Dimethylformamide clusters: non-covalent bondings, structures and temperature-dependence

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**ABSTRACT**

Thermodynamics properties as well as infrared spectra of liquids can be determined using the quantum cluster equilibrium (QCE) theory. The QCE theory requires the knowledge of the structures of the clusters formed by the solvent molecules. In prelude to this determination, in this work, we studied the non-covalent bondings, the structures and the temperature-dependence of the clusters of dimethylformamide (DMF) from dimer to tetramer. To perform this study, we used classical molecular dynamics to sample initial geometries of DMF clusters. Then, optimisation of the geometries is carried out at the MP2/aug-cc-pVDZ level of theory. Besides, we carried out a quantum theory of atoms in molecule analysis. The results show that the structures of the DMF dimer exhibit a stacking configuration, and mainly stabilised by CH\ldots O hydrogen bondings. For the DMF trimer and DMF tetramer, the structures exhibit an amorphous behaviour. Moreover, it has been found that the CH\ldots O hydrogen bondings are the main non-covalent bondings in DMF clusters. CH\ldots C, CH\ldots N, N\ldots O, N\ldots C, C\ldots O and H\ldots H bonding interactions are also located in the studied DMF clusters. In addition, the temperature-dependence study shows that only isomers with relative energy within $\sim$ 1.0 kcal/mol have meaningful contribution to the population of DMF clusters.

**1. Introduction**

Thermodynamics properties as well as infrared spectra of liquids can be determined using the quantum cluster equilibrium (QCE) theory developed by Weinhold [1, 2]. The QCE theory has been applied in its earliest by Weinhold and coworkers to determine the thermodynamics properties, chemical shifts and vibrational frequencies of liquid ammonia [3, 4]. The accuracy of QCE theory...
in determining these properties depends on the accurate exploration of the potential energy surfaces (PESs) of molecular clusters constituting the liquid. For the case of dimethylformamide (DMF), this accuracy depends on the accurate description of the PESs of DMF clusters, by identifying all possible isomers and the energy landscape of the clusters. The structures, their vibrational frequencies and their energies will be used in the QC theory to determine the properties of the liquid DMF. Therefore, one can see that the determination of the properties of liquid DMF is directly linked to the accuracy of DMF clusters. Moreover, it is important to note that DMF clusters are important to describe processes occurring in liquid DMF (or solution). Molecular clusters have been used in previous works to calculate proton solvation free energies and proton transfer free energies [5–20]. DMF clusters can also be used to determine the free energies of solvating ions in liquid DMF. In fine, DMF clusters are important for the calculation of several properties of processes taking place in liquid DMF.

Although DMF clusters are important, the literature mining shows that very few works have been devoted to its investigation. Desfrançois et al. [21] have reported few configurations of the DMF dimer studied both experimentally and theoretically. Theoretical work has been performed using a potential model. Their work revealed that the lowest energy structures of the DMF dimer are not cyclic structures. They argued that the methyl groups in DMF do not allow the construction of cyclic DMF dimer. The lowest lying energy isomer has a binding energy of 8.0 kcal/mol and a dipole moment of 1.2 Debye [21]. This isomer has a stacking configuration in which the two DMF molecules are nearly parallel. Vargas et al. [22] investigated the strength of C–H· · ·O = C hydrogen bonding using several levels of theory. For this investigation, they have calculated the binding energies of some isomers of the DMF dimer stabilised by C–H· · ·O = C bondings. The binding energies at the MP2/aug-cc-pVTZ level of theory vary from −5.8 kcal/mol to −12.1 kcal/mol [22]. The most stable isomer with highest binding energy is a stacking dimer while the less stable isomer is a cyclic DMF dimer. Tukhvatullin and coworkers [23, 24] have investigated the intermolecular interactions in liquid DMF using Raman spectroscopy. They have also reported some properties of the DMF monomer and DMF dimer using ab-initio calculations (HF/6-31G(d) level of theory). Their located DMF dimer has a cyclic configuration with 0.0 Debye dipole moment, and 8.0 kcal/mol binding energy [24]. Besides, Shan et al. [25] investigated the two configurations of the DMF dimer and the interaction between DMF and some aromatic molecules. The reported DMF dimers have cyclic configurations. After considering basis set superposition errors, the authors have classified the binding strength between DMF and the studied aromatic molecules [25]. Using B3LYP DFT (density functional theory) functional, DMF dimers have been investigated by Shundalau and coworkers [26]. The authors have calculated the binding energies and reported the vibrational spectroscopy of the DMF dimer. It should be noted that their investigation yielded the cyclic configuration to be the lowest energy isomer [26]. This result is in contradiction with the prediction of Vargas et al. [22] at the MP2/aug-cc-pVTZ level of theory, for which the most stable structure of the DMF dimer has a stacking configuration. Another investigation on the DMF dimer has been reported by Zhang et al. [27]. They used MP2/6-31+G(d) level of theory for geometric and energetics study, while the B3LYP/6-31+G(d) level of theory has been used to study the theoretical IR spectroscopy of the DMF dimers. They have located five DMF dimers with three cyclic and two stacking configurations. The results show that the stacking configurations are found to be more stable than the cyclic configuration at the MP2/6-31+G(d) level of theory. In addition, the authors found that the most stable cyclic configuration lies 4.2 kcal/mol above the most stable stacking configuration. This shows that cyclic configurations have high relative energies, and evidences their negligible importance. Very recently, two DMF dimers and one DMF trimer have been studied by Hushvaktov et al. [28] at the B3LYP/6-31++G(d,p) level of theory. The authors have reported the binding energies, the atomic charges, the dipole moments, as well as the Raman spectroscopy of the studied clusters. Their non-cyclic dimer has been found to be more stable than the cyclic configuration. The authors have not indicated any information about the full exploration of the PESs of the studied clusters, which highlights the limit of the investigation.

Apart from the aforementioned studies on the DMF dimer and DMF trimer, to the best of our knowledge, no other work has been reported on DMF clusters. Nevertheless, interaction of DMF with adducts and microsolvent of DMF have been reported previously [29, 30]. Thus, only the investigation of the DMF dimer and trimer has been reported in the literature. Furthermore, even for the DMF dimer and DMF trimer, the exploration of the PES remains unclear. To allow application of DMF clusters in the determination of liquid’s properties, as emphasised previously, it becomes necessary to carry out a thorough exploration of the PESs of the DMF clusters. Consequently, in this work, we explored the PESs of (DMF)_n for n = 2 to n = 4 at the MP2/aug-cc-pVDZ level of theory. Thus, we generated all possible geometries using ABCluster [31, 32] before optimisation using Gaussian 16 [33]. In addition, we performed a quantum
theory of atoms in molecule (QTAIM) analysis on the five lowest energy structures to gain insights on non-covalent bondings in DMF clusters.

2. Methodology

In this section, we are briefly presenting the theory and the computational tools/details used in this work to carry out the investigations.

2.1. Sampling of geometries

To undertake the current investigation, we started by sampling possible structures on the potential energy surfaces (PESs) of the DMF clusters. For this sampling, we use the ABCluster code [31, 32] which is based on classical molecular dynamics. The reader is reminded that ABCluster has been used in our previous works on ammonia clusters [15, 34, 35], water clusters [36], and ethanol clusters [37, 38]. For these aforementioned clusters, ABCluster has been able to successfully sample all possible geometries within few kcal/mol around the ground-state geometry. Furthermore, ABCluster has been used in atmospheric and environmental sciences in order to locate the most stable structures of atmospheric clusters [39–42]. Recently, a compilation of several studies, which have successfully used ABCluster for different applications, has been reported by Zhang and Glezakou [43]. Therefore, we are very confident that the geometries generated by ABCluster are reliable and can be used for higher order optimisation. It is recommended to read the original work of Zhang and Dolg for further insights on ABCluster [31, 32].

2.2. Computational details

ABCluster generates several geometries with negligible differences. These geometries will converge to the same isomer after optimisation at higher level. Therefore, redundant geometries have been eliminated before optimisation. All selected geometries are optimised at the MP2/aug-cc-pVDZ level of theory. The choice of the MP2 level of theory considers both the accuracy and the affordability. It is well known that the accuracy of ab-initio methods such as MP2 increases with the size of the basis set. Thus, aug-cc-pVTZ or aug-cc-pVQZ basis sets would be more accurate than aug-cc-pVDZ associated with MP2. However, considering the size of system especially the DMF tetramer, MP2 associated with aug-cc-pVTZ or aug-cc-pVQZ basis sets is almost intractable. Consequently, for better compromise between time and accuracy, we carried out the calculations in this work using the MP2/aug-cc-pVDZ level of theory. All optimisations and frequencies calculations are performed using the Gaussian 16 program [33]. To reach a high accuracy level, we performed a tight optimisation and we used ultrafine grid for integrals.

2.3. Temperature-dependent structural stability

After optimisation of the selected structures, we examine the structural stability change as function of temperature. It is well known that the structural stability of clusters is highly temperature dependent [44–53]. Thus, we calculated the probabilities of the selected structures between 20 and 500 K. The probabilities, \( W_m^\ell(T) \), of an isomer \( m \) of the DMF \( \ell \)-mer are calculated using the Boltzmann distribution:

\[
W_m^\ell(T) = \frac{\exp \left( -\beta G_m^\ell(T) \right)}{\sum_i \exp \left( -\beta G_i^\ell(T) \right)}
\]

In Equation (1), \( \beta = 1/kT \) is the Boltzmann constant, and \( G_m^\ell(T) \) is the free energy of an isomer \( m \) of the DMF \( \ell \)-mer at temperature \( T \). In this work, \( G_m^\ell(T) \) are calculated using the program Tempo of Fifen and coworkers [54, 55]. One could also use the freqchk module of Gaussian 16 to calculate \( G_m^\ell(T) \). It should be noted that we have used Tempo in our previous works on molecular clusters [56–62]. In some investigations, we have been able to validate the prediction from Tempo using experimental infrared spectra [56, 57, 62]. We have found that the isomers which are predicted to dominate the population of the clusters at the experimental temperature, have their theoretical IR spectra in agreement with experiment. Therefore, although we do not have experimental IR spectra for DMF clusters, we are confident that the predicted probabilities are reliable.

2.4. Non-covalent bondings

Intermolecular bondings or interactions are important to understand the bonding network, and the structural stability of the DMF clusters. In this work, we carried out a QTAIM analysis of the five lowest energy structures of the investigated clusters. The AIMAll program [63] was used for the QTAIM analysis.

3. Results and discussion

In the present section, the selected structures of the DMF clusters are presented after optimisation. In addition, their non-covalent bonding are discussed directly after presenting the structural stability. Finally, the temperature-dependent structural stability is examined for the DMF dimer, DMF trimer and DMF tetramer.
3.1. DMF dimer

The investigation shows that the DMF dimer has three low lying energy structures within 0.7 kcal/mol, as reported in Figure 1.

The general trend shows that the two DMF molecules in the dimers are parallel leading to stacking configurations such as in benzene clusters [64–66], thiophene clusters [67–69], furan clusters [70, 71] and other clusters of ring-membered molecules. All the three isomers display a symmetric behaviour having at least one $C_2$ symmetric operator. The lowest energy structure belongs to the $C_2$ symmetry point group. It is worth mentioning that the three isomers reported here, are not the only possible structures of the DMF dimer. These are the lowest lying energy structures generated by ABCluster. As will be seen in the next paragraph these three isomers are stabilised by strong hydrogen bonding besides other non-covalent bondings. Previously, Desfrançois et al. [21] reported a stacking configuration of the DMF dimer using a potential model. In addition, using MP2/aug-cc-pVTZ level of theory, four configurations of the DMF dimer are reported: two stacking configurations and two cyclic DMF dimers [22]. The authors found that the stacking configurations are lowest energy structures. Furthermore, they reported that the two cyclic DMF dimers lie 5.2 kcal/mol and 6.3 kcal/mol above the most stable stacking isomer [22]. The considerable relative energy of cyclic configurations will lead to negligible participation of these isomers in the population of the DMF dimer. This supports also the fact that only stacking configurations have been located by ABCluster in this work. Another investigation on the DMF dimer has reported a cyclic dimer to be the most stable configuration at the B3LYP/cc-pVDZ level of theory [26], in contradiction with our results and those of Vargas et al. [22]. This discrepancy could be ascribed to the fact that the B3LYP functional does not properly describe dispersion interactions. Thus, B3LYP has underestimated the structural stability of the stacking configurations of the DMF dimer. The reader is reminded that only few investigations have been reported on DMF clusters (especially the dimer). Thus, we hope that the results provided in this work will lay a route to further investigations on DMF clusters.

To comprehend the bonding network in DMF dimer, we have carried out a QTAIM calculations on the three structures of the DMF dimer. The located Critical points and the bond paths of the DMF dimer are reported in Figure 2. The symmetry of the isomers appears in the bonding interactions. The lowest energy isomer $\text{DMF}_2$ has four strong CH···O hydrogen bondings and two C···N stacking interactions. At the BCPs of the four CH···O bondings, the electron density average value is 0.0096 au, while the Laplacian of the electron density is evaluated to be 0.0316 au. These values of $\rho$ and $\nabla^2 \rho$ at the BCPs characterise a hydrogen bondings. The bond critical points of the two C···N bondings, $\rho = 0.0081$ au and $\nabla^2 \rho = 0.0283$ au $\rho = 0.0081$ au and $\nabla^2 \rho = 0.0283$ au characterise a weak non-covalent bondings. Previously, Desfrançois et al. [21] reported a stacking configuration of the DMF dimer using a potential model. In addition, using MP2/aug-cc-pVTZ level of theory, four configurations of the DMF dimer are reported: two stacking configurations and two cyclic DMF dimers [22]. The authors found that the stacking configurations are lowest energy structures. Furthermore, they reported that the two cyclic DMF dimers lie 5.2 kcal/mol and 6.3 kcal/mol above the most stable stacking isomer [22]. The considerable relative energy of cyclic configurations will lead to negligible participation of these isomers in the population of the DMF dimer. This supports also the fact that only stacking configurations have been located by ABCluster in this work. Another investigation on the DMF dimer has reported a cyclic dimer to be the most stable configuration at the B3LYP/cc-pVDZ level of theory [26], in contradiction with our results and those of Vargas et al. [22]. This discrepancy could be ascribed to the fact that the B3LYP functional does not properly describe dispersion interactions. Thus, B3LYP has underestimated the structural stability of the stacking configurations of the DMF dimer. The reader is reminded that only few investigations have been reported on DMF clusters (especially the dimer). Thus, we hope that the results provided in this work will lay a route to further investigations on DMF clusters.

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![Figure 1](image1.png)

Figure 1. Structures of the DMF dimer and their relative energies as optimised at the MP2/aug-cc-pVDZ level of theory. The relative energies are reported in kcal/mol and they are zero-point vibrational energy corrected.

![Figure 2](image2.png)

Figure 2. Critical points and bond paths of the structures of DMF dimer. Detailed properties of the system at the bond critical points are given in the supporting information.
interaction. The isomer DMF2_2 has four CH···O hydrogen bondings and two N···O bonding interactions. For the hydrogen bondings, the values of $\rho$ and $\nabla^2 \rho$ are similar to those reported for DMF2_1. However, the value of $\rho$ and $\nabla^2 \rho$ for the N···O bonding interactions are 0.0076 au and 0.0261 au, respectively. These values are characteristic of a weak non-covalent interaction. For detailed insights in the intermolecular interactions in the DMF dimer, we have provided the values of $\rho$, $\nabla^2 \rho$ at the BCP of the CH···O hydrogen bondings for the DMF dimer are considerably smaller than those reported for DMSO (dimethylsulfoxide) dimer [72, 73]. For the DMSO dimer, the values are reported to be 0.0160 au and 0.0453 au, respectively [72, 73]. Considering the values of the electron density at BCPs, this indicates that the CH···O hydrogen bondings in DMF dimer are weaker than those in DMSO dimer. This conclusion is also supported by the values of the binding energy of the two dimers. The binding energy for the DMF dimer is calculated to be –11.0 kcal/mol, while that of DMSO dimer is reported to be –13.8 kcal/mol at the MP2/aug-cc-pVDZ level of theory (see Table 2).

After locating the most favourable isomers of the DMF dimers, we examined the temperature-dependent structural stability. For that, we calculated the probability of the three isomers to contribute in the population of the DMF dimer. The probability as function of temperature is reported in Figure 3 for the DMF dimer. It can be seen in Figure 3 that the isomer DMF2_1 has the highest probability between 20 and 500 K. The strong stability of DMF2_1 makes it to be dominant even at high temperatures. This indicates that the increase of temperature is not enough to weaken to bondings in DMF2_1 to loose its stability. Besides, the results show that the isomers DMF2_2 and DMF2_3 have almost the same stability trend as function of temperature. These two isomers contribute increasingly to the population of the DMF dimer from 100 K to 500 K. At 500 K, their probability reaches almost 25% (see Figure 3). The fact that the most stable isomer dominates the population of the cluster for all investigated temperatures has been reported in our previous works on thiophene clusters [68] and dimethylsulfoxide clusters [72].

### 3.2. DMF trimer

The obtained structures of the DMF trimer after optimisation of ABCluster’s geometries are reported in Figure 4. As can be seen in Figure 4, 17 stable structures were identified within 1.8 kcal/mol energy cut-off. Although, 17 isomers are reported, up to 67 initial geometries have been optimised at the MP2/aug-cc-pVDZ level of theory. Several isomers end up to be identical one to another after full optimisation. To obtain the 17 reported isomers, we eliminated all redundant structures. Three isomers are located within 0.2 kcal/mol. Based on the negligible difference in their relative energies, these three

### Table 1. Range of values of the electron density and its second-order derivative for all the bondings identified in DMF clusters from dimer to tetramer.

| Bonding | $\rho$ (e$\cdot$a$_0^{-3}$) Min | $\rho$ (e$\cdot$a$_0^{-3}$) Max | $\nabla^2 \rho$ (e$\cdot$a$_0^{-5}$) Min | $\nabla^2 \rho$ (e$\cdot$a$_0^{-5}$) Max |
|---------|-------------------------------|-------------------------------|----------------------------------|----------------------------------|
| CH···O  | 0.0046                        | 0.0144                        | 0.0191                           | 0.0420                           |
| CH···C  | 0.0051                        | 0.0077                        | 0.0205                           | 0.0336                           |
| CH···N  | 0.0067                        | 0.0118                        | 0.0229                           | 0.0346                           |
| N···O   | 0.0059                        | 0.0100                        | 0.0179                           | 0.0343                           |
| C···O   | 0.0068                        | 0.0104                        | 0.0277                           | 0.0436                           |
| N···C   | 0.0059                        | 0.0096                        | 0.0224                           | 0.0330                           |
| H···H   | 0.0020                        | 0.0077                        | 0.0073                           | 0.0288                           |

### Table 2. Comparison of binding energy, binding enthalpy and binding free energy calculated for DMF clusters and DMSO clusters at the MP2/aug-cc-pVDZ level of theory.

| n     | $\Delta$En | $\Delta$Hn | $\Delta$Gn | $\Delta$En | $\Delta$Hn | $\Delta$Gn |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|
| 2     | –11.0       | –10.9       | 0.8         | –13.8       | –13.6       | –1.9        |
| 3     | –21.4       | –20.8       | 1.3         | –28.1       | –27.5       | –5.3        |
| 4     | –37.3       | –36.8       | –0.6        | –43.6       | –42.8       | –8.9        |

### Figure 3. Contribution of isomers to the population of the DMF dimer presented as probability as function of temperature.
isomers, DMF3_1, DMF3_2, DMF3_3, can be considered isoenergetic. These isomers are constituted of one dimer system with one DMF molecule attached on its side. The difference between the three comes from the position of the methyl groups in the clusters, which also explains the negligible relative energy difference. Exploration of the isomers shows that most of them can be seen as a dimer with one DMF molecule on its side. However, there are few isomers which do not follow this trend, including DMF3_13, DMF3_15 and DMF3_17.

It is worth mentioning that the present work is the first attempt to explore the PES of the DMF trimer using an ab-initio method. Hushvaktov et al. [28] have reported recently one isomer of the DMF trimer at the B3LYP/6-31+G(d,p) level of theory. The authors were not interested in the full exploration of the DMF trimer’s PES to locate different configurations. Moreover, even at a low cost computational level of theory, there is no previous work reported on the exploration of DMF trimer’s PES. The lack of the investigations on the DMF trimer comes from the complexity of its PES, and the computational cost related to its exploration. It is important to note that, without a global optimisation (through ABCcluster in this work), one would not be able to accurately locate the most stable structure of the DMF trimer. Contrary to the case of the dimer, the number of possible interactions in DMF trimers makes intuitive guessing almost impossible. This reason justifies also the importance of using a global optimisation code for accurate exploration of the PESs of complex systems such as the DMF clusters.

Despite the lack of previous works on the DMF clusters higher than the dimer, investigations on similar systems such as the DMSO clusters have been reported previously [72–75]. Similar to the case of the DMF trimer, it has been found that the structures of DMSO trimer can be built from the dimer with one DMSO molecule appended on its side [72, 74]. Another similarity between the DMF trimer and the DMSO trimer is that most of non-covalent interaction are built through the CH···O hydrogen bondings [72, 73]. However, as emphasised

Figure 4. Structures of the DMF trimer and their relative energies as optimised at the MP2/aug-cc-pVDZ level of theory. The relative energies are reported in kcal/mol and they are zero-point vibrational energy corrected.
previously for the dimer, the binding energy of the DMF trimer is smaller than that of the DMSO trimer (see Table 2). This highlights that the intermolecular binding in the DMF trimer is weaker than the binding in the DMSO trimer.

To study the interaction between the DMF molecules in the trimers, we carried out a QTAIM analysis of the five most stable structures of the DMF trimer. The critical points and the located bond paths are reported in Figure 5. The most stable isomer \textbf{DMF3\textsubscript{1}} has 11 intermolecular interactions: six CH···O hydrogen bonding, two C···N, one N···O and one H···H bonding interactions (see Figure 5). The isomers \textbf{DMF3\textsubscript{2}} and \textbf{DMF3\textsubscript{3}} have similar number of non-covalent bondings as \textbf{DMF3\textsubscript{1}}. Thus, it comes out from the analysis that four types of non-covalent interaction can be identified in DMF trimers: CH···O hydrogen bonding, C···N, N···O and H···H bonding interactions. For detailed insights in the intermolecular interactions in the DMF trimer, we have provided the values of $\rho$, $\nabla^2 \rho$, ellipticity and kinetic energy at all bond critical points in the supporting information. This information is provided only for the five most stable structures for which the QTAIM analysis has been performed.

Temperature effects on the located isomers of the DMF trimer show that the low temperatures are dominated mainly by the most stable structure \textbf{DMF3\textsubscript{1}}. However, around room temperature and above, several isomers compete to the population of the trimer (see Figure 6). We noted that the isomers that have meaningful contribution to the population of the trimer have their relative energies within $\sim 1.0 \text{ kcal/mol}$ (see Figure 6). It is worth noting that the relative population trend obtained in this work is similar to that of DMSO trimer where the most stable structure dominate the population of trimer [72].
Figure 7. Structures of the DMF tetramer and their relative energies as optimised at the MP2/aug-cc-pVDZ level of theory. The relative energies are reported in kcal/mol and they are zero-point vibrational energy corrected.
3.3. DMF tetramer

Regarding the PES of the DMF tetramer, 106 initial geometries have been optimised at the MP2/aug-cc-pVDZ level of theory. After elimination of redundant structures, 42 isomers have been found to be different from each other within a cut-off energy of 7.0 kcal/mol. The first 20 isomers of the DMF tetramer are reported in Figure 7, while the remaining structures are provided in the supporting information to avoid cumbersome results. Examination of the isomers shows that they do not have a definite symmetry, and they present amorphous configuration. In addition, for all the structures, there is a stacking dimer acting as a building block of the system. Based on this result, we can anticipate that the structures of larger-sized DMF clusters will be constituted of dimers as building blocks. Besides, we found that the most stable isomer, DMF4_1 has compact structure, and strongly stabilised by mainly CH···O hydrogen bondings.

The QTAIM analysis shows that seven different non-covalent bondings can be localised in DMF tetramers: CH···O hydrogen bonding, CH···C, CH···N, N···O, N···C, C···O and H···H bonding interactions. Critical points and bond paths of the five most stable structures of the DMF tetramer are reported in Figure 8. We have provided in Table 1 the range of values of the electron density and its second order derivative for all the identified non-covalent bondings. Based on the values of ρ at BCPs, the CH···O hydrogen bondings are the strongest non-covalent interactions, while the H···H bonding interactions are found to be the weakest (see Table 1). The same result has been found for the DMSO clusters as reported in our previous work [72, 73]. Although both systems (DMF clusters and DMSO clusters) are stabilised mainly by strong hydrogen bondings, comparison of their binding energies indicates that the non-covalent bondings in DMSO clusters are stronger than those of DMF clusters (see Table 2).

Figure 8. Critical points and bond paths of the structures of DMF tetramer. Detailed properties of the system at the bond critical points are given in the supporting information.

Figure 9. Contribution of isomers to the population of the DMF tetramer presented as probability as function of temperature.
The temperature-dependence analysis is reported in Figure 9 as probability of participation to the cluster’s population. The analysis revealed that the most stable isomer \textbf{DMF4}_1 dominates the population of the tetramer for temperatures varying from 20 to 500 K. Nevertheless, some isomers \textbf{DMF4}_2 to \textbf{DMF4}_6 contribute in trace to the population for temperatures higher than 100 K. For temperatures above the room temperature, the six most stable structures compete to the cluster’s population with dominance of \textbf{DMF4}_1. The relative population trend of the DMF tetramer follow the same trend as the population behaviour in thiophene clusters [67], furan clusters [70] and DMSO clusters [72, 73].

4. Conclusions

In this work, we studied the non-covalent bondings, the structures and the temperature-dependence of DMF clusters from dimer to tetramer. To undertake this investigation, we used molecular dynamics simulations to sample initial geometries. Then, the geometries are optimised at the MP2/aug-cc-pVDZ level of theory. Frequencies have been calculated to assess the thermodynamics properties especially the temperature-dependence. Finally, we carried out a QTAIM analysis to understand the bonding network in DMF clusters.

The results show that 3, 17 and 42 isomers have been located on the PESs of the DMF dimer, trimer and tetramer, respectively. The isomers of the DMF dimer exhibit a stacking configuration, and they are mainly stabilised by CH···O hydrogen bondings. We have noted that the isomers of the DMF trimer can be built by appending one DMF molecule to the located dimers. The structures of the DMF trimer and tetramer exhibit an amorphous behaviour without any definite symmetry. Similar to the dimer, the trimer and tetramer are mainly stabilised by CH···O hydrogen bondings. It comes out from the QTAIM analysis that seven different non-covalent bondings can be identified in DMF clusters, including: CH···O hydrogen bonding, CH···C, CH···N, N···O, N···C, C···O and H···H bonding interactions. Besides, the temperature-dependence analysis shows that the most stable structure dominates the population of the sample for the assessed temperatures (from 20 to 500 K). In addition, we found that only isomers with relative energy within \( \sim 1.0 \text{kcal/mol} \) have meaningful contribution to the cluster’s population.

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Disclosure statement

There are no conflicts of interest to declare.

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Supplementary material

Optimised Cartesian coordinates of the investigated structures, QTAIM analysis data, and all the isomers of the DMF tetramer as well as their relative energies.

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References

[1] F. Weinhold, J. Chem. Phys. 109, 367–372 (1998). doi:10.1063/1.476573
[2] F. Weinhold, J. Chem. Phys. 109, 373–384 (1998). doi:10.1063/1.476574
[3] R. Ludwig, F. Weinhold and T. Farrar, Ber. Bunsen. Phys. Chem. 102, 197–204 (1998). doi:10.1002/bbpc.19981020210
[4] R. Ludwig, F. Weinhold and T. Farrar, Ber. Bunsen. Phys. Chem. 102, 205–212 (1998). doi:10.1002/bbpc.19981020211
[5] M.D. Tissandier, K.A. Cowen, W.Y. Feng, E. Gundlach, M.H. Cohen, A.D. Earhart, J.V. Coe and T.R. Tuttle, J. Phys. Chem. A. 102, 7787–7794 (1998). doi:10.1021/jp982638r
[6] M.D. Tissandier, K.A. Cowen, W.Y. Feng, E. Gundlach, M.H. Cohen, A.D. Earhart, T.R. Tuttle and J.V. Coe, J. Phys. Chem. A. 102, 9308–9308 (1998). doi:10.1021/jp983807a
[7] T.R. Tuttle, S. Malaxos and J.V. Coe, J. Phys. Chem. A. 106, 925–932 (2002). doi:10.1021/jp013242+
[8] S. Nigam and C. Majumder, J. Mol. Struct.: Theochem. 907, 22–28 (2009). doi:10.1016/j.theochem.2009.04.013
[9] D. Himmel, S.K. Goll, I. Leito and I. Krossing, Chem. Eur. J. 17, 5808–5826 (2011). doi:10.1002/chem.v17.21
[10] N.F. Carvalho and J.R. Pliego, Phys. Chem. Chem. Phys. 17, 26745–26755 (2015). doi:10.1039/C5CP03798K
[11] Z. Marković, J. Tošović, D. Milenković and S. Marković, Comput. Theor. Chem. 1077, 11–17 (2016). doi:10.1016/j.comptc.2015.09.007
[12] A. Ishikawa and H. Nakai, Chem. Phys. Lett. 650, 159–164 (2016). doi:10.1016/j.cplett.2016.03.004
[13] A. Malloum, J.J. Fifen, Z. Dhaoudi, E.S.G. Nana and N.-D. Jaidane, J. Chem. Phys. 146, 134308 (2017). doi:10.1063/1.4979568
[57] A. Malloum, J.J. Fifen, Z. Dhaouadi, E.S.G. Nana and N.-D. Jaidane, Phys. Chem. Chem. Phys. 18, 26827–26843 (2016). doi:10.1039/C6CP03240K

[58] A. Hattab, Z. Dhaouadi, A. Malloum, J.J. Fifen, S. Lahmar, N. Russo and E. Sicilia, J. Comput. Chem. 40, 1707–1717 (2019). doi:10.1002/jcc.v40.18

[59] O. Boukar, J.J. Fifen, A. Malloum, Z. Dhaouadi, H. Ghalila and J. Conradie, New J. Chem. 43, 9902–9915 (2019). doi:10.1039/C9NJ02462J

[60] T.E. Da-yang, J.J. Fifen, A. Malloum, S. Lahmar, M. Nsangou and J. Conradie, New J. Chem. 44, 3637–3653 (2020). doi:10.1039/C9NJ05169D

[61] A. Malloum, J.J. Fifen and J. Conradie, Int. J. Quantum Chem. 120, e26222 (2020). doi:10.1002/qua.26222

[62] A. Malloum, J.J. Fifen and J. Conradie, Phys. Chem. Chem. Phys. 22, 13201–13213 (2020). doi:10.1039/D0CP01393E

[63] T.A. Keith, Tk gristmill software, Overland Park KS, USA 11 (2019) 16, <aim.tkgristmill.com>.

[64] H. Takeuchi, J. Phys. Chem. A. 116, 10172–10181 (2012). doi:10.1021/jp305965r

[65] E. Miliordos, E. Aprà and S.S. Xantheas, J. Phys. Chem. A. 118, 7568–7578 (2014). doi:10.1021/jp5024235

[66] E.E. de Moraes, M.Z. Tonel, S.B. Fagan and M.C. Barbosa, J. Mol. Model. 25, 1–15 (2019). doi:10.1007/s00894-019-4185-2

[67] A. Malloum and J. Conradie, Int. J. Quantum Chem. 122, e26840 (2022). doi:10.1002/qua.v122.4

[68] A. Malloum and J. Conradie, J. Mol. Liq. 347, 118301 (2022). doi:10.1016/j.molliq.2021.118301

[69] A. Malloum and J. Conradie, Data Brief. 40, 107818 (2022). doi:10.1016/j.dib.2022.107818

[70] A. Malloum and J. Conradie, J. Mol. Graph. Mod. 111, 108102 (2022). doi:10.1016/j.jmgm.2021.108102

[71] A. Malloum and J. Conradie, Data Brief. 40, 107766 (2022). doi:10.1016/j.dib.2022.107766

[72] A. Malloum and J. Conradie, J. Mol. Liq. 350, 118522 (2022). doi:10.1016/j.molliq.2022.118522

[73] A. Malloum and J. Conradie, Data Brief. 42, 108024 (2022). doi:10.1016/j.dib.2022.108024

[74] N.S. Venkataramanan and A. Suvitha, J. Mol. Graph. Model. 81, 50–59 (2018). doi:10.1016/j.jmgm.2018.02.010

[75] N.S. Venkataramanan, A. Suvitha and Y. Kawazoe, J. Mol. Liq. 249, 454–462 (2018). doi:10.1016/j.molliq.2017.11.062