# Complexes of sulfuric acid with *N,N*-dimethylformamide: An ab initio investigation*

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*Abstract*: The $(H_2SO_4)_2$, $H_2SO_4$-DMF, and $(H_2SO_4)_2$-DMF complexes have been investigated, using the B3LYP functional with cc-pVQZ basis set. The characteristics of structure and energetics for binary complexes of sulfuric acid with dimethylformamide (DMF) have been obtained for the first time. The H-bond formation both between molecules of sulfuric acid as well as sulfuric acid-DMF were studied, on the basis of Weinhold's natural bond orbital (NBO) analysis. It was shown that the H-bond formation between sulfuric acid and DMF molecules is stronger than ones for the acids dimer. The value of charge transfer from lone pair (LP) orbitals of DMF oxygen to the antibonding orbital of acid OH-bond significantly exceeds the criterion of H-bond existance (0.01 *e*). As follows from energy, among the complexes under investigation the most preferable one was found to be $(H_2SO_4)_2$-DMF in which sulfuric acid molecules are linked with each other by three H-bonds.

*Keywords*: complexes; dimethylformamide; hydrogen bonding; structures; sulfuric acid.

## INTRODUCTION

The study of the hydrogen-bonded clusters by various experimental physical-chemical methods unfortunately does not provide detailed information about the structure and composition complexes formed. There are various approaches in computational chemistry for investigating the nature of intermolecular interactions and mechanisms of some processes at the molecular level. A geometric-energetic criterion of H-bond existence is commonly used for analysis of H-bonding. In this approach, the interatomic distances, angles, interaction energies, and H-bond lifetimes apply for the identification of H-bond existence. Another well-known approach to characterize H-bonding by use of quantum-chemical methods is Reed–Weinhold's natural bond orbital (NBO) analysis [1], which allows the study of intermolecular charge-transfer process. The advantage of NBO analysis for the study of H-bonded clusters contains an opportunity to mark out the orbitals, which contribute to formation of H-bonds as well as to estimation of the energy effects arising at the interaction of these orbitals.

Nowadays, the level of the fundamental studies concerning the structure of nonaqueous solutions of protonic acids is still insufficient, whereas hydrated sulfuric acid complexes of different composition have been extensively investigated [2–8]. In addition, the application of strong acids (sulfuric acid,

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$H_2SO_4$) as proton donors for gel electrolyte preparation leads to stable gel electrolytes with relatively high proton conductivity [9,10].

In the previous works, the structure of binary $H_3PO_4$-DMF system was investigated using quantum-chemical calculations [11,12] and molecular dynamics simulations [13,14]. The structures of most stable $(H_3PO_4)_n$-DMF ($n$ = 1, 2) configurations, typical for the condensed phase, were obtained. The geometrical characteristics and partial charges on atoms were used as parameters of pair interaction potential for computer simulation. As a result, the detailed structures of the $H_3PO_4$-DMF complex as a function of composition have been investigated.

This work is a starting point for similar investigation of the $H_2SO_4$-DMF system.

## COMPUTATIONAL DETAILS

To gain insight into this problem, we used density functional theory (DFT) using the B3LYP functional [15] to investigate the molecular structures and energies of the hydrogen-bonded complexes of $H_2SO_4$ and $(H_2SO_4)_n$-DMF ($n$ = 1, 2). The 6-31++G(d,p) and cc-pVQZ basis sets were used. All calculations were performed with the GAUSSIAN 03 program package [16]. The vibrational analysis was carried out using the analytical second derivative method for the structures of all complexes to confirm the energy minima. Those structures that have one or more negative frequencies were excluded from this study.

The basis set superposition error (BSSE) was assessed by the counterpoise (CP) correction [17]. The energy of complexation is calculated as follows:

$$\Delta E = E(AB, aUb, R) - [E(A, a, R) + E(B, b, R)] \tag{1}$$

and

$$\Delta E_{corr} = E(AB, aUb, R) - [E(A, aUb, R) + E(B, aUb, R)] \tag{2}$$

where $E$(AB; $aUb$; $R$), $E$(A; $a$; $R$), $E$(B; $b$; $R$) are the energies of the complex and the A and B monomers, respectively. $R$ is the distance between the A and B molecules in the AB complex; $a$ and $b$ are the basis functions of A and B monomers and $aUb$ is the basis function of the AB complex. The CP-corrected energy of complexation is given as $\Delta E - \Delta E_{corr}$.

Complementary information on hydrogen bonding was obtained from analysis of the NBOs, associated with hydrogen and oxygen atoms [1]. Calculations of NBOs were performed on the optimized configurations of the $(H_2SO_4)_2$ and $(H_2SO_4)_n$-DMF ($n$ = 1,2).

Stabilization energy was calculated from the second-order perturbation approach:

$$E_{STAB} = \frac{n_O \cdot F_{IJ}^2}{\Delta E} \tag{3}$$

where $n_O$ is the population of the lone pair (LP) orbital of the proton acceptor, $F_{IJ}$ is off-diagonal Fock matrix element, and $\Delta E$ is the difference between energies of interacting NBOs.

Correspondingly, the charge-transfer value at H-bond formation was calculated in the following way:

$$q_{CT} = 2\left(\frac{F_{IJ}}{\Delta E}\right)^2 \tag{4}$$

### Test calculation for free $H_2SO_4$ and DMF molecules

Since there are no experimental data available for the $H_2SO_4$ complexes, we tested the accuracy of our calculations on a single $H_2SO_4$ molecule for which the experimental geometries are available. Table 1 shows bond lengths and angles corresponding to optimized structures of $H_2SO_4$, calculated with dif-

ferent approaches [4,5,18] and their experimental values [19]. The results of our calculations at B3LYP/6-31++G(d,p) and B3LYP/cc-pVQZ levels of theory are also presented in Table 1.

**Table 1** Bond lengths and angles of $H_2SO_4$ molecule.

| Methods | Bond lengths, Å | | | Angles, ° | | | | |
|---|---|---|---|---|---|---|---|---|
| | $S_1–O_1$ | $S_1–O_3$ | $O_3–H_1$ | $O_1–S_1–O_2$ | $O_1–S_1–O_3$ | $O_1–S_1–O_4$ | $O_3–S_1–O_4$ | $S_1–O_3–H_1$ |
| HF/6-311++G(2d,2p) [5] | 1.39 | 1.55 | 0.95 | 123.4 | – | – | 102.1 | 110.7 |
| MP2/6-311++G(2d,2p) [5] | 1.429 | 1.602 | 0.967 | 124.8 | 108.8 | 105.3 | 101.7 | 107.6 |
| B3LYP/6-31++G(d,p) our data | 1.448 | 1.628 | 0.974 | 124.6 | 108.7 | 105.4 | 101.6 | 108.8 |
| B3LYP/6-311++G(2d,2p) [4] | 1.429 | 1.609 | 0.968 | – | 108.3 | 105.4 | – | – |
| B3LYP/cc-pVQZ [18] and our data | 1.426 | 1.599 | 0.967 | 124.0 | 108.6 | 105.7 | 102.0 | 109.0 |
| Kuczkowski et al. [19] (gaseous) | 1.422 | 1.574 | 0.970 | 123.3 | 108.6 | 106.4 | 101.3 | 108.5 |

The symbol is given in Figs. 1 or 2.

It is clearly seen that all bond lengths of the $H_2SO_4$, as calculated from Hartree–Fock (HF) method, are smaller in comparison with the experimental values. This is due to the fact that the self-consistent field (SCF) calculation neglects the electron correlation, which is essential for accurate description of the molecular structure. The geometrical parameters of $H_2SO_4$ obtained with Møller–Plesset perturbation theory (MP2) and DFT methods with 6-311++G(2d,2p) basis set [4,5] are shown to agree with data determined from microwave spectra of gaseous $H_2SO_4$ molecules [19].

Earlier [11], a comparative analysis of calculation results with use of HF, second-order MP2 and DFT methods in a variety of basis sets and experimental data for $H_3PO_4$ and DMF molecules were performed. We showed that the fully optimized geometrical parameters of initial molecules, calculated by B3LYP/6-31++G(d,p), are in excellent agreement with gas-phase electron diffraction [20] for DMF molecule and X-ray diffraction data [21] and neutron diffraction [22] of phosphoric acid. Unfortunately, the B3LYP/6-31++G(d,p) calculation are not applicable for sulfuric acid molecule. The differences for intramolecular distances of $H_2SO_4$ between those calculated from that basis set and experimental data are relatively high, especially for the $S_1–O_1$ and $S_1–O_3$ bonds (see Table 1). The extension of the basis set from 6-31++G(d,p) (and similar basis sets [7,8]) to cc-pVQZ shows the well-known sensitivity of the $S_1–O_1$ bond lengths with respect to computational efforts. The geometric parameters of molecule, which are calculated using B3LYP/cc-pVQZ, are in excellent agreement with experimental data.

One should note that the structure of $H_2SO_4$ was also studied by MP2/6-31G(d) [7] and 6-311G+(d,p) [8], local density approximation (LDA) in DFT [6], BLYP [6], and B3LYP approach with 6-311G* [18] and D95++(d,p) [2] basis sets. However, calculations show a slightly less satisfactory estimation of the molecular geometry in comparison to experimental data.

The IR spectra for the deuterated sulfuric acid (referred to as $D_2SO_4$) are listed in Table 2. The theoretical values of the vibration frequencies are very close to the experimentally observed values. However, the OD stretching frequencies are calculated to be 2737.7 and 2734.4 cm$^{-1}$, whereas the experimental antisymmetric OD stretching is reported to be 2631.4 cm$^{-1}$ (in argon matrices at 5 K [23]) and 2663 cm$^{-1}$ (vapor phase [24–27]). It is likely that this discrepancy is due to the defect of describing the $S_1–O_3$ bond with the B3LYP method as seen from Table 1.

**Table 2** Observed and calculated vibrations of $D_2SO_4$ ($cm^{-1}$) (abbreviations: s – strong, m – medium, w –weak, vw – very weak).

|  | Our data | Ar matrix [23] | Vapor [24–27] |
|---|---|---|---|
| Antisymmetric O–D stretch | 2737.7 (s) | 2631.4 (s) | 2663 |
| Symmetric O–D stretch | 2734.4 (m) | – | – |
| Antisymmetric S=O stretch | 1435.0 (m) | 1442.6 (m) | 1446 |
| Symmetric O=S=O stretch | 1204.1 (s) | 1217.7 (s) | 1223 |
| Antisymmetric S–O–D bend | 907.1 (w) | 903.7 (w) | 820 |
| Symmetric S–O–D bend | 860.3 (vw) | 854.0 (vw) | – |
| Symmetric S–O bend | 796.0 (m) | 829.2 (m) | – |
| Antisymmetric S–O bend | 853.9 (s) | 877 (s) | 883 |
| O–S=O wag | 450.6 (m) | 467.5 (m) | – |
| Symmetric OD torsion | 180.1 (w) | 208.0 (w) | – |

The structural characteristics of the DMF molecule, as obtained in our calculations, in comparison with the data available in the literature are listed in Table 3. The obtained parameters at B3LYP with 6-31++G(d,p) and cc-pVQZ levels of theory are very close in value. Both approaches give good agreement with the experimental data from electron diffraction of the gaseous DMF molecule [20].

**Table 3** Bond lengths and angles of $H_2SO_4$ molecule.

| Methods | Bond lengths, Å | | | Angles, ° | | |
|---|---|---|---|---|---|---|
|  | $C_1$–$N_1$ | $C_1$–$O_9$ | $C_1$–$H_5$ | $C_2$–$N_1$–$C_3$ | $N_1$–$C_1$–$O_9$ | $N_1$–$C_1$–$H_5$ |
| MM3 [28] | 1.381 | 1.217 | 1.117 | 120.8 | 126.6 | – |
| HF/4-31G(d) [29] | 1.343 | 1.221 | – | 118.5 | 124.8 | 114.1 |
| MP2/6-31+G(2d,p) [30] | 1.365 | 1.222 | 1.105 | 120.6 | 125.7 | 111.7 |
| B3LYP/6-31G(2d,p) [30] | 1.359 | 1.216 | 1.105 | 120.5 | 125.8 | 112.1 |
| B3LYP/6-31++G(d,p) [11] | 1.37 | 1.23 | 1.11 | 121.7 | 124.8 | 113.0 |
| BLYP/DZVP [31] | 1.381 | 1.240 | – | 118.15 | 125.70 | – |
| B3LYP/cc-pVQZ our data | 1.363 | 1.215 | 1.104 | 121.6 | 124.8 | 112.7 |
| Schultz et al. [20] (gaseous) | 1.391(0.007) | 1.224(0.003) | 1.112(0.003) | 120.8(0.3) | 123.5(0.6) | 117.0(2.8) |

The symbol is given in Fig. 2.

As can be seen in Fig. 1, the theoretically predicted IR spectrum of DMF molecule at the B3LYP/cc pVQZ level of theory is quite close to the experimental spectrum [32].

Thus, we are using the B3LYP/cc-pVQZ level of theory to investigate the energetics and molecular structures of the $(H_2SO_4)_2$, $H_2SO_4$-DMF, and $(H_2SO_4)_2$-DMF H-bonded complexes. In addition, B3LYP is the most popular DFT functional [33], which gives reasonable results for H-bonded complexes [34].
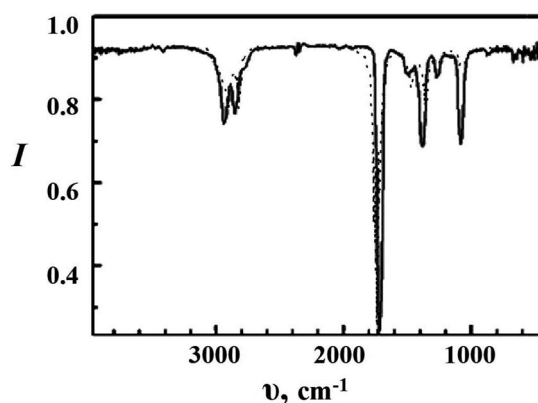
**Fig. 1** Calculated (dashed line) and observed (full line) IR spectra of DMF molecule.

## RESULTS AND DISCUSSION

## $(H_2SO_4)_2$

In the first place, we performed ab initio quantum-chemical calculations of the structures and the formation energies of the $H_2SO_4$ dimers. The calculated structures of the $(H_2SO_4)_2$ are shown in Fig. 2, whereas structural parameters and formation energies of these dimers are given in Table 4.
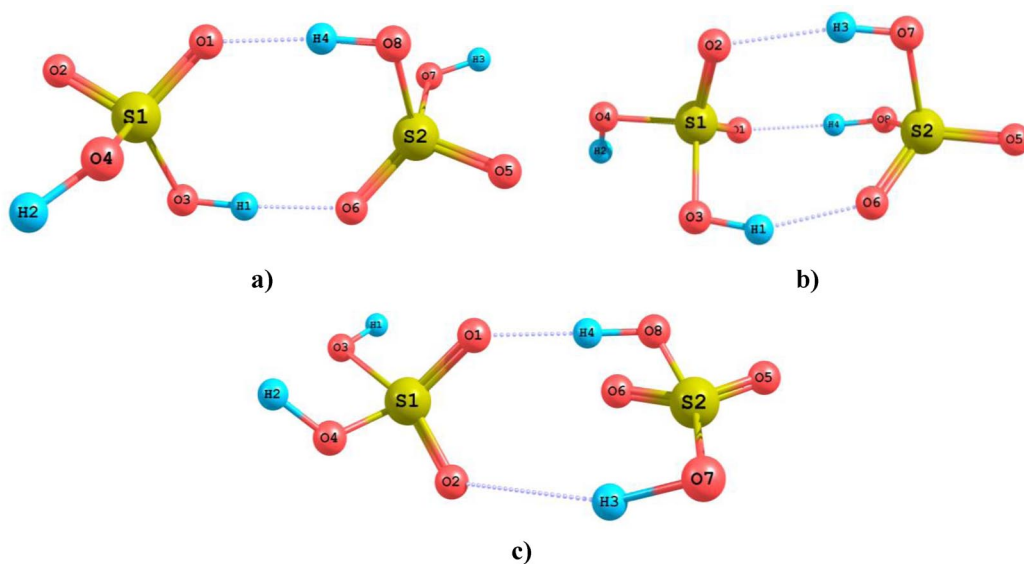


**Fig. 2** Optimized geometries of three configurations of the $H_2SO_4$ dimers.

**Table 4** Geometrical and energetic characteristics of the $(H_2SO_4)_2$ (Fig. 2).

| Parameters | Fig. 2a | Fig. 2b | Fig. 2c |
|---|---|---|---|
| | Bond lengths, Å | | |
| $O_3$–$H_1$ | 0.996 | 0.996 | 0.967 |
| $O_8$–$H_4$ | 0.996 | 0.981 | 0.978 |
| $O_7$–$H_3$ | 0.968 | 0.980 | 0.978 |
| $H_1 \cdots O_6$ | 1.671 | 1.704 | – |
| $H_4 \cdots O_1$ | 1.671 | 1.888 | 2.238 |
| $H_3 \cdots O_2$ | – | 1.899 | 2.238 |
| $O_3 \cdots O_6$ | 2.665 | 2.659 | |
| $O_8 \cdots O_1$ | 2.665 | 2.850 | 3.210 |
| $O_7 \cdots O_2$ | – | 2.859 | 3.210 |
| | Angles, ° | | |
| $O_3$–$H_1 \cdots O_6$ | 175.4 | 159.0 | – |
| $O_8$–$H_4 \cdots O_1$ | 175.4 | 165.4 | 165.8 |
| $O_7$–$H_3 \cdots O_2$ | – | 165.9 | 165.8 |
| | Formation energy, kJ/mol | | |
| $-\Delta E$ | 65.37 | 61.44 | 43.54 |
| $-\Delta E_{corr}$ | 63.23 | 59.21 | 41.41 |
| BSSE | 2.14 | 2.13 | 2.23 |

*r(O–H) = 0.967 Å for free $H_2SO_4$ molecule.

There are three possible configurations of $(H_2SO_4)_2$ (Fig. 2), according to the obtained data, two of them have almost identical energies but very different structure. All dimers are stable mainly due to formation of the ring-like structure in which most of the atoms are arranged around the center. In the first dimer (Fig. 2a), the O⋯H (1.671 Å) and O⋯H (2.665 Å) distances are equal for both H-bonds. The obtained O⋯H distances are shorter than the ones determined with the SCF calculation (1.809 Å) [35] and B3LYP/6-311++G(2d,2p) level theory (1.683 Å) [36]. As one may expect, inclusion of electron correlation through the DFT approach and extension of the basis set considerably reduces the length of the intermolecular bonds.

It is interesting to note that the difference in formation energy values of the dimer calculated by these methods is relatively large. The formation energy of the $(H_2SO_4)_2$ is –71.9 kJ/mol with HF/6-31++G(d,p) and –52.72 kJ/mol with B3LYP/6-311++G(2d,2p), whereas in this work $\Delta E$ corresponds to –65.37 kJ/mol. For an accurate description of the energetic characteristics of the complex, we calculated the CP correction by eq. 2. However, as one can see from Table 4, the use of B3LYP with the cc-pVQZ basis set leads to an almost negligible BSSE error ($\Delta E_{corr}$ = –63.23 kJ/mol).

The formation energy of the acid dimer with three H-bonds (Fig. 2b) is close to the energy of the previous complex (see Table 4). The $\Delta E_{corr}$ value is found to be –59.21 kJ/mol. Three H-bonds in the $(H_2SO_4)_2$ are not equivalent [$r$(O⋯O) = 2.659, 2.850, and 2.859 Å]. The H–O⋯H angles are distorted from 180°, being 159.0°, 165.4°, and 165.9°.

The dimer of acid in which the two O–H groups of the one acids molecule are bonded with O(=S) atoms of the other acid (Fig. 2 ) has the lowest value of formation energy ($\Delta E_{corr}$ = –41.41 kJ/mol). The O⋯O distances are equivalent and considerably longer than ones for dimers 2a and 2b (see Table 4). The O⋯O distance between the two oxygen atoms in the H-bond (–O–H⋯O=) has been introduced as an indicator of the H-bond strength [37]. The obtained distance for this complex may be classified as weak bonds with r(O⋯O) > 2.8 Å.

Furthermore, we considered the most stable H-bonds between the sulfuric acid molecules, represented by Figs. 2a and b. As it is known, the strength of the H-bond correlates with the charge density and, in general, the large charge transfer leads to the strong H-bond. The NBO analysis allows one to calculate the charge transfer ($q_{CT}$) and the energetic effects ($E_{STAB}$) of the orbitals, interacting at H-bond formation. In compliance with the NBO concepts, the formation of the H-bond is accompanied by charge transfer from oxygen LP orbitals of one acid molecule to non-Lewis valent antibonding orbital (BD*) of the other acid molecule. According to Weinhold et al. [1], the charge transfer for a H-bond formation should exceed 0.01 $e$.

As one can see from Table 5, the two orbitals corresponding to the LPs of $H_2SO_4$ oxygen take part in the H-bond formation. The contribution of the oxygen LP orbitals is equal to the acid dimer as follows from Fig. 2a. The energetic effect of the two orbitals forming the H-bond corresponds to 98.95 kJ/mol (whereas for the strong H-bond, it is 60 ÷ 160 kJ/mol [38]). For this dimer, the charge transfer from LP orbitals to the antibonding orbital of the acid O–H bond is much more than the threshold value of conventional H-bonds (0.01 $e$). In other words, there are two fairly strong intermolecular H-bonds between the $H_2SO_4$ molecules.

**Table 5** Stabilization energy of the H-bond and charge transfer in the $(H_2SO_4)_2$ dimers.

| Donor–acceptor | $E_{STAB}$, kJ/mol | | $q_{CT}$ | |
|---|---|---|---|---|
| | Fig. 2a | Fig. 2b | Fig. 2a | Fig. 2b |
| $LP(1)O_6$–$BD*(1)O_3$–$H_1$ | 49.47 | 41.63 | 0.017 | 0.016 |
| $LP(2)O_6$–$BD*(1)O_3$–$H_1$ | 49.48 | 48.37 | 0.017 | 0.017 |
| $LP(1)O_1$–$BD*(1)O_8$–$H_4$ | 49.47 | 14.68 | 0.017 | 0.005 |
| $LP(2)O_1$–$BD*(1)O_8$–$H_4$ | 49.48 | 29.58 | 0.017 | 0.011 |
| $LP(1)O_2$–$BD*(1)O_7$–$H_3$ | – | 14.43 | – | 0.004 |
| $LP(2)O_2$–$BD*(1)O_7$–$H_3$ | – | 27.74 | – | 0.010 |

The obtained values of $E_{STAB}$ and $q_{CT}$ for the dimer of acid with three H-bonds (Fig. 2b) indicate that one of them is strong and two other have medium strength. Our calculations also show that the H-bonds between $H_2SO_4$ molecules lead to a significant increase of the occupancy BD* OH-bond of acid in comparison with ones for the isolated molecule (0.006 $e$). So, the antibonding orbital occupancy is 0.054 $e$ ($O_3$–$H_1$, $O_8$–$H_4$) for the dimer with two H-bonds and 0.047 $e$ ($O_3$–$H_1$), 0.029 $e$ ($O_8$–$H_4$), and 0.028 $e$ ($O_7$–$H_3$) for the dimer with three H-bonds.

## $(H_2SO_4)_n$-DMF ($n$ = 1, 2)

The results from the calculation on the $H_2SO_4$ and $(H_2SO_4)_2$, mentioned above, were used for investigation of the $(H_2SO_4)_n$-DMF ($n$ = 1, 2) complexes. The optimized $H_2SO_4$-DMF and $(H_2SO_4)_2$-DMF H-bonded complexes are shown in Fig. 3.
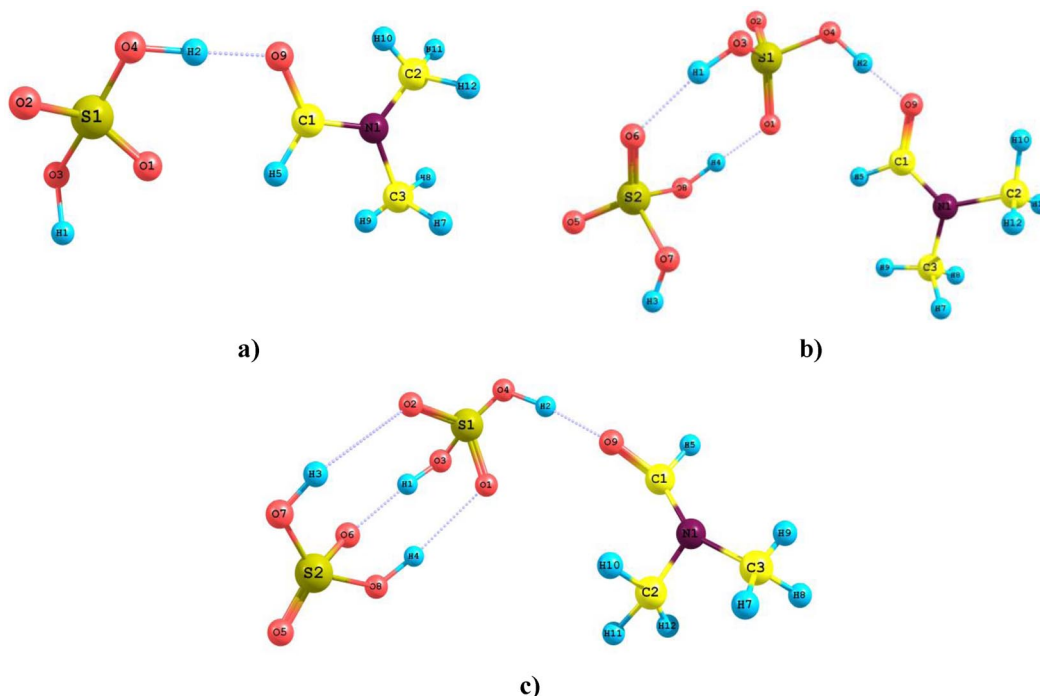
**Fig. 3** Structure of the $(H_2SO_4)_n$-DMF ($n = 1, 2$) H-bonded complexes.

One stable configuration (Fig. 3a) was found for the $H_2SO_4$-DMF complex. The O–H bond of the sulfuric acid elongates by 0.058 Å (see Table 6), due to the formation of H-bond between $H_2SO_4$ and DMF molecules. The energy of formation with CP correction of the $H_2SO_4$-DMF is equal to –78.06 kJ/mol, and it is close to –64.64 kJ/mol calculated for $H_2SO_4$-$NH_3$ (B3LYP/6-31G(d,p)), whereas for sulfuric acid monohydrate the $\Delta E_{corr}$ is only –52.1 kJ/mol (MP2/6-311++G(2d,2p)). This fact allows us to suppose that the interactions of ammonia and DMF with $H_2SO_4$ are stronger than the ones between $H_2SO_4$ and water molecules.

We considered two possible configurations for the $(H_2SO_4)_2$-DMF (Figs. 3b and c). As can be seen in Table 6, the H-bond formation between the acid dimer and the DMF molecule causes the significant elongation of the O–H bond of sulfuric acid for both complexes (Fig. 3a). The distance between the $(H_2SO_4)_2$ proton and the O(DMF) is shorter for complex 3c (1.386 Å) than ones for complex 3b (1.483 Å). The calculated H···O distance for complex containing sulfuric acid dimer with two H-bonds and cis-pinonic acid (1.496 Å) [39] is close to ones obtained for $(H_2SO_4)_2$-DMF (Fig. 3b). The H-bond angles O–H···O(DMF) in both configurations of $(H_2SO_4)_2$-DMF are around 180º.

**Table 6** Geometrical and energetic characteristic of the $(H_2SO_4)_n$-DMF ($n$ = 1, 2) (Fig. 3).

| Parameters | $H_2SO_4$-DMF | $(H_2SO_4)_2$-DMF | |
|---|---|---|---|
| | (Fig. 3a) | Fig. 3b | Fig. 3c |
| | Bond lengths, Å | | |
| $O_3–H_1$ | 0.966 | 0.986 | 0.991 |
| $O_8–H_4$ | 1.025 | 1.010 | 0.988 |
| $O_4–H_2$ | – | 1.038 | 1.076 |
| $O_7–H_3$ | – | 0.968 | 0.987 |
| $H_1\cdots O_6$ | – | 1.752 | 1.741 |
| $H_4\cdots O_1$ | – | 1.596 | 1.784 |
| $H_2\cdots O_9$ | 1.532 | 1.483 | 1.386 |
| $H_3\cdots O_2$ | – | – | 1.793 |
| $O_3\cdots O_6$ | – | 2.732 | 2.699 |
| $O_8\cdots O_1$ | – | 2.604 | 2.763 |
| $O_4\cdots O_9$ | 2.556 | 2.520 | 2.461 |
| $O_7\cdots O_2$ | – | – | 2.766 |
| | Angles, ° | | |
| $O_3–H_1\cdots O_6$ | – | 171.6 | 161.3 |
| $O_8–H_4\cdots O_1$ | – | 176.6 | 170.5 |
| $O_4–H_2\cdots O_9$ | 177.5 | 176.7 | 176.4 |
| $O_7–H_3\cdots O_2$ | – | – | 167.5 |
| | Formation energy, kJ/mol | | |
| $-\Delta E$ | 80.08 | 138.89 | 157.27 |
| $-\Delta E_{corr}$ | 78.06 | 134.79 | 152.78 |
| BSSE | 2.02 | 4.10 | 4.49 |

*$r$(O–H) = 0.967 Å for free $H_2SO_4$ molecule.

It should be noted that the addition of the DMF molecule to the dimer of $(H_2SO_4)_2$ changes the characteristics of the initial H-bonds in the acids dimer. As one can see from Table 4, there are two symmetric H-bonds with O$\cdots$O distance of 2.665 Å for the $(H_2SO_4)_2$ (Fig. 2a), whereas in $(H_2SO_4)_2$-DMF complex (Fig. 3b) these distances are different (2.604 and 2.732 Å). The similar distortion of the $(H_2SO_4)_2$ structure is observed at the formation of the sulfuric acid trimer [35] and the $(H_3PO_4)_2$-DMF complex [11].

As shown in Table 5, the formation energy with CP correction for $(H_2SO_4)_2$-DMF (Fig. 3c) is higher than the one for the $(H_2SO_4)_2$-DMF complex (Fig. 3b). It should be noted that the BSSE for the complexes is not significant. According to our computations, the BSSE slightly increases with the loss of simplicity of the molecular structure.

We applied the NBO analysis to investigate the charge-transfer process responsible for the H-bond formation between $H_2SO_4$ and DMF molecules. The values of charge transfer and stabilization energy of H-bond for complexes under investigation are listed in Table 7.

The NBO results shows that the charge-transfer value from the LP orbitals of O(DMF) to the antibonding orbital of the O–H for all complexes are larger than the accepted standard of the H-bond formation ($q_{CT} \geq 0.01\ e$). It is interesting to note that the contribution of these LPs completely differ: the charge transfer with LP(2)O orbital is considerably larger than with LP(1)O. The obtained values indicate that the H-bond formation between $H_2SO_4$ and DMF is stronger in comparison with the one for the acid dimer.

**Table 7** Stabilization energy of the H-bond and charge-transfer value of the $(H_2SO_4)_n$-DMF ($n$ = 1, 2).

| Donor–acceptor | $E_{STAB}$, kJ/mol | | $q_{CT}$ | |
| --- | --- | --- | --- | --- |
| | Acid–acid | | | |
| | Fig. 3b | Fig. 3c | Fig. 3b | Fig. 3c |
| LP(1)$O_6$–BD*(1)$O_3$–$H_1$ | 53.97 | 38.53 | 0.018 | 0.015 |
| LP(2)$O_6$–BD*(1)$O_3$–$H_1$ | 107.86 | 41.17 | 0.063 | 0.016 |
| LP(1)$O_1$–BD*(1)$O_8$–$H_4$ | 36.11 | 27.53 | 0.011 | 0.011 |
| LP(2)$O_1$–BD*(1)$O_8$–$H_4$ | 37.61 | 46.36 | 0.012 | 0.017 |
| LP(1)$O_2$–BD*(1)$O_7$–$H_3$ | – | 26.77 | – | 0.011 |
| LP(2)$O_2$–BD*(1)$O_7$–$H_3$ | – | 42.38 | – | 0.015 |

| Donor–acceptor | Acid–DMF | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | Fig. 3a | Fig. 3b | Fig. 3c | Fig. 3a | Fig. 3b | Fig. 3c |
| LP(1)$O_9$–BD*(1)$O_4$–$H_2$ | 39.66 | 45.19 | 52.55 | 0.015 | 0.017 | 0.021 |
| LP(2)$O_9$–BD*(1)$O_4$–$H_2$ | 180.50 | 223.26 | 346.73 | 0.098 | 0.124 | 0.188 |

As shown in Table 7, values of $q_{CT}$ and ESTAB are larger for $(H_2SO_4)_2$-DMF complexes than for $H_2SO_4$-DMF. As expected, the high values of the charge transfer are due to the donation of electron density from an O(DMF) LP orbital to the BD* O–H bond of acid dimer with three H-bonds.

The formation of H-bond between sulfuric acid dimer (Fig. 2a) and DMF (Fig. 3b) leads to the increasing of the $E_{STAB}$ and $q_{CT}$ values for one from H-bonds and decreasing these values for other bonds. The increase of the $E_{STAB}$ and $q_{CT}$ values was observed for two of three H-bonds of the acid dimer (Fig. 2b) in $(H_2SO_4)_2$-DMF (Fig. 3c). As results, there are three strong H-bonds between acid molecules with nearly equal length (Table 6).

It needs to be pointed out that formation of strong H-bond leads to significant increasing of the antibonding orbital occupancies of acid in comparison with ones for the isolated molecule. This can easily be seen in Table 8.

**Table 8** The antibonding orbital (BD*) occupancy of acid OH–bond.

| | BD* orbital occupancy |
| --- | --- |
| $H_2SO_4$ | 0.006 |
| $H_2SO_4$-DMF   (Fig. 3a) | 0.100 ($O_4$–$H_2$) |
| $(H_2SO_4)_2$-DMF   (Fig. 3b) | 0.116 ($O_4$–$H_2$); 0.038 ($O_8$–$H_4$); 0.075 ($O_3$–$H_1$) |
| (Fig. 3c) | 0.156 ($O_4$–$H_2$); 0.042 ($O_3$–$H_1$); 0.040 ($O_8$–$H_4$); 0.040 ($O_7$–$H_3$) |

## CONCLUSION

In this paper, the structure and energetics of H-bonded complexes have been calculated using the B3LYP/cc-pVQZ level of theory. According to obtained data, two $H_2SO_4$ molecules may form dimers both with two H-bonds and with three H-bonds. Moreover, the $(H_2SO_4)_2$ with two equal H-bonds is most stable. The strength of the H-bond differs in the acid–acid and acid–DMF complexes. The H-bond formation between $H_2SO_4$ and DMF molecules is stronger than ones between $H_2SO_4$ molecules. Among complexes under investigation, the highest formation energy is observed for the $(H_2SO_4)_2$-DMF complex in which $H_2SO_4$ molecules are bonded with each other by three H-bonds. For this complex, the O–H···O(DMF) bond is very strong. The charge-transfer value from O(DMF) LP orbitals to antibonding orbital of the OH-bond significantly exceeds the criteria of H-bond formation.

In the future, we are planning a study of the $H_2SO_4$-DMF complexes in the condensed phase using molecular dynamics. This will enable us to give further assessments relating to the processes of proton transfer and the nature of acid–base interactions.

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