Research article

An account of noncovalent interactions in homoleptic palladium(II) and platinum(II) complexes within the DFT framework: A correlation between geometries, energy components of symmetry-adapted perturbation theory and NCI descriptors

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GRAPHICAL ABSTRACT

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ABSTRACT

The present work addresses the underlying nature of weak noncovalent interactions (NCIs) in the self-assembled dimers of two square planar palladium(II) and platinum(II) complexes trans-[Pd(Hida)_2] (1) and trans-[Pt(Hida)_2] (2) (Hida = monoprotonated iminodiacetate) within the framework of density functional theory (DFT) in gas phase. Initial geometries of the dimers in different spatial orientations were extracted from the X-ray crystal structures, reported earlier, and optimized with three dispersion-corrected functionals that are frequently used to explore NCIs. The BP86-D3, M062X-D3 and oB97X-D3 functionals have been used to test their performances over the present systems. The SARC-ZORA-TZVP and ZORA-def2-TZVP basis sets were applied for the metals and the remaining elements, respectively. The optimizations resulted in equilibrium geometries where the monomers are self-assembled through NCIs to form dimers in a cyclic fashion. This type of structural pattern is absent in the crystal structures of both 1 and 2. Physical components of interaction energies were investigated by symmetry-adapted perturbation theory (SAPT). The UV-Vis absorption spectra of the dimers are described by time-dependent density functional theory (TD-DFT). Global reactivity parameters for the dimers have been computed within the framework of conceptual density functional theory (C-DFT). Detailed investigations on NCIs were performed for all dimer geometries. Simulated IR and 1H NMR spectra, charge transfer, QTAIM, NCI-RGD, IGM, ETS-NOCV and ELF studies confirmed the presence of intermolecular hydrogen bonds (HBs) and weak van der Waals interactions. Energies of the hydrogen bonds and associated orbital interaction energies were computed by QTAIM and ETS-NOCV methods, respectively.

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1. Introduction

Over the last few decades, inclination towards supramolecular chemistry has resulted in the synthesis of a growing number of elegant and intricate functional structures. In this context, accurate comprehension and characterization of weak noncovalent interactions (NCIs) have become one of the major goals of contemporary chemistry [1, 2]. It has been established that the hydrogen and halogen bonds, π–π stacking, π-cation, σ-anion, C–H⋯σ and hydrophobic interactions [3, 4, 5, 6, 7, 8, 9] can govern the conformation, aggregation, and higher order structures of the molecules in the construction of supramolecular architectures. NCIs are also the driving force for many biological processes where the structures as well as the interactions between the biomolecules such as proteins, DNAs and several host-guest systems are largely controlled by the noncovalent forces [10, 11, 12, 13, 14, 15, 16].

Noncovalent interactions have a wide range of applications in the field of nanoscience and nanotechnology. To date, various computational methods have been used to analyze these interactions in order to design nanomaterials with greater precision and performance, to develop nanocarriers for site-specific drug delivery, and to fabricate nanosensors for the detection of HCFC-124 on nanotubes and nanosheets [17, 18, 19, 20].

The rich variety of weak interactions has prompted researchers to investigate the physical nature of these forces and quantify them experimentally as well as theoretically [21, 22, 23, 24, 25]. In this regard, metal-carboxylates have been extensively studied for their potential role in demonstrating impressive NCIs [26, 27, 28, 29, 30]. In this study we have explored the nature and strength of noncovalent interactions for the dimers of two square planar Pd(II) and Pt(II) complexes, trans-[Pd(Hida)]_2 (1) and trans-[Pt(Hida)]_2 (2) (Hida = monoprotonated iminodiacetate) in gas phase. The structures of the compounds were reported previously by our group [30]. Both 1 and 2 were synthesized and structurally characterized by single crystal X-ray diffraction technique. The crystal structures of 1 and 2 revealed O⋯H⋯O and N⋯H⋯O intermolecular hydrogen bonds resulting in self-assembled two-dimensonal supramolecular networks. The propagation of the networks along a particular direction was governed by a specific type of HB. To account for the individual contribution of different intermolecular hydrogen bonding interactions in gas phase, it is convenient to consider the substructures generated by each type of HB. The initial geometries of the monomers and the corresponding dimers (D1 and D2) have been generated from the crystallographic fragments of both 1 and 2 and were optimized using the DFT method. Latest dispersion-corrected functionals such as BP86-D3, M062X-D3 and αB97X-D3, frequently used to explore NCIs were employed to test their performance over the present systems. The valence triple-ζ ZORA-def2-TZVP basis set was applied on the functionals for all atoms except Pd(II) and Pt(II) for which the element-specific modifications SARC-ZORA-TZVP were applied. The supermolecular approach was used to calculate intermolecular interaction energies for the relaxed dimer geometries of 1 (D1 and D2) and 2 (D1 and D2). In addition, the symmetry-adapted perturbation theory (SAPT) [31] has been applied on the dimers to decompose the interaction energies into various meaningful components. Quantum theory of atoms-in-molecules (QTAIM) [32, 33], noncovalent interaction-reduced density gradient (NCI-RDG) [34], independent gradient model (IGM) [35, 36], electron localization functions (ELF) [37, 38], molecular electrostatic potential (MEP) [39], extended transition state-natural orbitals for chemical valence (ETS-NOCV) [40] and charge transfer (CT) analysis [41] have been used to understand the intermolecular interactions. Parr’s conceptual density functional theory (CDFT) was applied [42] to compare the global reactivities of the present chemical systems.

2. Computational details

All density functional calculations were carried out using the ORCA Program Version 5.0.2 computational package [43]. The input files were prepared using Avogadro 1.2.0 [44, 45]. The molecular and electronic structures of 1 and 2 and their dimers in different geometrical arrangements were studied in gas phase by performing complete structural optimization of the geometries in singlet spin state using restricted Kohn-Sham (RKS) formalism. Initial coordinates were extracted from the CIF files [38] and no constraints on symmetry, bond lengths, bond angles and dihedral angles were applied in the optimization calculations.

To account for the long-range dispersion energies, Grimme’s atom-pairwise dispersion correction method (DFT-D3) [46, 47, 48, 49] was applied. The dispersion-corrected pure GGA functional BP86-D3 [50, 51], hybrid meta-GGA Minnesota functional M062X-D3 [52] and range-separated hybrid functional αB97X-D3 [53, 54] were chosen. The D3(BJ) scheme [47, 48] was applied for BP86-D3 while for the other functionals the D3(0) scheme [47, 55] was applied.

The basis set was a scalar implementation of the zeroth-order regular approximation (ZORA) [56] adapted version of the def2 [57] family: ZORA-def2-TZVP (recontracted for ZORA by D. A. Pantazis) for all atoms except Pd(II) and Pt(II) for which the recommended element-specific modifications SARC-ZORA-TZVP [58, 59] were applied. The calculations utilized segmented all-electron relativistically contracted auxiliary basis set (SARC/J) [59] for the metals and Weigend’s decontracted Coulomb-fitting auxiliary basis set def2/J [60] for the remaining elements.

Harmonic vibrational frequency calculations were carried out for 1 and 2 and their dimers to confirm the absence of any imaginary frequency. Single-point energy calculations were performed with the ZORA-def2-TZVPP basis set for elements other than Pd(II) and Pt(II) for which the SARC-ZORA-TZVPP basis set was applied. To remove the basis set superposition errors (BSSE), Grimme’s geometrical counterpoise correction (gCP) [61] was applied.

SAPT calculations at the SAPTO level were performed with the aug-cc-pVDZ-pp basis set for Pd(II) and Pt(II) and the recommended jun-cc-pVQZ basis set for the remaining elements on all equilibrium dimer geometries. The Psi4 code (version 1.5) [62] was employed for the SAPTO analyses.

1H-NMR chemical shifts were investigated by gauge including atomic orbitals (GIAO) method [63, 64] with simulated spectrometer frequency 300 MHz and corresponding field strength 7.05 Tesla. The excitation energies in gas phase were calculated by TD-DFT method [65, 66]. Lowest 50 singlet-singlet electronic transitions have been computed. Charge transfer calculations were performed with the JANPA computational package [67]. Global reactivity descriptors, and noncovalent interactions were analyzed by Multiwfn software (version 3.8) [68]. Chemcraft [69] and VMD (version 1.9.3) [70] were used to visualize the molecular and electronic structures.

3. Results and discussion

3.1. Geometry of the dimers

Both 1 and 2 are mononuclear square planar complexes of Pd(II) and Pt(II), respectively, having similar structures (Fig. S1). Two monoprotonated iminodiacetates (Hida) act as ligands in trans configuration. Computed structural parameters for 1 and 2 are given in Table S1. Fig. 1 shows the optimized structures with atom numbering schemes for the cyclic hydrogen bonded dimers of 1. Selected structural parameters for the optimized geometries of 1D1 and 1D2 along with the experimental values have been presented in Table 1. Calculated values of bond
lengths and angles for the dimers of both 1 and 2 are in good agreement with the experimentally observed values [30]. The atom positional root-mean-square deviations (RMSDs) fall within the range 0.007-0.031 Å for 1D1 and 0.009-0.041 Å for 1D2, confirming that all the geometries are very similar at all levels. Similar bond distances are also noticed for the dimers of 2 where numerical estimations of RMSD lie within the range 0.008-0.026 Å for 2D1 and 0.009-0.036 Å for 2D2 (Table S2).

Structural parameters for hydrogen bonding with their RMSDs are listed in Table 2. Intermolecular HBs are observed in the dimers 1D1 and 2D1. In each system the free –COOH group of one monomer acts...
Table 1. Selected bond lengths (Å), bond angles (°) and RMSDs (Å) for the dimers of 1 computed with different functionals and ZORA-def2-TZVP/SARC-ZORA-TZVP basis sets.

| Bond angles | Functional | RMSD |
|-------------|------------|------|
| O2–Pd1–N26 | B97X-D3 | 0.097 |
| N11–Pd1–N26 | M062X-D3 | 0.009 |
| O2–Pd1–O17 | aB97X-D3 | 0.089 |
| Pd1–N17 | B97X-D3 | 0.089 |
| O2–Pd1–N26 | M062X-D3 | 0.097 |
| O2–Pd1–O17 | aB97X-D3 | 0.089 |
| Pd1–N17 | B97X-D3 | 0.089 |

Table 2. Hydrogen bond distances (Å), angles (°) and RMSDs (Å) for the dimers of 1 and 2 computed at different levels of theory with ZORA-def2-TZVP/SARC-ZORA-TZVP basis sets. Experimental parameters are also tabulated for comparison.

| Bond angles | Functional | RMSD |
|-------------|------------|------|
| O24–H25–O34 | B97X-D3 | 0.097 |
| O24–H25–O34 | M062X-D3 | 0.009 |
| O24–H25–O34 | aB97X-D3 | 0.089 |
| Pd1–N17 | B97X-D3 | 0.089 |
| O2–Pd1–O17 | M062X-D3 | 0.097 |
| O2–Pd1–O17 | aB97X-D3 | 0.089 |
| Pd1–N17 | B97X-D3 | 0.089 |

as HB donor while the C=O group of the bound carboxylate of the other monomer acts as HB acceptor forming O–H–O = C type HB as shown in Fig. 1a. Thus, the D1s are stabilized by O–H–O intermolecular HB interactions. The solid-state structures for a dimeric pair of 1 and 2 include only a single intermolecular O–H–O HB as viewed down the crystallographic b-axis. In contrast, the gas phase geometries of D1 and D2 feature two O–H–O intermolecular HBs (O9–H10–O34 and O40–H41–O18 for D1 and O24–H25–O34 and O55–H56–O18 for D2).
2D1). Self-assembly of this type gives rise to a R^2(18) motif in both cases (Fig. 1a and S2). This type of cyclic motif is formed as a result of inward orientation of O–H covalent bond towards C–O in gas phase, favoring closest proximity of participating atoms to interact strongly to form HBs. The O–H distances fall within the range 1.457-1.622 Å for 1D1 and 1.555-1.633 Å for 2D1 where shortest contacts are found for the geometries computed with the BP86-D3 functional (1.457 and 1.549 Å for 1D1, 1.459 and 1.555 Å for 2D1). RMSDs of O–H distances range from 0.238 to 0.339 Å for 1D1 and 2D1. The differences in O–H distances within the dimers can be ascribed to the extent of intermolecular interactions that have linked the monomers together in gaseous state, thus changing the structural parameters, compared to the dimers in solid state. The Pd–Pd separations in 1D1 fall within the range 8.814-8.897 Å (Table S3) and are shorter than the experimental Pd–Pd distance (9.285 Å). The Pt–Pt distances range within 8.805-8.906 Å (Table S3) in 2D1. These distances are also shorter than those found in the crystal structure (9.248 Å) of 2. Considerable intermolecular interactions in gas phase also led to shortening of intermetallic distances, favorable for the formation of additional HBs in both 1D1 and 2D1.

Optimizations with the functionals reveal N–H–O HB interactions in 1D2 and 2D2. The –NH group acts as HB donor and the C=O group of the bound carboxylate acts as HB acceptor forming N–H–O=C type HBs in all the dimers 2D2 except 2D2, computed with BP86-D3. As shown in Fig. 1b, the H12 and O49 atoms of the respective monomers construct the first intermolecular N–H–O HB (N11–H12–O49), whereas the second intermolecular HB (N42–H43–O3) is formed by the interaction between H43 and O3 atoms of the respective monomers in 1D2. This self-assembly leads to a R^2(11) motif in 1D2 for all the functionals.

Optimized geometries calculated with M062X-D3 and oB97X-D3 for 2D2 exhibit similar structural patterns that have been observed for 1D2. In contrast to the crystal structure, two N–H–O=C HBs are seen in 2D2 where the oxygen atoms O34 and O18 of the bound carboxylates are linked to the H27 and H58 imino hydrogen atoms, respectively (N26–H27–O34 and N57–H58–O18). A different feature of HB for the optimized structure of 2D2 calculated with BP86-D3 has been noticed. Apart from the N–H–O=C type HB (N57–H58–O18) another HB of the type N–H–O=Pt is formed where the metal-bound (Pt32) oxygen atom O33 acts as HB acceptor (N26–H27–O33) as can be seen in Fig. 1c. The Pt1–Pt32 distance is shortest in this case and found to be 5.204 Å. Both intermolecular HBs within 2D2 reinforce the dimer through R^2(9) cyclization.

The O–H distances range from 1.829 to 2.071 Å for 1D2 and 1.817 to 2.037 Å for 2D2 with RMSDs 0.238 to 0.339 Å. The RMSD values clearly express the difference between experimental and computed hydrogen bonding parameters. The Pd1–Pd32 separations in 1D2 fall within the range 5.419-5.643 Å that are considerably shorter than the crystallographic Pd–Pd distance (6.793 Å). Calculated Pt1–Pt32 distances for 2D2 are within the range 5.204-5.594 Å (Table S3), much smaller than the crystallographic Pt–Pt distance of 6.816 Å. Structural differences between the dimers D1 and D2 of 1 and 2 resulted in additional NCIs which will be discussed in subsequent sections of this article.

3.2. Frontier molecular orbitals of the dimers

The HOMO and the LUMO for the dimers of 1 and 2 predicted at the BP86-D3/ZORA-def2-TZVP/SARC-ZORA-TZVP level are shown in Fig. 2. It is evident that there is considerable reorganization in the electronic distribution in these dimers. Fig. 2a shows that the HOMO of 1D1 is mostly nonbonding in character, localized on one monomer and the LUMO is localized on the other monomer. Similar feature has been obtained for 1D2 (Fig. 2b). The electronic nature of HOMO and LUMO in 1D1 and 1D2 is closely related to that of 1 (Fig. S3). For 1D1 the energy difference, ∆E (∆E = E_LUMO – E_HOMO) between these frontier orbitals is largest for oB97X-D3 (9.56 eV) and minimum for BP86-D3 (2.63 eV). Similar trend has been noticed for 1D2 where the values of ∆E range between 9.49-2.53 eV.

The HOMO of 2D1 and 2D2 is a π*-MO localized on one monomer. The LUMO is a π-MO localized on free –COOH group of the other monomer within the dimer (Fig. 2c and 2d). Frontier MOs of 2D1 and 2D2 closely resemble those of 2 (Fig. S3). ∆E values are found to be
greater in 2D1 and 2D2 than those in 1D1 and 1D2 for respective functionals. Largest value of \( \Delta E \) is obtained for \( \omega B97X-D3 \) (10.19 and 10.09 eV for 1D2 and 2D2, respectively) while smallest value is obtained for BP86-D3 (3.19 and 2.97 eV for 1D1 and 2D2, respectively).

### 3.3. Interaction energies across supermolecular approach

Interaction energy (\( \Delta E_{\text{int}} \)) is one of the most crucial quantities to characterize the noncovalent dimer. It is calculated as the difference between the energy of the dimer and the sum of the energies of the monomers possessing geometry of the complex dimer, implying that structural relaxation of the monomers is ignored. \( \Delta E_{\text{int}} \) of the dimer is calculated according to Eq. (1)

\[
\Delta E_{\text{int}} = E_{\text{Dimer}} - (E_{\text{Monomer}1} + E_{\text{Monomer}2}) \tag{1}
\]

Interaction energies ranging from -41.07 to -29.98 kcal/mol have been obtained for the dimer geometries of 1 and 2 (Table 3). A large negative value of \( \Delta E_{\text{int}} \) implies greater stability of the dimer. Comparable values of \( \Delta E_{\text{int}} \) are noted for 1D1 and 2D1 with respective functionals and the values are more negative than those of 1D2 and 2D2 for corresponding functionals. Same trend has been noticed for D2s where the magnitudes of \( \Delta E_{\text{int}} \) are comparable for corresponding functionals. As can be seen in the table, stabilization of the geometries for 1D1 and 2D1 follows the order BP86-D3 > M062X-D3 > \( \omega B97X-D3 \) with \( \Delta E_{\text{int}} \) of -40.95 (1D1) and -41.07 (2D1) kcal/mol to be largest negative for BP86-D3. Computation of interaction energies for 1D2 and 2D2 reveals the trend in stability BP86-D3 > M062X-D3 > \( \omega B97X-D3 \) where \( \Delta E_{\text{int}} \) ranges from -31.94 to -30.20 kcal/mol for 1D2 and -31.00 to -29.98 kcal/mol for 2D2.

The interaction energy term includes dispersion energy (\( \Delta E_{\text{disp}} \)). In Table 3, comparable values of \( \Delta E_{\text{disp}} \) are noticed for 1D1 and 2D1 with the respective functionals where \( \Delta E_{\text{disp}} \) (including sign) follows the order \( \Delta E_{\text{disp, BP86-D3}} < \Delta E_{\text{disp, M062X-D3}} < \Delta E_{\text{disp, \omega B97X-D3}} \). Dispersion energy of 1D2 and 2D2 also follows the same order. Contribution of \( \Delta E_{\text{disp}} \) to \( \Delta E_{\text{int}} \) is small for D1s of both 1 and 2 and lowest contribution is obtained for the geometries computed with M062X-D3 in both cases. In contrast, significant contribution of \( \Delta E_{\text{disp}} \) to \( \Delta E_{\text{int}} \) is found for 1D2 and 2D2 except the geometries computed with M062X-D3 for which less negative \( \Delta E_{\text{disp}} \) values (-2.30 and -2.33 kcal/mol for 1D2 and 2D2, respectively) have been obtained. \( \Delta E_{\text{disp}} \) values are comparatively more negative for 1D2 and 2D2 (-18.86 and -20.99 kcal/mol, respectively) computed with BP86-D3. Thus, it can be rationalized that the noncovalent dispersive forces play a dominant role in the stabilization of both 1D2 and 2D2 when their geometries are computed with BP86-D3 functional.

### 3.4. Decomposition of interaction energies

SAPT is one of the stringent methods for indirect estimation of interaction energies (\( E_{\text{int}} \)) in systems where NCIs are recognized. This approach also allows the decomposition of \( E_{\text{int}} \) into several physically meaningful components as expressed by Eq. (2) [71]

\[
E_{\text{int}} = E_{\text{elec}} + E_{\text{disp}} + E_{\text{vdw}} + E_{\text{elec}} \tag{2}
\]

where \( E_{\text{elec}} \) denotes the classical electrostatic interaction between two monomers, the exchange-repulsion contribution is reflected by \( E_{\text{exchange}} \), the \( E_{\text{disp}} \) term corresponds to the induction contribution due to polarization and charge transfer effects between two monomers, \( E_{\text{vdw}} \) is the dispersion contribution arising from Coulomb correlation between electrons of the monomers. The electrostatic, induction and dispersion terms contribute to \( E_{\text{int}} \) as attractive forces, representing negative energy values, while the exchange-repulsion term acts as a repulsive force, characterized by positive energy value. In this study SAPTO, which is the simplest SAPT method, has been applied with the recommended jun-cc-pVDZ basis set. It has been demonstrated that performance of SAPTO is best with this truncated double-\( \zeta \) basis set due to favorable cancellation of errors [71].

To probe the nature of interactions between the monomers of each dimer geometry and the factor(s) playing the pivotal role, the components of SAPTO-derived interaction energies were computed and the results are summarized in Table 4. From the table it is evident that the sum of the electrostatic, induction and dispersion terms overcomes the exchange-repulsion term, thus yielding negative values of \( E_{\text{int}} \) (SAPTO). More precise information about the nature of NCIs has been obtained after the magnitudes of each attractive energy term given in the table were converted into contribution percentage as \( \frac{E_{\text{elec}}}{E_{\text{elec}} + E_{\text{disp}} + E_{\text{vdw}}} \times 100\% \), where \( E_{\text{elec}} = E_{\text{elec}}, E_{\text{vdw}} \) and \( E_{\text{disp}} \). The results are presented graphically in Fig. 3. The plot reveals that the predominant component of \( E_{\text{int}} \) (SAPTO) is the electrostatic term that comprises about 53-58% of total attractive interaction energy in all the dimers. The induction component is also quite significant in 1D1 and 2D1, accounting for 29-33% of the attractive forces. Dispersion plays an important role in the stabilization of 1D2 and 2D2 contributing 26-29% to \( E_{\text{int}} \) (SAPTO). Thus, it can be inferred that apart from prevalent electrostatic attraction, induction interaction plays a significant role in the stabilization of 1D1 and 2D1. On the other hand, dispersion interaction is the key component of \( E_{\text{int}} \) (SAPTO) in 1D2 and 2D2. Subject to the same functional employed for the computational purpose concerned to the dimers of 1 and 2, it is evident from the plot that each of the energy components contributes in a similar fashion, however, the magnitude varies in a subtle manner.

### 3.5. Infrared spectroscopy

In the realm of computational chemistry, frequency calculations not only characterize the stationary points (as minima, transition states
to weakening of the O–H bonds as a result of HB formation. For all computed geometries of 1D1 and 2D1, values of $\nu$(O–H) lie within 2236-3024 (experimental value 3300 cm$^{-1}$) and 2246-3055 cm$^{-1}$ (experimental value 3400 cm$^{-1}$), respectively. Computation with BP86-D3 for both 1D1 and 2D1 shows maximum red-shift in $\nu$(O–H) with $\Delta\nu$ values $\sim$1353 and $\sim$985 cm$^{-1}$ for 1D1 and $\sim$1343 and $\sim$966 cm$^{-1}$ for 2D1. Red-shift is also observed for the C=O stretching frequencies of metal-bound carboxylates where $\nu$(C=O) values range from 1570 to 1739 cm$^{-1}$ for 1D1 (experimental value 1586 and 1734 cm$^{-1}$) and 1576 to 1746 cm$^{-1}$ for 2D1 (experimental value 1598 and 1734 cm$^{-1}$). This confirms the HB accepting ability of the oxygen atoms O34 and O18 in these dimers. Thus, both 1D1 and 2D1 are stabilized by strong intermolecular O–H...O=C HBs. Apart from intermolecular O–H...O=C HBs, weaker intramolecular N–H...O=C HBs are found in the geometries of both 1D1 and 2D1 computed with BP86-D3 where small red-shifts in N–H stretching frequencies with $\Delta\nu$ values $\sim$107 (N11–H12–O8) and $\sim$111 cm$^{-1}$ (N57–H58–O54) for 1D1 and 2D1, respectively have been observed. No notable change in N–H stretching frequencies has been observed for the geometries computed with M062X-D3 and oB97X-D3.

The stretching vibrations for both free and hydrogen bonded N–H groups have been computed for 1D2 and 2D2 and listed in the table. The monomers are associated through intermolecular N–H...O=C HBs to form the dimers where values of $\nu$(N–H) range from 3065 to 3422 cm$^{-1}$ for 1D2 and 3088 to 3407 cm$^{-1}$ for 2D2. Experimental $\nu$(N–H) were observed at 3100 and 3200 cm$^{-1}$ for I and 2, respectively. Formation of HBs is confirmed by the red-shifting of N–H stretching frequencies. For 1D2 maximum red-shift in $\nu$(N–H) occurs for the geometry computed with BP86-D3 with $\Delta\nu$ values $\sim$204 and $\sim$311 cm$^{-1}$. For 2D2 values of $\Delta\nu$ are maximum for the geometry computed with the same functional and found to be 240 and 270 cm$^{-1}$. These $\Delta\nu$ values are quite small than those computed for O–H...O=C intermolecular HBs in 1D1 and 2D1, reflecting much weaker strength of N–H...O=C HBs compared to O–H...O=C HBs.

As mentioned in section 3.1, the geometry of 2D2 computed with BP86-D3 shows both N–H...O=C (O33–P332) and N–H...O=C intermolecular HBs. Calculated $\nu$(N–H) for the former is $\sim$3104 cm$^{-1}$ and

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**Table 5. Assignment of selected vibrational stretching frequency data for the dimers of 1 and 2.**

| Functional | 1D1 | 2D1 | 1D2 | 2D2 |
|------------|-----|-----|-----|-----|
| BP86-D3    | 3589.20 (free) | 3590.66 (free) | 3590.66 (free) | 3590.66 (free) |
|            | 3330.67 (free) | 3357.74 (free) | 3343.62 (free) | 3343.62 (free) |
| M062X-D3   | 3786.74 (free) | 3783.72 (free) | 3789.56 (free) | 3789.56 (free) |
|            | 3457.66 (free) | 3473.09 (free) | 3473.09 (free) | 3473.09 (free) |
|            | 3787.15 (free) | 3807.65 (free) | 3807.65 (free) | 3807.65 (free) |
|            | 3634.56 (free) | 3634.56 (free) | 3634.56 (free) | 3634.56 (free) |
| oB97X-D3   | 3804.24 (free) | 3800.64 (free) | 3800.64 (free) | 3800.64 (free) |
|            | 3490.54 (free) | 3502.99 (free) | 3502.99 (free) | 3502.99 (free) |
|            | 3482.29 (free) | 3517.21 (free) | 3517.21 (free) | 3517.21 (free) |
|            | 3487.55 (free) | 3525.57 (free) | 3525.57 (free) | 3525.57 (free) |
|            | 3476.35 (free) | 3546.11 (free) | 3546.11 (free) | 3546.11 (free) |

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Fig. 3. Contribution percentage plot of SAPT0-derived attractive energy components.
that for the latter is 3088 cm\(^{-1}\). A \(\Delta v\) value of 16 cm\(^{-1}\) suggests comparable strengths of both HBs.

3.6. \(^1\)H NMR spectroscopy

NMR spectroscopy has evolved as one of the most powerful techniques to investigate the presence of hydrogen bonding interactions [25]. It is known that when a hydrogen atom participates in hydrogen bonding its isotropic nuclear magnetic shielding constant decreases; that is, the \(^1\)H NMR signal suffers a downfield displacement. The shift of the \(^1\)H signal to higher frequencies is associated with a shortening of the HB; a shorter HB distance is indicated by larger proton deshielding [72, 73, 74]. The downfield chemical shift upon HB formation is mostly explained by the loss of electron density around the hydrogen nucleus [75, 76]. It has also been suggested that deshielding effect at the proton site arises from the electronic currents of the acceptor atom [77].

\(^1\)H NMR spectra were simulated for the optimized dimers of 1 and 2 with the dispersion-corrected functionals and def2-TZVP ECP basis set. The results are summarized in Table 6. The OH protons (H41 and H10) participating in intermolecular hydrogen bonding interactions have strong downfield signals with \(\delta\) values ranging from 11.22 to 14.88 ppm for 1D1 (H41 and H10) and 11.11 to 14.29 ppm for 2D1 (H25 and H56). The nonparticipating OH protons (H56 and H25) show upfield \(\delta\) values in between 3.18-4.28 ppm for 1D1 and 3.30-3.73 ppm (H10 and H41) for 2D1.

The chemical shifts of the NH protons participating in hydrogen bonding appeared in between 3.03-4.37 ppm for 1D2 (H12 and H43) and 3.30-5.37 ppm for 2D2 (H27 and H58). The \(\delta\) values are higher than those of the other nonparticipating NH protons. The hydrogen bonded OH protons in 1D1 and 2D1 have strongly deshielded signals compared to the signals of the participating NH protons in 1D2 and 2D2, confirming greater strength of O—H—O HBs compared to the N—H—O HBs.

All CH\(_2\) protons appeared as singlets with upfield chemical shifts below 2.00 ppm for the dimer geometries of both 1 and 2 (Fig. S5).

Experimental \(^1\)H NMR spectra of 1 and 2 were recorded in D\(_2\)O with TMS as internal standard. Two equally intense peaks of AB pattern at 3.52 and 3.58 ppm and a singlet at 3.22 ppm appeared for 1 (Fig. S5). Similar spectral feature was noted for 2 where the signal of the AB pattern appeared at 3.97 and 3.99 ppm and that for the singlet appeared at 3.22 ppm. The AB pattern and the singlet were assigned to the ring and free CH\(_3\) protons, respectively, for both 1 and 2. Due to rapid proton exchange with the deuterated solvent, no OH and NH proton signal was recorded. Thus the \(^1\)H NMR spectra recorded in solution are quite different than those recorded in gas phase.

3.7. TD-DFT study

To obtain the electronic excitation energies (\(E_{\text{exc}}\)), oscillator strengths (\(f\)) and associated orbital contributions, TD-DFT calculations were performed at singlet ground state \((S_0)\) in gas phase for the optimized dimers of 1 and 2. Spectral data have been reported in Table 7 and corresponding absorption spectra are presented in Fig. 4. The simulated spectra were generated by Gabelid 2.5.0 software [78]. Computation of UV-Vis spectra with BP86-D3 for 1D1 has shown absorption peaks \((\lambda_{\text{max}})\) at 402 and 330 nm with oscillator strengths 0.02487 and 0.02214, respectively. The peak corresponding to the highest oscillator strength appeared mainly due to the H—2—L+1 transition with \(E_{\text{exc}}\) 3.094 eV. Computation with the same functional for 2D2 yielded three absorption maxima at 404, 364 and 338 nm corresponding to the oscillator strengths 0.02197, 0.02518 and 0.02645, respectively. The peak with highest oscillator strength appeared due to the H—7—L+1 transition with \(E_{\text{exc}}\) 3.698 eV. The major transitions for 1D1 and 2D2 may be attributed to the \(\pi \rightarrow \pi^*\) electron excitation. Simulation with the other functionals resulted in different spectral patterns for 1D1 and 2D2 as can be seen in Fig. 4a. In both cases the spectral bands are blue-shifted to a in comparison to those simulated with BP86-D3 with \(\lambda_{\text{max}}\) ranging from 174-178 nm. The excitation energies are high and fall within the range 6.693-7.297 eV. Oscillator strengths are found to be the largest for \(\omega\)97X-D3 in both cases and are found to be 0.40727 and 0.38000 for 1D1 and 2D2, respectively. Relatively high intensity bands at shorter wavelengths may arise due to the \(\sigma \rightarrow \pi^*\) transitions.

TD-DFT study for 2D1 and 2D2 with BP86-D3 revealed almost identical spectral pattern (Fig. 4b) where the absorption maxima are red-shifted. In 2D1 the spectral bands are slightly blue-shifted (315 and 281 nm) than those in 2D2 (379 and 300 nm). The H—2—L+3 and H—L+7 transitions for 2D1 may be assigned to n—\(\pi^*\) and \(\pi \rightarrow \pi^*\) excitations with \(E_{\text{exc}}\) 4.015 \((f = 0.01139)\) and 4.4850 \((f = 0.02964)\) eV, respectively. Same type of excitations is seen in 2D2 with \(E_{\text{exc}}\) 3.245 \((f = 0.00370)\) and 4.270 eV \((f = 0.01552)\). The peaks originated due
to H→L+1 and H→L+7 transitions. Analysis with the other functionals for both 2D1 and 2D2 shows \( \lambda_{\text{max}} \) between 203-210 and 170-173 nm corresponding to \( n \rightarrow \pi^\ast \) and \( \pi \rightarrow \pi^\ast \) transitions, respectively.

### 3.8. Charge transfer interactions

Charge transfer (CT) interaction is regarded as the transfer of electron density from one monomer to the other monomer within a dimer upon HB formation. CT is considered as a part of the stabilization energy of intermolecular systems [79]. Transfer of charge usually takes place from the lone pair orbital of the HB acceptor atom to the antibonding \( \sigma^\ast_{D-H} \) orbital. CT interaction is enhanced by a larger orbital overlap as well as smaller energy gap. As a result of HB formation, accumulation of charge occurs in the \( \sigma^\ast_{D-H} \) orbital, thereby increasing its antibonding character. This results in weakening of the D–H bond [80, 81, 82]. CT may therefore be considered as evidence for covalent character of HBs.

To study intermolecular CT interactions, an approximate charge transfer analysis with chemist’s localized property-optimized orbitals (CLPOs) has been carried out for the dimer geometries of 1 and 2 using the JANPA package (version 2.02) [67, 83]. CLPOs are the localized orbitals portraying a Lewis structure possessing one-electron physical properties that are closest to those calculated with the true delocalized many-electron wavefunction [83]. The amount of CT was calculated using Eq. (3) [41]

\[
Q_{i \rightarrow j} = 2 \left( \frac{V_{ij}}{\epsilon_i - \epsilon_j} \right)^2
\]

where \( Q_{i \rightarrow j} \) is the charge, transferred from the \( i^{th} \) orbital of the donor to the \( j^{th} \) orbital of the acceptor, \( V_{ij} \) is the matrix element between the corresponding CLPOs and \( \epsilon_i - \epsilon_j \) is the energy difference between the donor and acceptor CLPOs in a.u.

Occupancies of donors and acceptors and the amount of CT for the hydrogen bonded dimers are listed in Table 8. Values of CT fall in the range 0.11-0.01 for all dimer geometries. Both lone pairs on the oxygen atoms of bound carboxylates are involved in CT process for 1D1 and 2D1, while for 1D2 and 2D2, CT is associated with the involvement of only one lone pair on the oxygen atoms. As given in the table, a relatively high electron density shift is observed for \( nO \rightarrow \sigma^\ast_{O-H} \) CT in 1D1 and 2D1 and the extent of CT decreases in the order BP86-D3 > M062X-D3 > \( \omega \)B97X-D3. In contrast, the \( nO \rightarrow \sigma^\ast_{N-H} \) CT involves negligible electron density shift for 1D2 and 2D2. Stronger intermolecular interactions with greater covalency are thus favored by the \( nO \rightarrow \sigma^\ast_{O-H} \) CT in 1D1 and 2D1.

### 3.9. Global reactivity descriptors

Conceptual density functional theory (CDFT), developed by R. G. Parr, is the basis for the global reactivity descriptors. These are useful parameters in understanding the global reactivity and local site selectivity, respectively. To investigate the structure-activity (QSAR),

### Table 7. Selected parameters for the vertical excitation (UV-Vis absorption) of the dimers.

| Functional | Electronic transition | \( \lambda_{\text{max}} \) (nm) | \( E_i \) (eV) | \( \lambda \) (nm) | \( f \) | Major transitions |
|------------|-----------------------|------------------|---------|---------|---------|-----------------|
| BP86-D3    | S\(_0\) → S\(_1\)     | 402              | 3.094   | 401     | 0.02467 | H→2→L+1 (93%)  |
| S\(_0\) → S\(_3\)     | 330              | 3.854            | 322     | 0.02214 | H→9→L+1 (40%) |
| S\(_0\) → S\(_{15}\)  | 340              | 3.105            | 399     | 0.02197 | H→4→L (89%)   |
| S\(_0\) → S\(_{22}\)  | 207              | 0.02518          |         |         | H→5→L (37%)   |
| S\(_0\) → S\(_{32}\)  | 238              | 3.698            | 335     | 0.02651 | H→7→L+1 (72%) |
| M062X-D3   | S\(_0\) → S\(_1\)     | 174              | 7.297   | 170     | 0.34427 | H→15→L+1 (14%) |
| S\(_0\) → S\(_{32}\)  | 210              | 5.898            | 207     | 0.03094 | H→6→L (25%)   |
| \( \omega \)B97X-D3 | S\(_0\) → S\(_1\)     | 176              | 7.130   | 174     | 0.40727 | H→23→L (25%)  |
| S\(_0\) → S\(_{22}\)  | 178              | 6.693            | 186     | 0.38007 | H→7→L+1 (18%) |

### Fig. 4. Simulated UV-Vis absorption spectra for the dimers of 1 (a) and 2 (b) in gas phase.
Table 8. Charge transfer (in e) between orbitals participating in intermolecular hydrogen bonding.

| Functional   | Donor   | Occupancy of donor | Acceptor   | Occupancy of acceptor | CT (Ql ↔ n) |
|--------------|---------|--------------------|------------|------------------------|-------------|
| BP86-D3      | n O34   | 1.7766             | n O9–H10   | 0.1396                 | 0.1125      |
| n O18        | 1.7962  | n O40–H41          | 0.1900     | 0.07793                | 0.0585      |
| M062X-D3     | n O34   | 1.8188             | n O9–H10   | 0.1075                 | 0.08305     |
| n O18        | 1.8336  | n O40–H41          | 0.0810     | 0.05612                | 0.05471     |
| αB97X-D3     | n O34   | 1.8262             | n O9–H10   | 0.0911                 | 0.06607     |
| n O18        | 1.8324  | n O40–H41          | 0.0784     | 0.05330                | 0.02007     |
| BP86-D3      | n O18   | 1.7780             | n O55–H56  | 0.1392                 | 0.11305     |
| n O34        | 1.7983  | n O24–H25          | 0.1074     | 0.07705                | 0.0523      |
| M062X-D3     | n O34   | 1.8200             | n O55–H56  | 0.1057                 | 0.08199     |
| n O34        | 1.8344  | n O24–H25          | 0.0790     | 0.05471                | 0.01035     |
| αB97X-D3     | n O18   | 1.8274             | n O55–H56  | 0.0899                 | 0.06517     |
| n O34        | 1.9612  | n O24–H25          | 0.0757     | 0.01294                | 0.0348      |

Structure-property (QSPR) and structure-toxicity (QSTR) relationships [84, 85, 86, 87, 88] quantitatively, the reactivity descriptors are used routinely.

Chemical potential (μ) and chemical hardness (η) are the first- and second-order partial derivatives, respectively, of the Kohn-Sham (KS) energy with respect to the number of particles at fixed external potential ω(r) [89, 90] as given in Eqs. (4) and (5)

\[
\mu = \left( \frac{\partial E}{\partial N} \right)_{\omega(r)}
\]

(4)

\[
\eta = \left( \frac{\partial^2 E}{\partial N^2} \right)_{\omega(r)} = \left( \frac{\partial \mu}{\partial N} \right)_{\omega(r)}
\]

(5)

where E and N are the total energy and the number of electrons in the system, respectively. Eq. (6) expresses the electronegativity of a system, proposed by Iczkowski and Margrave [91]

\[
\chi = -\left( \frac{\partial E}{\partial N} \right)_{\omega(r)}
\]

(6)

where χ is Mulliken’s electronegativity. Comparing the above relations, Parr et al. [92] suggested an important relationship between μ and χ as given in Eq. (7)

\[
\chi = -\mu = \left( \frac{\partial E}{\partial N} \right)_{\omega(r)}
\]

(7)

Thus, the electronic chemical potential of a molecule can be interpreted as the propensity of an electron charge cloud to escape from the system.

Global hardness indicates the overall stability of a system. Pearson [93] proposed the maximum hardness principle (MHP) which relates hardness to the stability of the system at a constant external potential. The concept of hardness of a species implies its resistance toward deformation. The inverse of hardness is known as softness, S, related to polarizability of a species [42] and is given by Eq. (8)

\[
S = \frac{1}{\eta} = \left( \frac{\partial N}{\partial \mu} \right)_{\omega(r)}
\]

(8)

Global electrophilicity index (ω) is another descriptor of reactivity. It is defined as the stabilization energy gained by a system after it reaches equilibrium. Eq. (9) is used to relate the global electrophilicity index of a system with its electronic chemical potential and hardness [94]

\[
\omega = \frac{\mu^2}{2\eta}
\]

(9)

The three-point finite difference approximation is used in the operational definitions to compute the reactivity parameters, μ and η can be expressed with the help of ionization potential (I) and electron affinity (A) [95] as shown in Eqs. (10) and (11)

\[
\mu = -\chi = -\frac{1}{2}(I + A)
\]

(10)

\[
\eta = (I - A)
\]

(11)

In this study, vertical ionization potential and electron affinity were calculated with the ΔSCF method using Eqs. (12) and (13)

\[
I \approx E(N - 1) - E(N)
\]

(12)

\[
A \approx E(N) - E(N + 1)
\]

(13)

Values of global reactivity descriptors for the dimer geometries of 1 and 2 are listed in Table S5. The chemical potential of any molecular system assesses the escaping tendency of the electron cloud. The higher the value of μ (less negative), the greater is the tendency of electrons to escape from the system. For 1D1 most negative value of μ has been found for the M062X-D3 functional (−5.30 eV) following the order M062X-D3 < αB97X-D3 < BP86-D3. Same trend is noticed for 1D2 where most negative value of μ has been found to be −5.15 eV for the M062X-D3 functional. Chemical potential for both 2D1 and 2D2 follows the order M062X-D3 < BP86-D3 < αB97X-D3. It is evident from the table that values of μ for D1 are more negative than those for D2 with each corresponding functional in both dimers. Chemical hardness (η) signifies the resistance offered by the electron cloud upon perturbation of chemical processes. Hard systems are relatively less polarizable. The chemical hardness follows the trend BP86-D3 < M062X-D3 < αB97X-D3 for 1D1 and BP86-D3 < M062X-D3 < αB97X-D3 for 2D1. For the dimers of 2, η follows the order BP86-D3 < M062X-D3 < αB97X-D3 for 2D1 and BP86-D3 < αB97X-D3 < M062X-D3 for 2D2. Stability of a molecule decreases with increasing global softness. Identical trends in S have been noticed for the dimers of both 1 and 2 where M062X-D3 ≈ αB97X-D3 < BP86-D3. The global electrophilicity index is considered as an indicator of the electrophilic force of a molecular system against a nucleophile. ω follows the trend αB97X-D3 < M062X-D3 < BP86-D3 for 1D1 and 1D2. Same trend has been noticed for 2D1 and 2D2. For each corresponding functional D1s appear to be more electrophilic than D2s.

3.10. Noncovalent interactions within the dimers

3.10.1. Molecular electrostatic potential (MEP) surfaces

As a first approximation to rationalize the NCIs, molecular electrostatic potential (MEP) surfaces were computed [96] for the optimized gas phase geometries of 1 and 2. MEP surfaces can be used to find suitable regions for electrophilic/nucleophilic attack on the molecular systems. MEP maps were generated for the monomer geometries computed at BP86-D3/ZORA-def2-TZVP/SARC-ZORA-TZVP level of theory and the results are shown in Fig. 5a and 5b. Red, green and blue colors on the map indicate the possible points that favor electrophilic/nucleophilic attack. The extent of MEP in decreasing order is found as blue > green > red. As expected, the most negative regions (red surface) correspond to the C=O oxygen atoms of bound carboxylates, well suited to interact with electron deficient atoms. The hydrogen atoms covalently
bonded to nitrogen and oxygen atoms are electrophilic as they have been in the electron-deficient zones indicated by blue MEP surfaces.

### 3.10.2. QTAIM topology analysis

To unravel inter- and intramolecular interactions as well as their strengths, Bader’s quantum theory of atoms-in-molecules (QTAIM) [33] has been used routinely as a conventional theoretical tool. The usage of QTAIM allows us to inspect comprehensively the electron density and associated real space functions such as the Laplacian of electron density and electron energy density at the bond critical point (BCP). Topology analysis of electron density is performed to search the critical points. The electron density, \( \rho(r) \), plays the central role at BCP. A larger value of \( \rho(r) \) at BCP corresponds to greater HB strength. Strong hydrogen bonding interactions involve appreciably greater covalent character [97] that may manifest itself in the values of \( E_{\text{min}} \), obtained from SAPT analysis [98]. The Laplacian of electron density, \( \nabla^2 \rho(r) \), at BCP is frequently used to probe the nature of the interaction [99]. A negative value of \( \nabla^2 \rho(r) \) generally implies that the interaction is predominantly covalent in origin while a positive value indicates the noncovalent nature of the interaction. The ratio of absolute potential energy density, \( V(r) \), to the Lagrangian kinetic energy density, \( G(r) \), at BCP is also a useful parameter to characterize the type of interactions. Magnitudes of \( \frac{|V(r)|}{G(r)} \) less than 1 correspond to closed-shell interactions. Intermediate interactions are suggested for \( 1 < \frac{|V(r)|}{G(r)} < 2 \). When \( \frac{|V(r)|}{G(r)} > 2 \), the interactions are covalent [100]. Accordingly, \( \frac{|V(r)|}{G(r)} \) may be treated as a useful parameter to ascertain the nature of HBs.

Table 9 presents the QTAIM parameters for the dimer geometries of 1 and 2. The Poincaré-Hopf relationship was satisfied, indicating that all CPs had been found. The distribution of CPs and bond paths for the self-assembled dimers of 2 are shown in Fig. 6. Largest values of \( \rho(r) \) were found for 1D1 and 2D1 optimized with BP86-D3, implying strongest O—H—O interactions (Fig. 6a). For all the dimers V\(^2\)\(\rho(r)\) at O—H BCPs is positive, which indicates that the O—H contacts do not correspond to typical covalent bonds [1]. However, the negative values of total electron density energy \( |H(r)| \) imply partially covalent interactions. Largest negative values of \( H(r) \) have been found for 1D1\(_{\text{BP86-D3}}\) and 2D1\(_{\text{BP86-D3}}\) confirming maximum covalency within the \( H—O \) interactions. Values of \( \rho(r) \) for the geometries of both 1D2 and 2D2 are much smaller than those computed for 1D1 and 2D1. This is in line with the long N—O and H—O distances in 1D2 and 2D2 (Table 2) where positive values of both \( V^2\rho(r) \) and \( H(r) \) at BCPs suggest weak and electrostatic H—O interactions [101]. The nature of interaction in each dimer geometry corroborates the magnitude of \( \frac{|V^2\rho(r)|}{G(r)} \) (Table 9).

Apart from N—H—O HBs, O—O intermolecular interactions have been noticed (Fig. 6b) as indicated by a bond path with \( V^2\rho(r) \) and \( H(r) \) 0.027 e/Å\(^3\) and 0.002 hartree/Å\(^3\), respectively, in 1D2 \( \rho(r) = 0.006 \) e/Å\(^3\) for O49—O50 and 0.030 e/Å\(^3\) and 0.002 hartree/Å\(^3\), respectively, in 2D2 \( \rho(r) = 0.007 \) e/Å\(^3\) for O23—O34). Positive values of these parameters affirm very weak electrostatic interactions prevailing in the O—O contacts.

Table 9. Topological parameters and hydrogen bond energies obtained at the critical points for the dimer geometries.

| Functional Interaction | 1D1 | 1D2 |
|------------------------|-----|-----|
| \( \rho(r) \) (e/Å\(^3\)) | V\(^2\)\(\rho(r)\) (e/Å\(^6\)) | H(r) (hartree/Å\(^3\)) | G(r) (hartree/Å\(^3\)) | \( |\nabla^2 \rho(r)| \) (hartree/Å\(^6\)) | \( \frac{|V^2\rho(r)|}{G(r)} \) | E\(_{\text{H}}\) (kcal/mol) |
|------------------------|-----|-----|
| BP86-D3 | O34—H10 | 0.088 | 0.101 | -0.036 | 0.061 | 0.098 | 1.61 | -18.89 | 0.078 | 0.000 | 0.001 | 0.022 | -0.021 | 0.95 | -5.50 |
| BP86-D3 | O18—H41 | 0.069 | 0.109 | -0.023 | 0.050 | 0.073 | 1.46 | -14.65 | 0.035 | 0.107 | -0.001 | 0.028 | -0.029 | 1.04 | -7.07 |
| BP86-D3 | O34—H10 | 0.076 | 0.119 | -0.030 | 0.059 | 0.089 | 1.51 | -16.21 | 0.020 | 0.082 | 0.003 | 0.018 | -0.015 | 0.83 | -7.62 |
| BP86-D3 | O18—H41 | 0.058 | 0.120 | -0.017 | 0.047 | -0.064 | 1.36 | -12.20 | 0.025 | 0.100 | 0.002 | 0.023 | -0.020 | 0.87 | -4.83 |
| aB97X-D3 | O34—H10 | 0.064 | 0.128 | -0.019 | 0.051 | -0.071 | 1.39 | -13.53 | 0.028 | 0.098 | 0.001 | 0.024 | -0.023 | 0.96 | -5.50 |
| aB97X-D3 | O18—H41 | 0.055 | 0.122 | -0.014 | 0.044 | -0.058 | 1.32 | -11.53 | 0.034 | 0.106 | 0.002 | 0.025 | -0.023 | 0.92 | -5.50 |

Fig. 5. Molecular electrostatic potential surface and color scheme for 1 (a) and 2 (b).
To probe the strength of the HBs in the dimers of 1 and 2, the HB binding energy \( E_{\text{HB}} \) was calculated using Eq. (14) [102] applicable for neutral HBs

\[
E_{\text{HB}} = -223.08 \times \rho(r)_{\text{HCP}} + 0.7423
\]

(14)

where the unit of \( E_{\text{HB}} \) is expressed in kcal/mol. Table 9 reveals that the O—H—O HBs in 1D1 and 2D1 enjoy maximum binding energy compared to the N—H—O HBs in 1D2 and 2D2. In 1D1s the values for \( E_{\text{HB}} \) decrease (including sign) in the order BP86-D3 > M062X-D3 > oB97X-D3 while those for 2D2s decrease (including sign) as BP86-D3 > oB97X-D3 > M062X-D3. The regression plot of \( E_{\text{HB}} \) versus \( d(O-H) \) for the entire set has been shown in Fig. 7. In this case a second-order polynomial fit has been used since it offers much better fitting quality compared to the linear fit. The plot exhibits a good correlation with \( R^2 = 0.995 \).

### 3.10.3. Reduced density gradient

NCIs have a unique signature and their presence can be revealed solely from the electron density. To investigate different types of NCIs in real space, the reduced density gradient (RDG) method [34, 103] has been applied. RDG, a fundamental dimensionless function of the electron density gradient norm, is used to describe the deviation from a homogeneous electron distribution within the framework of DFT. RDG \( S \), obtained from the density and its first derivative, is expressed by Eq. (15)

\[
S = \frac{1}{2 (3\pi^2)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{2/3}}
\]

(15)

Fig. 8 shows the color-mapped isosurfaces and corresponding scatter graphs for the dimers of 1 and 2. Sign(\( \lambda_2 \))\( \rho(r) \) is the electron density multiplied by the sign of the second largest eigenvalue of the Hessian matrix \( (\lambda_2) \). It is a useful quantity to predict the nature of interaction. Attractive interactions such as hydrogen bonding are indicated by large and negative sign(\( \lambda_2 \))\( \rho(r) \), while repulsive interactions (steric effect) are indicated by large and positive sign(\( \lambda_2 \))\( \rho(r) \). Values of sign(\( \lambda_2 \))\( \rho(r) \) very close to zero suggest weak van der Waals interactions. In the visualization of NCI isosurfaces the color-coding scheme is as follows: blue for attractive, red for repulsive and green for intermediate interactions. The darker the color, the stronger is the interaction.

NCI-RDG analysis was performed on the dimer geometries of both 1 and 2, computed at the BP86-D3/ZORA-def2-TZVP/SARC-ZORA-TZVP level of theory. In the RDG isosurface map of 1D1 (Fig. 8a), the green and red regions indicate the presence of weak van der Waals and steric interactions, respectively. In addition, the blue elliptical slabs suggest the presence of intermolecular HBs. Deep blue isosurfaces confirm strong nature of O9—H10—O34 and O40—H41—O18 HBs. A very small blue region indicates weak N11—H12—O8 HB. Steric effects are located within the chelate rings in both monomers as shown by red isosurfaces. Similar is the observation for 2D1. Wide green isosurfaces in 1D2 and 2D2 (Fig. 8b and 8c) indicate van der Waals interactions. Steric interactions are noted within the chelate rings as shown by red isosurfaces. The small blue regions correspond to N—H—O HBs.
Characteristics of various types of regions are also expressed by the scatter graphs where \(\text{sign}(\lambda_2)\rho(r)\) ranges from \(-0.05\) to \(0.05\) a.u. In 1D1 the spike on the left shows the negative \(\text{sign}(\lambda_2)\rho\) value 0.029 a.u. corresponding to N11—H12—O8 intramolecular HB. The green and red spikes characterize the van der Waals and steric interactions, respectively (Fig. 8d). N—H—O HBs are indicated by the spikes at the negative regions of \(\text{sign}(\lambda_2)\rho(r)\) in 1D2 and 2D2. Spikes at \(\rho(r)\) critical values 0.028 and 0.035 a.u. correspond to N11—H12—O49 and N42—H43—O3 HBs, respectively, in 1D2 (Fig. 8e) while the spikes at \(\rho(r)\) critical values 0.036 and 0.031 a.u. correspond to N26—H27—O33 and N57—H58—O18 HBs, respectively, in 2D2 (Fig. 8f). Green and red spikes appeared in the scatter graphs for both dimers. The results of NCI-RDG analysis are consistent with those obtained from Bader's topology analysis discussed in Section 3.10.2.

3.10.4. Independent gradient model (based on promolecular density)

IGM is a recent electron density-based computational method [35] that enables us to detect intermolecular interactions using promolecular density (frozen electron density) in real space. Like RDG, IGM is also associated with the electron density gradient and confers a new descriptor \(\delta g\) that locally accounts for the difference between a virtual upper limit of the electron density gradient \(|\nabla \rho(r)|_{\text{IGM}}\) and the true electron density gradient, \(|\nabla \rho(r)|\), as given in Eq. (16)

\[
\delta g = |\nabla \rho(r)|_{\text{IGM}} - |\nabla \rho(r)|
\]  

(16)
Thus, the signature of interactions between two molecular fragments ($\delta_{\text{inter}}$) can easily be found out with the help of $\delta g$. The $\delta_{\text{inter}}$ description has been used in this work since we are interested in intermolecular interactions.

To identify and quantify the noncovalent interactions, the IGM plot [36], an improved NCI plot tool, has been used. Fig. 9 reveals the intermolecular interactions in the dimers of 1 and 2. The $\delta_{\text{inter}}$ function outlines two strong O–H–O HBs in both 1D1 and 2D1 as shown by the blue isosurfaces (Fig. 9a and 9c). A deep blue isosurface corresponds to strong attractive interaction. A green isosurface is also noticed in between the monomers, indicating weak van der Waals interaction. IGM plots for 1D2 and 2D2 (Fig. 9b and 9d) feature more combined interactions where both hydrogen bonding and van der Waals interactions are prominent. In addition to two N–H–O HBs, weak C–H–O HBs are noticed which are characterized by green color with small IGM surfaces. In 2D2 the small light blue isosurface on the C–H–O bond path corresponds to relatively greater HB strength than that in 1D2. All these findings corroborated the QTAIM topology analysis mentioned in Section 3.10.2.

### 3.10.5. Extended transition state-natural orbitals for chemical valence (ETS-NOCV)

By charge and energy decomposition based on the Kohn-Sham model, the ETS-NOCV scheme allows us to gain a thorough understanding about the intermolecular interactions. The ETS scheme [104, 105] and NOCV theory [106] are combined in the ETS-NOCV approach [40]. Within the ETS scheme, total interaction energy ($\Delta E_{\text{total}}$) of the interacting fragments can be decomposed into the following components as given in Eq. (17)

$$\Delta E_{\text{total}} = \Delta E_{\text{dist}} + \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}}$$  (17)

$\Delta E_{\text{orb}}$ signifies the stabilizing interactions between filled MOs of one fragment with the empty MOs of the other, together with intrafragment polarization. The $\Delta E_{\text{orb}}$ term is expressed according to Eq. (18) [104, 105] as

$$\Delta E_{\text{orb}} = \sum_{\mu} \sum_{\lambda} \Delta P_{\mu\lambda} F_{\lambda\mu}^{TS}$$  (18)

where $\Delta P$ is the deformation density matrix and $F_{\mu\lambda}^{TS}$ is the diagonal Kohn-Sham Fock matrix element, interpreted in terms of a transition state potential that lies halfway between that of the assembled fragments and the complete molecule.

Diagonalization of the electron density deformation matrix is performed by NOCV. The complementary eigenfunctions $\psi_{-k}$ and $\psi_{k}$, also called the NOCV pair, decompose the deformation density $\Delta \rho(r)$ into NOCV contributions ($\Delta \rho_k$) as shown in Eq. (19) [40, 107]

$$\Delta \rho(r) = \sum_{k=1}^{M/2} \lambda_k \left[ \psi_{-k}^2(r) + \psi_{k}^2(r) \right] = \sum_{k=1}^{M/2} \Delta \rho_k(r)$$  (19)

where NOCV eigenvalues and the number of basis functions are designated by $\lambda_k$ and $M$, respectively.

The eigenvalues of NOCV are used to express the $\Delta E_{\text{orb}}$ component of ETS mathematically, [Eq. (20)] following the combined ETS-NOCV approach [40].
Estimations of $\Delta \rho_k$ in terms of energy are obtained from $\Delta E_{\text{orb}}(k)$, which is extremely important in understanding the characteristics of hydrogen bonding interactions between two molecular units.

All calculations were performed by ORCA Program Version 5.0.2 computational package \[43\]. The results unveiled the presence of intermolecular HBs as shown in Fig. 10. Accumulation and depletion of electron density are indicated by green and blue isosurfaces, respectively. The isosurface maps show that orbital interaction effect is responsible for discernible concentration of electron density between hydrogen and the acceptor atom, thus confirming the presence of O—H—O HBs in 1D1 and 2D1 (Fig. 10a and 10b) and N—H—O HBs in 1D2 and 2D2 (Fig. 10c and 10d). Strengths of the HBs are reflected in corresponding $\Delta E_{\text{orb}}(k)$ values. Table 10 displays significant values of $\Delta E_{\text{orb}}(k)$ and their contribution to total orbital energy ($\Delta E_{\text{orb}}$) for the dimer geometries of both 1 and 2 computed with different functionals and ZORA-def2-TZVP/SARC-ZORA-TZVP basis sets. From the table it is evident that O9—H10—O34 and O40—H41—O18 HBs in 1D1 and O24—H25—O34 and O55—H56—O18 HBs in 2D1 are the core contributors to $\Delta E_{\text{orb}}$. In both cases largest negative values of $\Delta E_{\text{orb}}(k)$ have been found for 1D1$_{\text{PR6-D3}}$ and 2D1$_{\text{PR6-D3}}$. Values of $\Delta E_{\text{orb}}(k)$ for N11—H12—O49 and N42—H43—O3 HBs in 1D2 and N57—H58—O18 and N26—H27—O33 (O34 for the geometries computed with M062X-D3 and aB97X-D3) in 2D2 are much higher (less negative) than those of the O—H—O HBs in 1D1 and 2D1.

Orbital interactions from the ETS-NOCV scheme are more favorable than the induction interactions in SAPT0 (Table 4). Because of the differences in methodologies, the energies cannot be compared quantitatively. However, values of $\Delta E_{\text{orb}}$ are in good qualitative agreement with those of $\varepsilon_{\text{orb}}$ for corresponding geometries. Comparable relative trends of these energy parameters have been observed as given in Fig. 11.

Regression plots of $\Delta E_{\text{orb}}(k)$ versus O—H distances and $\rho(r)$ at BCP are sketched in Figure S7. The plots clearly indicate the dependence of $\Delta E_{\text{orb}}(k)$ on these parameters. Satisfactory correlations have been obtained with R$^2$ 0.960 and 0.971, respectively.

3.10.6. Electron localization function

To identify the essential fingerprints for hydrogen bonding interactions and to probe the dependence of such interactions on intermolecular distances, the electron localization function (ELF), proposed by Becke and Edgecombe \[37\], has proved to be an extremely valuable tool. To study different hydrogen bonded complexes in gas phase \[108, 109\], this method has been successfully applied. ELF furnishes an orbital independent description of electron localization. Topological analysis of the ELF gradient field renders basins which partition the molecular space exhibiting the chemical pictures of lone or bonded electron pairs. Expression of the dimensionless scalar ELF, $\eta(r)$, is given in Eq. (21)

$$
\eta(r) = (1 + [(T - T_W)/T_F]^2)^{-1}
$$

where $T$ is the kinetic energy computed with the MOs. $T_W$ and $T_F$ are the von Weizsäcker and Thomas-Fermi kinetic energy functionals, respectively \[90\]. The domain of ELF is $0 \leq \eta(r) \leq 1$ as the above equation is of Lorentzian type. $\eta(r)$ highlights the distinct environment around the atoms participating in hydrogen bonding.

Shaded surface maps with projection effect and the contours of ELF for 1D1 and 1D2 have been shown in Fig. 12 where the ELF patterns exhibit intermolecular hydrogen bonding between the monomers. In 1D1 the nonbonding attractors of O34 are pointed towards the ELF holes in the electron shell of H10 (Fig. 12a), thereby favoring strong intermolecular HB. Similarly, the nonbonding attractors in the valence shell of O18 are pointed towards the ELF holes in the electron shell of H41 (Fig. 12b). Thus, the monomers are associated through intermolecular HBs to form a cyclic dimer. On the other hand, the nonbonding attractors of O49 and O3 are projected inefficiently at the ELF holes in the electron shells of H12 and H43, respectively, in 1D2. This results in the weakening of N—H—O HBs (Fig. 12c and 12d).
Table 10. Orbital interaction energies (in kcal/mol) calculated at different DFT levels and ZORA-def2-TZVP/SARC-ZORA-TZVP basis sets.

| Geometry   | Interacting atoms | \(\Delta E_{\text{orb}}(\text{kcal/mol})\) | \(\Delta E_{\text{ind}}(\text{kcal/mol})\) | Contribution of \(\Delta E_{\text{orb}}(\text{kcal/mol})\) to \(\Delta E_{\text{ind}}(\text{kcal/mol})\) |
|------------|-------------------|----------------------------------------|------------------------------------------|------------------------------------------------------------------|
| 1D1_{BP86-D3} | H10—O34           | -21.75                                 | -50.84                                   | 42.78                                                            |
| 1D1_{BP86-D3} | H41—O18           | -15.47                                 | 30.43                                    | 0.50                                                            |
| 2D1_{BP86-D3} | H25—O34           | -15.20                                 | -50.18                                   | 30.29                                                           |
| 2D1_{BP86-D3} | H56—O18           | -21.58                                 | 43.01                                    | 53.86                                                           |

4. Conclusion

The present work has addressed a detailed study on the structural and electronic properties and noncovalent interactions within the self-assembled cyclic dimers of two square planar Pd(II) and Pt(II) complexes, trans-[Pd(Hida)_2] (1) and trans-[Pt(Hida)_2] (2). Initial geometries of the dimers in different orientations were extracted from X-ray crystal structures and optimized with BP86-D3, M062X-D3 and oB97XD3 functionals and ZORA-def2-TZVP/SARC-ZORA-TZVP basis sets. To probe the nature and strength of interactions between the monomers within the dimers, interaction energies were computed according to supermolecular and SAPT concept. In both methods largest negative values of interaction energy were obtained for the geometries computed with BP86-D3. SAPT0 analysis revealed that electrostatic and induction forces play the major role to stabilize 1D1 and 2D1 while electrostatic and dispersion forces are the predominant factors for the stability of 1D2 and 2D2. Intermolecular interactions have been characterized by QTAIM and ETS-NOCV methods. Largest negative values of HB binding and orbital energies were obtained for the geometries computed with BP86-D3. NCI-RDG and IGM analyses confirmed the presence of hydrogen bonds and weak van der Waals interactions within the dimers. The observations of the NCI studies are in well accord with the SAPT0 and ETS-NOCV results. Essential fingerprints of hydrogen bond were located by The ELF method. CDFT was applied to delineate the global reactivity of all dimer geometries.

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Data will be made available on request.

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Fig. 12. Shaded surface maps with projection effect and corresponding electron localization functions for H10—O34 (a), H41—O18 (b) in 1D1 and H12—O49 (c), H43—O3 (d) in 1D2 (equilibrium geometries were computed at BP86-D3/ZORA-def2-TZVP/SARC-ZORA-TZVP level).

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