular structures bound by S–H···S and Se–H···Se hydrogen bonds, respectively.(Reproduced from Ref. [160]with permission from Royal Society of Chemistry via Copyright Clearance Centre).

The propensity of occurrence of hydrogen bonds involving sulfur and selenium in nature has been highlighted by examples from biological systems and these have been supported by investigations on model systems. The ramifications of substitution of heavier chalcogens instead of oxygen into biological systems like nucleobases as well as binding modes of small molecules (like selenourea) to proteins have been discussed. Furthermore, it is amazing to note the efficacy of these hydrogen bonds in crystal engineering that helps in design of novel materials like alloys, piezoelectric compounds, and organic superconductors. Hence, if we could just look beyond the second row, the versatile S/Se/Te-centered hydrogen bonds are, indeed, well poised to emerge as the "hydrogen bonds for the future".

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