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Hydrogen Bonding in Substituted Formic Acid Dimers

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The hydrogen-bonded dimers of formic acid derivatives XCOOH (X = H, F, Cl, and CH_3) have been investigated using density functional theory (B3LYP) and second-order Møller−Plesset perturbation (MP2) methods, with the geometry optimization carried out using 6-311++G(2d,2p) basis set. The dimerization energies calculated using aug-cc-pVXZ (with X = D and T) basis have been extrapolated to infinite basis set limit using the standard methodology. The results indicate that the fluorine-substituted formic acid dimer is the most stable one in comparison to the others. Topological analysis carried out using Bader's atoms in molecules (AIM) theory shows good correlation of the values of electron density and its Laplacian at the bond critical points (BCP) with the hydrogen bond length in the dimers. Natural bond orbital (NBO) analysis carried out to study the charge transfer from the proton acceptor to the antibonding orbital of the X−H bond in the complexes reveals that most of the dimers are associated with conventional H-bonding except a few, where improper blue-shifting hydrogen bonds are found to be present.

1. Introduction

Hydrogen bonding has been one of the most interesting areas of research mainly due to its vital role in many chemical and biological processes.[1−3] During the past few decades, a large number of experimental and theoretical studies have been devoted to the elucidation of structures where intra- and intermolecular hydrogen bonding plays a crucial role in determining the stability of the molecular systems. The hydrogen bonds are conventionally shown as A−H···B where the H atom is shared between A and B atoms. Usually A is an electronegative atom and B is either an electronegative atom having one or more lone electron pairs or a region of excess electron density such as aromatic π-systems. In a normal hydrogen bond, there is significant charge transfer from the proton acceptor B to the proton donor (A−H), resulting in a weakening of the A−H bond leading to bond elongation and a consequent decrease of the A−H stretching vibration frequency. This red shift in A−H stretching vibration, which is often of the order of several tens of wavenumbers, is usually considered to be the most important and easily detectable manifestation of the formation of an H-bond, even in an O−H···O system.[4,5]

The scenario is, however, different in the case of a C−H···O hydrogen bond,[6] which is relatively weak and is also associated with a blue-shift[7,8] of the C−H stretching frequency instead of the commonly observed red shift discussed above. Widespread appearance of the weak C−H···O hydrogen bond,[6] and its importance in biological structures has resulted into increasing interest in the investigation of its properties. Reasonable rationalization of the C−H bond shortening and the consequent blue-shift of the C−H stretching frequency has been provided by Hobza et al.,[9] and Kolandaivel et al.[10] Unlike in a red-shifting hydrogen bond, where considerable charge transfer occurs from B to the antibonding σ* orbital of the A−H bond resulting into lengthening of this bond, in a blue-shifting hydrogen bond only a small amount of electron density goes to the σ* antibonding orbital of the C−H bond of the proton donor with the larger portion transferred to its remote (nonparticipating) part. The consequent structural reorganization of the proton donor leads to contraction of the C−H bond. Investigations involving the electron density reorganization can thus shed light and provide insight into the formation of this type of hydrogen bond. The objective of this work is to employ the well-known density based theory of atoms in molecules (AIM) of Bader for an understanding of this type of C−H···O hydrogen bonds. As illustrative examples, we have chosen a few systems that are of importance in atmospheric chemistry.

Formic acid is the simplest carboxylic acid, which is a major constituent of cloud and fogwater. The nature of hydrogen bonding between formic acid and water has thus been a key area of research[11−16] for a long time, leading to many theoretical and experimental studies on the subject. Recently several studies[17−19] have been devoted to formic acid dimers involving the weak C−H···O hydrogen bonds. However, only one structure for the dimer has been considered,[18] and also, halogen-substituted formic acid dimers have not been investigated in the literature. Since halogen compounds are known to be atmospheric pollutants[20,21] having the ability to form hydrogen bond, it would be interesting to study the nature of the hydrogen bond formed in formic acid dimers in which H is replaced by halogen. It is also important to note that both halogens and formic acid are constituents of the atmosphere.

There has been considerable recent interest in complete basis limit (CBS) methods to study the interaction energies of the hydrogen-bonded systems.[19] In the present study, we have obtained results for interaction energies of the hydrogen-bonded formic acid dimers by employing separate extrapolation of Hartree−Fock and correlation[22] energies, which is called[23] the

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infinite basis (IB) method, to obtain the infinite-basis MP2 limits. For this we employ the aug-cc-pVDZ and aug-cc-pVTZ basis sets with the MP2 part. The theoretical background for the calculations is presented in section 2.

In the present study, an analysis of hydrogen bonds formed in dimers of substituted formic acids XCOOH (X = H, F, Cl, CH_3) is carried out using quantum chemical methods. Systems with both types of hydrogen bonds (conventional X−H···X as well as nonconventional C−H···O bonds) are considered in order to obtain a detailed insight through a comparison of the two.

2. Computational Details

The geometry optimization of the structures has been carried out by using density functional theory (DFT) with B3LYP form of the exchange−correlation functional[24,25] as well as MP2 theory using 6-311++G(2d,2p) basis set. The interaction energies for the optimized complexes were corrected for the basis set superposition errors (BSSE), which were estimated using the counterpoise method of Boys and Bernardi.[26] IB extrapolated interaction energies were calculated using MP2/6-311++G(2d,2p) optimized geometries with aug-cc-pVDZ and aug-cc-pVTZ basis sets. The equations used[22] for calculating IB energies are discussed here. The total energy is a sum of HF and correlation components:

$$E^{\text{tot}} = E^{\text{HF}} + E^{\text{cor}} \tag{1}$$

The components of the energy are assumed to approach their basis set limits by power laws:

$$E_X{}^{\text{HF}} = E_\infty{}^{\text{HF}} + A^{\text{HF}} X^{-\alpha} \tag{2}$$

and

$$E_X{}^{\text{cor}} = E_\infty{}^{\text{cor}} + A^{\text{cor}} X^{-\beta} \tag{3}$$

Here $X = 2$ for the aug-cc-pVDZ basis and $X = 3$ for the aug-cc-pVTZ basis. Then the basis set limit for the total energy is obtained by

$$E_\infty{}^{\text{tot}} = E_\infty{}^{\text{HF}} + E_\infty{}^{\text{cor}} \tag{4}$$

Combining these equations yields

$$E_\infty{}^{\text{tot}} = \frac{3^\alpha}{3^\alpha - 2^\alpha} E_3{}^{\text{HF}} - \frac{2^\alpha}{3^\alpha - 2^\alpha} E_2{}^{\text{HF}} + \frac{3^\beta}{3^\beta - 2^\beta} E_3{}^{\text{cor}} - \frac{2^\beta}{3^\beta - 2^\beta} E_2{}^{\text{cor}} \tag{5}$$

(where $\alpha = 4.93$ and $\beta = 2.13$ from ref 19). Topological analysis was carried out using MP2 and B3LYP wave function files in Morphy 98 software.[27] The natural bond orbital (NBO) analysis has been carried out for the optimized structure at MP2 level using the same basis set by NBO 3.1 program.[28] All these calculations have been performed using the Gaussian 98W program.[29]

3. Results and Discussion

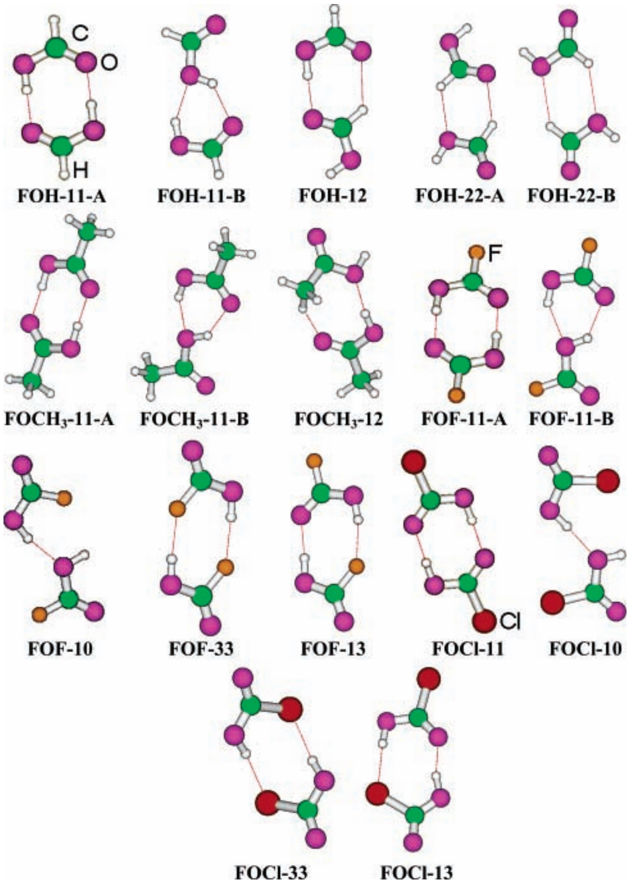

Figure 1. Optimized structures of the hydrogen-bonded formic acid dimer complexes considered in the present work. The correspondence between color and atom is as follows. Green: carbon atom. Purple: oxygen atom. Red: chlorine atom. Golden yellow: fluorine atom. White: hydrogen atom.

The search for minimum energy structures within the potential energy surface of the substituted formic acid dimers $(XCOOH)_2$ has led to 17 structures, five each for X = H and X = F, four for X = Cl, and three for X = CH_3. The optimized (with energy corresponding to global minimum or local minimum in its close neighborhood) structures of all these dimers are shown in Figure 1, while the corresponding interaction energies are reported in Table 1. The structures in this study are labeled with a common name FOX-*nn′* where FO stands for formic acid and X is the substituent as mentioned above. Here *n* and *n′* each has the value 1, 2, or 3 depending on the nature of hydrogen bond present in the structure viz., 0 means no H-bond, 1 means O−H···O type H-bond, 2 corresponds to C−H···O type H-bond, 3 indicates O−H···X type H-bond. The value of *n′* as zero indicates that there is only one H-bond and its type is indicated by the value of *n*. For example FOH-11 means two O−H···O hydrogen bonds between two simple formic acid molecules. Also, the structures with similar bonds but comparable energies have been distinguished with the letters A and B.

On surveying the structure of the dimers, it is found that most of the dimers have correspondence with the other dimers due to a similar type of hydrogen bonding. The dimer FOH-11-(A,B) is related to $FOCH_3$-11, FOF-11(A,B), FOCl-11, all of them having two O−H···O hydrogen bonds. $FOCH_3$-12 is related to FOH-12, both having one O−H···O and one C−H···O hydrogen bonds. The dimer FOCl-10 is related to FOF-10, with one O−H···O hydrogen bond. The dimer FOCl-33 is related to FOF-33, with two O−H···X hydrogen bonds. Further FOCl-13 is related to FOF-13 with one O−H···O hydrogen bond and one O−H···X hydrogen bond. The dimer FOH-22(A,B) is a unique dimer having two C−H···O hydrogen bonds. It is observed that most of the dimers are formed through O−H···O type hydrogen bonds, and only a few involve one or two C−H···O and O−H···X bonds. From

TABLE 1: Calculated Interaction Energies (kcal/mol) for the Substituted Formic Acid Dimers

	interaction energy					
system	$\Delta E_{\mathrm{B3LYP}}$[a]	ΔE_{MP2}[a]	$\Delta E_{\mathrm{PVDZ(MP2)}}$[b]	$\Delta E_{\mathrm{PVTZ(MP2}}$[b]	$\Delta E_{\mathrm{IB(HF)}}$[c]	$\Delta E_{\mathrm{IB(MP2)}}$[c]
FOH-11-A	−17.79	−15.92	−16.44	−16.75	−12.11	−17.05
FOH-11-B	−6.71	−6.84	−8.08	−8.11	−4.73	−8.27
FOH-12	−9.15	−8.87	−10.21	−10.18	−7.64	−10.35
FOH-22-A	−2.20	−2.83	−3.92	−3.76	−1.89	−3.88
FOH-22-B	−1.17	−1.98	−2.91	−2.58	−0.90	−1.84
FOCH$_3$-11-A	−18.53	−16.66	−17.18	−17.38	−12.43	−17.57
FOCH$_3$-11-B	−6.93	−7.15	−8.63	−8.53	−4.69	−8.59
FOCH$_3$-12	−4.97	−5.68	−7.39	−7.08	−3.19	−7.03
FOF-11-A	−19.23	−16.96	−17.31	−17.79	−13.51	−18.12
FOF-11-B	−7.14	−7.07	−8.52	−8.51	−5.02	−8.66
FOF-10	−3.77	−4.25	−4.18	−3.65	0.79	−3.58
FOF-33	−4.53	−4.56	−3.15	−1.91	5.31	−1.68
FOF-13	−11.29	−10.26	−9.89	−9.41	−3.69	−9.43
FOCl-11	−16.50	−15.09	−16.14	−16.57	−11.65	−16.89
FOCl-10	−3.72	−4.64	−5.40	−5.06	0.09	−5.09
FOCl-33	−3.58	−4.01	−3.84	−3.68	6.26	−3.89
FOCl-13	−10.52	−9.73	−9.57	−9.76	−2.84	−10.02

[a] BSSE-corrected interaction energies using B3LYP/6-311++G(2d,2p) and MP2/6-311++G(2d,2p) methods. [b] Interaction energies calculated using MP2/aug-cc-pVDZ//B3LYP/6-311++G(2d,2p) and MP2/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) methods. [c] Interaction energies extrapolated to infinite basis set using HF and MP2 methods and eq 5.

TABLE 2: Optimized Bond Length *R* (Å), Occupation Number of Lone Pair in the Proton Acceptor X, Occupation Number of σ*(H−Y) Involved in Hydrogen Bonds, and the Corresponding Stabilization Energies (kcal/mol), Where X = O, C and Y = O, Cl, F

		R (Å)		*N*(X)		*N*[σ*(H-Y)]		$E^{(2)}$	
system	bond	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
FOH-11-A	O−H···O	1.671	1.687	1.8454	1.8846	0.0702	0.0472	20.20	20.97
	O−H···O	1.671	1.687	1.8454	1.8846	0.0702	0.0472	20.20	20.97
FOH-11-B	O−H···O	2.035	1.981	1.9710	1.9780	0.0217	0.0139	3.80	4.80
	O−H···O	1.934	1.939	1.8473	1.8871	0.0344	0.0207	5.99	5.82
FOH-12	O−H···O	1.780	1.779	1.8466	1.8856	0.0487	0.0331	12.90	14.08
	C−H···O	2.377	2.344	1.8540	1.8910	0.0565	0.0437	0.92	1.05
FOH-22-A	C−H···O	2.447	2.412	1.8460	1.8862	0.0617	0.0477	1.15	1.04
	C−H···O	2.699	2.529	1.9806	1.9848	0.0634	0.0489	0.57	0.83
FOH-22-B	C−H···O	2.682	2.533	1.9797	1.9841	0.0636	0.0492	0.78	1.08
	C−H···O	2.682	2.532	1.9797	1.9841	0.0636	0.0492	0.78	1.08
FOCH$_3$-1 1-A	O−H···O	1.66	1.676	1.8528	1.8897	0.0707	0.0486	21.88	23.31
	O−H···O	1.66	1.676	1.8528	1.8897	0.0707	0.0486	21.88	23.29
FOCH$_3$-1 1-B	O−H···O	1.93	1.918	1.8573	1.8941	0.0328	0.0211	6.34	6.55
	O−H···O	2.00	1.940	1.9685	1.9753	0.0212	0.0143	4.35	5.68
FOCH$_3$-1 2	O−H···O	1.94	1.895	1.9688	1.9749	0.0273	0.0192	6.09	8.11
	C−H···O	2.41	2.346	1.8597	1.8953	0.0093	0.0062	1.06	1.00
FOF-11-A	O−H···O	1.648	1.666	1.8195	1.8620	0.0646	0.0432	21.08	21.05
	O−H···O	1.648	1.666	1.8195	1.8620	0.0646	0.0432	21.08	21.05
FOF-11-B	O−H···O	2.025	1.974	1.9668	1.9743	0.0150	0.0098	3.76	4.68
	O−H···O	1.893	1.913	1.8200	1.8622	0.0275	0.0159	6.86	6.18
FOF-10	O−H···O	1.955	1.909	1.9660	1.9731	0.0199	0.0134	6.10	7.75
FOF-33	O−H···F	1.929	1.910	1.9700	1.9778	0.0180	0.0110	3.58	3.74
	O−H···F	1.928	1.910	1.9700	1.9778	0.0180	0.0110	3.57	3.74
FOF-13	O−H···O	1.712	1.726	1.8214	1.8628	0.0505	0.0331	13.87	13.70
	O−H···F	1.849	1.857	1.9682	1.9773	0.0218	0.0130	5.93	5.65
FOCl-11	O−H···O	1.677	1.684	1.8016	1.8550	0.0645	0.0457	18.00	19.82
	O−H···O	1.677	1.684	1.8016	1.8550	0.0645	0.0457	18.00	19.82
FOCl-10	O−H···O	1.927	1.873	1.9646	1.9714	0.0243	0.0172	7.47	10.03
FOCl-33	O−H···C l	2.302	2.247	1.9243	1.9374	0.0374	0.0287	4.51	8.73
	O−H···C l	2.302	2.247	1.9243	1.9374	0.0374	0.0287	4.51	8.73
FOC1-13	O−H···O	1.710	1.716	1.8034	1.8570	0.0535	0.0360	13.46	14.38
	O−H···C l	2.229	2.209	1.9457	1.9583	0.0485	0.0342	11.60	14.16

the calculated hydrogen bond lengths presented in Table 2, it is observed that for the O−H···O type interaction, these values vary from 1.64 to 2.04 Å for B3LYP and 1.66 to1.98 Å for MP2 levels of theory, while the values for the C−H···O interaction, however, range between 2.3 and 2.7 Å. The shortest hydrogen bond length was found in the FOF-11 structure with the next larger one in FOCH$_3$-11, the hydrogen bonds in both cases being of O−H···O type which are known to be stronger hydrogen bonds.

The calculated interaction energies (BSSE-corrected and IB-extrapolated) are presented in Table 1, which shows that the fluorine-substituted dimer (FOF-11-A) is associated with maximum interaction energy that is due to the presence of the two strongest O−H···O type bonds in the structure. The other dimers that follow in their relative order of stability are the methyl (FOCH$_3$-11-A), hydrogen (FOH-11-A), and chlorine (FOCl-11) substituted ones which also have two O−H···O type bonds in them. Among the fluorine-substituted dimers, it is only FOF-11-A which is found to have a large interaction energy as compared to the others. This strong bonding is also reflected in the values of the H-bond length, which is small (1.65 Å and 1.66 Å from B3LYP and MP2 levels of theory, respectively).

The order of stability among the other dimers, viz. FOF-11-A > $FOCH_3$-11-A > FOH-11-A > FOCl-11 shows an inverse correlation with the H-bond length, i.e., the smaller the H-bond length, the more stable is the structure, which can be attributed to stronger overlap of orbitals between the two monomers. The infinite basis limit interaction energies determined by two-point extrapolation technique using aug-cc-pVDZ and aug-cc-pVTZ basis sets reveal that Hartree-Fock theory cannot describe H-bonding properly as compared to the MP2 method. This is due to the absence of correlation energies. The IB-corrected MP2 results predict fluorine-substituted dimer (FOF-11-A) to be the most stable among all the dimers considered here. This result is consistent with the BSSE-corrected interaction energy results obtained using 6-311++G(2d,2p) basis sets. The stability order obtained from these two sets of results remains almost unaltered (except a few), and hence it could be concluded that IB calculations have refined the interaction energy without disturbing the gross stability trend. The infinite basis extrapolated MP2 interaction energies follow the stability trend as follows: FOF-11-A > $FOCH_3$-11-A > FOH-11-A > FOCl-11 > FOH-12 > FOCl-13 > FOF-13 > FOF-11-B > $FOCH_3$-11-B > FOH-11-B > $FOCH_3$-12 > FOCl-1 > FOCl-33 > FOH-22-A > FOF-10 > FOH-22-B > FOF-33.

To obtain further insight into the nature of the H-bond in the substituted formic acid dimers, we invoke the electron density based topological parameters within the framework of Bader's atoms in molecule theory (AIM).[30] The interactions are investigated by considering the values of the electron density and its Laplacian at the bond critical points (BCP) of the O−H···O, O−H···X (X = Cl, F), and C−H···O bonds. A BCP (point corresponding to $\nabla\rho = 0$) is found between each pair of nuclei, which are considered to be linked by a chemical bond with two negative curvatures (λ_1 and λ_2) and one positive curvature (λ_3) denoted as the (3, −1) critical point. The bond ellipticity defined in terms of the two negative curvatures as $\epsilon = (\lambda_1/\lambda_2 - 1)$ reflects the deviation of the charge distribution of a bond path from axial symmetry, thus providing a sensitive measure of the susceptibility of a system to undergo a structural change. The Laplacian of the electronic density ($\nabla^2\rho$) indicates whether the electron density is locally concentrated ($\nabla^2\rho < 0$) or depleted ($\nabla^2\rho > 0$).

The calculated values of the electron density (ρ), Laplacian ($\nabla^2\rho$), and bond ellipticity (ϵ) at the BCP for O−H···O and C−H···O bonds in all the structures considered are presented in Table S1 of the Supporting Information. As expected, the strong bonds are found to be associated with higher electron density. It is observed for the structure FOF-11-A, which has higher BCP electron density and higher stability. Thus, the electron density values calculated at the BCPs augment the stability order predicted by overall interaction energy. The calculated values of other properties at the BCP, namely, the Laplacian of the electron density and the bond ellipticity also follow the same trend. The relative values of the electron density and other properties as obtained by DFT and MP2 methods show the same trend in most of the cases, except a few discrepancies with small differences. A comparison of various Bader's electron density properties for different substituted formic acid dimers indicate that these values are larger for fluorine substitution, followed by methyl, hydrogen, and chlorine substitutions. Further, we have established a correlation between the H-bond distance, electron density, and its Laplacian, as shown in Figures 2 and 3. The increase in H-bond length is found to correspond to a decrease in the electron density, which is natural as it results from a decrease in orbital overlap. Laplacian of the electron density and H-bond length also reveal an inverse correlation. The correlation coefficients for the plots of the electron density and the Laplacian of electron density with H-bond distance are respectively 0.908 and 0.979 for B3LYP and 0.909 and 0.973 for MP2. We have also analyzed the electron density and its Laplacian values for C−H···O type bonds for which the topological parameters are found to be very small in comparison to those for O−H···X bonds. Thus, AIM analysis is not able to provide much information on these types of bonds, and hence NBO analysis has been performed.

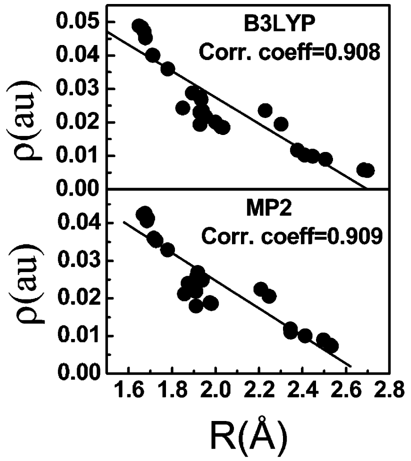

Figure 2. Correlation between electron density at the bond critical point and the H-bond distance calculated using B3LYP and MP2 levels of theory, respectively, for all the systems considered in this work.

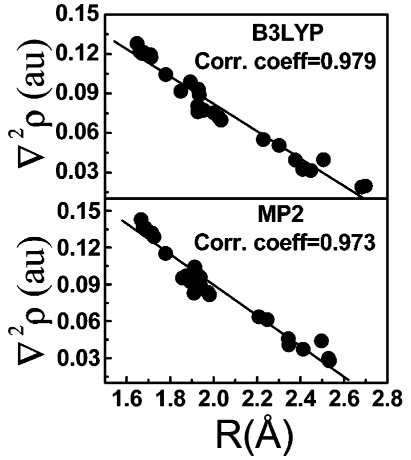

Figure 3. Correlation between the Laplacian of the electron density at the bond critical point and the H-bond distance calculated using B3LYP and MP2 levels of theory, respectively, for all the systems considered in this work.

The NBO analysis[31,32] has been a reliable tool for the rationalization of H-bonds, which correlate well with changes in bond length in accordance with the basic chemical concepts. It is also used to derive information on the changes of charge densities in proton donor and proton acceptor as well as in the bonding and antibonding orbitals. As we know, H-bonds are formed due to charge transfer from the proton acceptor to proton donor, and hence the amount of charge transfer plays a significant role in the elongation and contraction of the H−Y bond. For each donor and acceptor, the stabilization energy E associated with $i-j$ delocalization is given by the following equation:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F^2(i,j)}{\epsilon_j - \epsilon_i}$$

TABLE 3: Occupation Numbers (lone pair LP_1 and LP_2) of Proton Acceptor (Oxygen) and the Proton Donor σ^*(H−Y) Orbital (Y = O, Cl, F) in Monomers[a]

		N(O)[b]					$N[\sigma^*$(H−Y)][c]	
		B3LYP		MP2				
system	moiety	LP_1	LP_2	LP_1	LP_2	bond	B3LYP	MP2
FOH	H−C=O	1.9850	1.8408	1.9863	1.8814	O−H···O	0.0131	0.0079
	C−OH	1.9807	1.8195	1.9848	1.8741	C−H···O	0.0651	0.0651
$FOCH_3$	C−C=O	1.9783	1.8319	1.9799	1.8898	O−H···O	0.0104	0.0067
	C−OH	1.9786	1.8527	1.9997	1.9997	C−H···O	0.0033	0.0024
FOF	F−C=O	1.9805	1.8094	1.9821	1.8524	O−H···O	0.0053	0.0034
	C−OH	1.9756	1.8325	1.9803	1.8773			
FOCL	Cl−C=O	1.9759	1.7837	1.9776	1.8440	O−H···O	0.0112	0.0078
	C−O−H	1.9771	1.8201	1.9815	1.8707			

[a] All the values are calculated at both B3LYP and MP2 levels of theory using 6-311++G(2d,2p) basis sets. [b] Lone pairs occupation number of oxygen atom. [c] Occupation number of σ^*(H−Y) antibonding orbital of proton donor to be compared with the corresponding dimer values.

TABLE 4: Bond Length of Proton Donor in Complex and Monomer along with the Occupation Number of the Remote Z−X Antibonding Orbitals of Z−X−H−Y (X = C, Y = O, Z = H, O) System[a]

		bond length (X−H)				$N[\sigma^*$(Z−X)]				frequency (cm^{-1})	
	bond	complex		monomer		complex		monomer		complex	monomer
system	(Z−X−H−Y)	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	B3LYP
FOH-12	O−C−H···O	1.0922	1.0876	1.0953	1.0964	0.0159	0.0120	0.0144	0.0111	3108	3057
FOH-22-A	O−C−H···O	1.0944	1.0892	1.0953	1.0964	0.0148	0.0113	0.0144	0.0111	3084	3060
		1.0934	1.0890	1.0953	1.0964	0.0975	0.0728	0.0945	0.0705	3077	3060
FOH-22-B	O−C−H···O	1.0893	1.0891	1.0953	1.0964	0.0967	0.0724	0.0945	0.0705	3077	3060
		1.0893	1.0891	1.0953	1.0964	0.0967	0.0724	0.0945	0.0705	3077	3060
FOCH-12	H−C−H···O	1.0874	1.0869	1.0898	1.0862	0.0093	0.0062	0.0033	0.0024	3110	3057

[a] All the values are calculated at both B3LYP and MP2 levels of theory using 6-311++G(2d,2p).

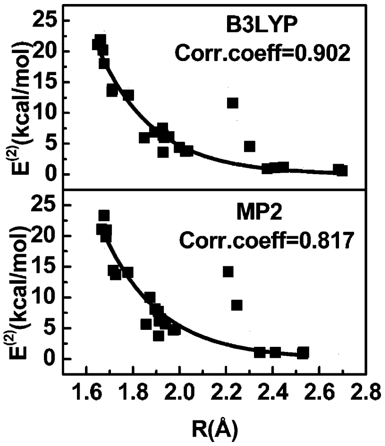

Figure 4. Correlation between the stabilization energy $E^{(2)}$ and the H-bond distance calculated using B3LYP and MP2 levels of theory, respectively, for all the systems considered in this work.

where q_i is the ith donor orbital occupancy, ϵ_j and ϵ_i are the diagonal elements (orbital energies), and $F(i,j)$ are the off diagonal elements, associated with the NBO Fock matrix.

Table 2 presents the values of NBO occupation numbers for the (H−Y) proton donor antibonding orbital $N[\sigma^*$(H−Y)] and the proton acceptor lone pairs N(X) for the dimers considered in the present study. The second-order perturbation energies $E^{(2)}$ (donor−acceptor) involving the σ^*(H−Y) orbital are also given. The data are with reference to the values for the isolated monomer molecules given in Table 3. When NBO results for the isolated molecules are compared, it is observed that σ^*-(H−Y) occupation numbers are in the range 0.01−0.07. It is important to note that the oxygen lone pair (acting as proton donor here) occupation numbers differ from the ideal one by an amount of 0.02−0.18 due to the charge transfer interaction between orbitals. Table 3 presents the values of occupation numbers of the oxygen lone pairs in substituted formic acid monomers (especially LP_2), which differs from the ideal case by an amount of 0.10−0.22. The lone pair of the oxygen atom acts as donor and (H−Y) as acceptor in the strong intermolecular charge transfer interaction. The $E^{(2)}$ terms corresponding to these interactions can be considered to be the charge transfer energy. Larger values of $E^{(2)}$ are found in FOF-11-A, $FOCH_3$-11-A, FOH-11-A, and FOCl-11 isomers. It is found that the charge transfer energy is high for $FOCH_3$-11-A when compared to FOF-11-A. It is also interesting to note that there is an exponential correlation between the bond length and stabilization energy $E^{(2)}$ given in Table 2, which indicates rapid fall in stabilization energy with increase in bond length as shown in the plots of Figure 4. Generally the H-bonds formed in all the complexes are of proper nature except for the dimers $FOCH_3$-12, FOH-12, and FOH-22-(A,B) which have the C−H···O type interaction. These bonds have been thoroughly analyzed by calculating the bond lengths of the C−H fragment, the occupation numbers of the antibonding orbital of the remote part Z−C fragment and the stretching frequency of C−H bond in the monomer as well as in the complex. All the values are presented in Table 4. It is evident that the C−H bond has contracted by approximately 0.001−0.01 Å when compared with the monomer, a trend found in all C−H···O bonded dimers. The reason for this kind of contraction is the structural reorganization induced by charge transfer from donor to the remote part of the acceptor which results in strengthening of the C−H bond and a possible change in its frequency, characteristics of the so-called improper H-bonding. We have analyzed the charge transfer to confirm this process, and the results indicate the transfer of a large amount of charge from the proton acceptor to the antibonding orbital of the remote part of the proton donor, confirming the bonds to be improper and the reason for shortening of the C−H bond. We have calculated the stretching frequency through vibrational analysis of the C−H bond in the complex as well as in the monomer at the B3LYP level. The values of the frequencies have shown considerable increase in going from the monomer to the dimer (17−53 cm^{-1}), which confirms that the bonds are improper blue shifting H-bonds. Further, the B3LYP calculated $E^{(2)}$ values for the C−H···O interactions in methyl-substituted as well as in unsubstituted dimers are almost the same and found to range from 0.57 to 1.15 kcal/mol.

4. Conclusion

In this work we have investigated the hydrogen-bonded dimers of substituted formic acids, $(XCOOH)_2$ with X = H, F, Cl, and CH_3 using density functional theory and second-order Møller−Plesset perturbation (MP2) methods. The energies calculated using aug-cc-pVXZ (with X = D and T) basis have been extrapolated to infinite basis set limit using the standard methodology. Among all the dimers considered, the fluorine-substituted dimer (FOF-11-A) is found to be the most stable one, followed by the methyl-substituted dimer, both associated with two strong H-bonds. The study of the topological parameters, viz., the charge density and the Laplacian of charge density defined by Bader's AIM theory on the bonds of dimers, reveals that all the bonds are H-bonds. The relative stability of a particular species as obtained from the calculated interaction energies is found to be consistent with the corresponding electron density based topological parameters. The correlation of H-bond length with charge density and its Laplacian shows linear fit for B3LYP as well as MP2 results.

The NBO analysis of the H-bond indicates that there is an increase in the population of the (H−Y) orbital in all the dimers when compared with the monomers. In case of the structures FOH-12, FOH-22-(A,B), and FOCH$_3$-12, the existence of improper C−H···O interaction has been found. The NBO study on C−H···O indicates a large charge transfer to remote antibonding orbitals of the C−H moiety from the second lone pair of oxygen. This results in shortening of the C−H bond distance, consequently increasing the stretching frequency (17 to 53 cm^{-1}) and thereby exhibiting blue-shift characteristics.

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Supporting Information Available: The calculated values of the electron density (ρ), Laplacian ($\nabla^2\rho$), and bond ellipticity (ϵ) at the BCP for various hydrogen bonds. This information is available free of charge via the Internet at http://pubs.acs.org.

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