

# A dispersion-corrected density functional theory study of hexamers of formic acid

Shane P. McCarthy, Amlan K. Roy, Sergey Kazachenko, and Ajit J. Thakkar

**Abstract:** Density functional theory with dispersion-correcting effective potentials is used to examine the low-lying isomers of the formic acid hexamer. The lowest-energy structure is a chairlike ring of six Z monomers.  $\pi$ -Stacked structures consisting of a dimer and tetramer lie higher in energy.

**Key words:** formic acid hexamer, clusters, hydrogen bonding,  $\pi$ -stacking, CH $\cdots$ O interaction.

**Résumé :** La théorie de la fonctionnelle de la densité avec potentiels effectifs corrigés pour la dispersion est appliquée à l'étude des isomères de basse énergie des hexamères d'acide formique. La structure dont l'énergie est la plus basse est un cycle de conformation « chaise » comprenant six monomères Z. Les empilements  $\pi$  constitués d'un dimère et d'un tétramère possèdent une plus haute énergie. [Traduit par la Rédaction]

**Mots-clés :** hexamère d'acide formique, agrégats, liaison hydrogène, empilements  $\pi$ , interaction CH $\cdots$ O.

## Introduction

The important role of formic acid in atmospheric and biochemical processes has led to considerable interest in the study of clusters of formic acid. Both experiment<sup>1</sup> and theory<sup>2</sup> show that the lowest-energy Z (trans) monomer is more stable than the E (cis) form by about 4 kcal/mol. The lowest-energy dimer, D in Fig. 1, has been known for decades experimentally<sup>3–5</sup> and theoretically.<sup>6,7</sup> It is a strong, resonance-assisted, cyclic dimer with  $C_{2h}$  symmetry and consists of two Z monomers held together by a pair of short and nearly linear O–H $\cdots$ O bonds. The next most stable dimer, F in Fig. 1, has one O–H $\cdots$ O hydrogen bond and one C–H $\cdots$ O bond.<sup>7</sup> The most stable trimer, T in Fig. 1, is a planar complex in which the D dimer is held to a Z monomer by an O–H $\cdots$ O hydrogen bond and a C–H $\cdots$ O bond.<sup>8</sup> The most stable tetramer, AS2 in Fig. 1, is a  $\pi$ -stack of two D dimers.<sup>9</sup> The most stable pentamer, P1 in Fig. 1, is a booklike folded ring of five Z monomers.<sup>10</sup>

Density functional theory (DFT) is an electronic structure theory with relatively modest computational demands. However, conventional DFT with a hybrid functional, such as the ubiquitous B3LYP,<sup>11,12</sup> cannot account correctly for dispersion interactions.<sup>13</sup> Recently, the use of B3LYP combined with dispersion-correcting potentials (DCP) that account for dispersion effects and also counterpoise errors has been advocated.<sup>14</sup> This method, referred to as the DCP method in the rest of this work, has been shown<sup>10</sup> to work quite well for formic acid tetramers where  $\pi$ -stacking is important and uncorrected B3LYP fails to predict correctly the order of the low-energy structures. This brief article reports a DCP investigation of formic acid hexamers.

## Methods

We began by generating 59 local minima energy structures of formic acid hexamers at the B3LYP/pc1a level using the search-and-screen method described earlier for pentamers.<sup>15</sup> We then added 15 other structures inspired partially by the  $\pi$ -stacking

structures found for the tetramers.<sup>9</sup> Energies for these 74 structures were computed with second-order Møller–Plesset (MP2) theory and the cc-pVTZ basis set.<sup>16</sup> The results were used to rank order the structures. The 25 structures with energies less than 5 kcal/mol above the lowest one were then further refined by energy minimization at the B3LYP-DCP/6-31+G(d,p) level and retained if a harmonic vibrational frequency computation confirmed that a local minimum had been obtained. Next, 14 of these minima whose energies were within 3 kcal/mol of the lowest energy were further optimized at the B3LYP-DCP/6-31+G(2d,2p) level to produce 12 unique hexamer structures corresponding to local DCP energy minima. All calculations were done with Gaussian 03.<sup>17</sup>

## Results and discussion

The best 12 structures are shown in Fig. 2 and their properties are listed in Table 1. All the structures have six hydrogen bonds. The two most stable structures, H01 and H02, are nearly isoenergetic and lower in energy than the other structures by more than 1.2 kcal/mol. They are both folded rings of six Z monomers. H01 is inversion symmetric, chair-shaped, and nonpolar, whereas the saddle-shaped H02 has a dipole moment of 1.1 D. The average length of the O–H $\cdots$ O bonds is 164 pm in both H01 and H02. Both contain two C–H $\cdots$ O bonds. Both can be thought of as two F dimers stacked one above the other and held tightly together by two side-capping monomers, each of which forms an O–H $\cdots$ O bond with both the upper and lower dimers. Global optimization is a difficult problem and it remains possible that we have missed a structure with an energy lower than that of H01; the latter is best referred to as a putative global minimum.

H03 and H05 are bag-shaped folded rings. Both H04 and H07 can be thought of as  $\pi$ -stacked tetramers with a D dimer held to one of the plates by a C–H $\cdots$ O bond. H06 can be visualized as a D dimer stacked above a cyclic tetramer (CE) with one E monomer forming

Received 13 December 2012. Accepted 20 December 2012.

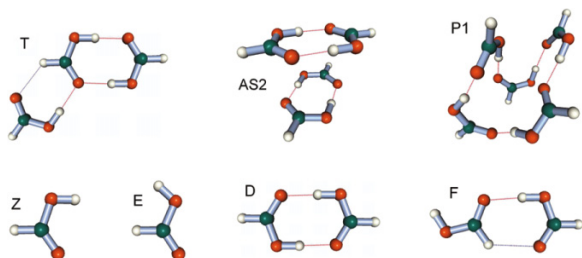
S.P. McCarthy, A.K. Roy\*, S. Kazachenko, and A.J. Thakkar. Department of Chemistry, University of New Brunswick, Fredericton, NB E3B 5A3, Canada.

Corresponding author: Ajit J. Thakkar (e-mail: [ajit@unb.ca](mailto:ajit@unb.ca)).

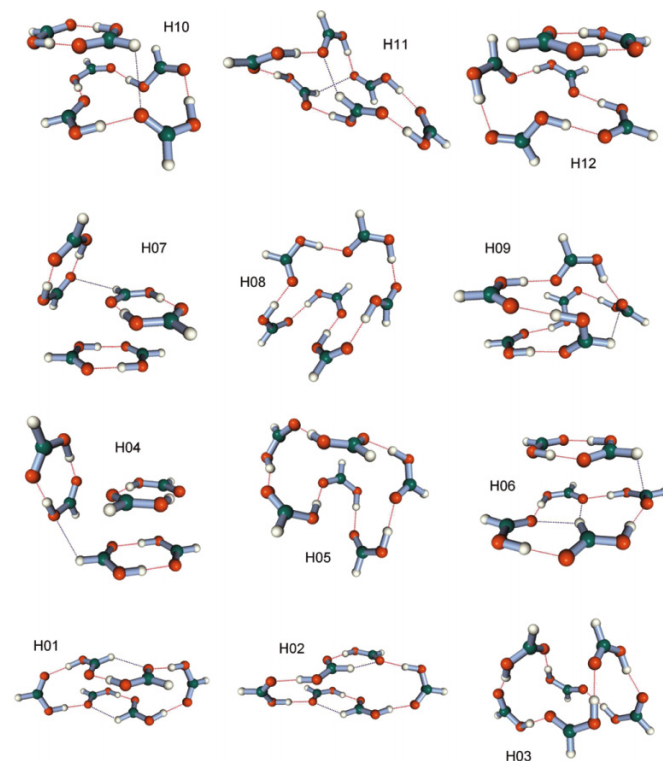
\*Present address: Division of Chemical Sciences, Indian Institute of Science Education and Research (IISER)-Kolkata, Mohanpur Campus, Nadia 741252, India.

It is a pleasure to dedicate this work to Dennis Salahub, one of the leaders of the world-wide DFT development community. This article is part of a Special Issue dedicated to Professor Dennis Salahub in recognition of his contributions to theoretical and computational chemistry.

**Fig. 1.** The lowest-energy monomers, dimers, trimer, tetramer, and pentamer of formic acid; see refs. <sup>1–10</sup> O–H...O and C–H...O bonds are shown as red dashes and blue dots, respectively.



**Fig. 2.** The lowest-energy hexamers of formic acid. O–H...O and C–H...O bonds are shown as red dashes and blue dots, respectively.



two endocyclic C–H...O bonds. A free CE tetramer lies about 2 kcal/mol above the lowest-energy AS2 tetramer.<sup>9</sup> H10 and H12 are similar to H06 but the endocyclic C–H...O bonds are absent in the tetramer moieties. There is a C–H...O bond between the D dimer and the CE tetramer in H06 and H10. The remaining hexamers H08, H09, and H11 are all folded rings. H08 and H09 contain one E monomer and H11 has two.

## Conclusions

The DCP method<sup>14</sup> has been used to obtain the structures and properties of low-lying formic acid hexamers. The lowest-energy structure is an inversion symmetric, chair-shaped ring of six Z monomers. The possibility that we have failed to locate the true global minimum energy structure should not be discounted.  $\pi$ -Stacked structures consisting of a dimer and tetramer lie higher in energy.

**Table 1.** Relative energies (RE) and binding energies (BE) in kcal/mol, rotational constants A, B, and C in MHz, and dipole moments ( $\mu$ ) in debye for the lowest-energy formic acid hexamers.

Isomer	RE	BE	A	B	C	$\mu$
H01	0.00	61.92	559.0	187.9	166.8	0.00
H02	0.25	61.67	584.2	173.7	171.9	1.07
H03	1.53	60.39	483.3	261.8	224.6	2.33
H04	1.76	60.16	506.7	243.8	224.8	0.37
H05	1.77	60.15	444.2	263.2	213.9	2.23
H06	1.82	60.10	371.6	306.8	237.2	3.99
H07	1.83	60.09	412.1	295.6	230.2	0.35
H08	1.87	60.05	416.9	263.2	202.7	2.74
H09	1.98	59.94	472.1	260.2	233.8	2.14
H10	2.01	59.91	449.0	267.6	236.7	2.82
H11	2.02	59.90	535.6	192.5	173.6	0.14
H12	2.46	59.46	411.6	279.4	269.0	2.99

**Note:** Binding energies are with respect to undistorted Z monomers at equilibrium. The B3LYP-DCP/6-31+G(2d,2p) energies of a Z monomer and H01 are  $-189.6106090 E_h$  and  $-1137.7623287 E_h$ , respectively.

## Acknowledgements

The Natural Sciences and Engineering Research Council of Canada (NSERC) supported this work.

## References

- Hocking, W. H. Z. *Naturforsch.* **1976**, 31A, 1113–1121.
- Császár, A. G.; Allen, W. D.; Schaefer, H. F. J. *Chem. Phys.* **1998**, 108, 9751–9764. doi:10.1063/1.476449.
- Pauling, L.; Brockway, L. O. *Proc. Nat. Acad. Sci. U.S.A.* **1934**, 20, 336–340. doi:10.1073/pnas.20.6.336.
- Karle, J.; Brockway, L. O. *J. Am. Chem. Soc.* **1944**, 66, 574–584. doi:10.1021/ja01232a022.
- Almenningen, A.; Bastiansen, O.; Motzfeldt, T. *Acta Chem. Scand.* **1969**, 23, 2848–2864. doi:10.3891/acta.chem.scand.23-2848.
- Schuster, P.; Funck, T. *Chem. Phys. Lett.* **1968**, 2, 587–588. doi:10.1016/0009-2614(68)80023-8.
- Turi, L. J. *Phys. Chem.* **1996**, 100, 11285–11291. doi:10.1021/jp960634l.
- Roy, A. K.; Thakkar, A. J. *Chem. Phys. Lett.* **2004**, 386, 162–168. doi:10.1016/j.cplett.2004.01.031.
- Karpfen, A.; Thakkar, A. J. *J. Chem. Phys.* **2006**, 124, 224313. doi:10.1063/1.2209687.
- Thakkar, A. J. *Chem. Phys. Lett.* **2013**, 560, 71–74. doi:10.1016/j.cplett.2013.01.010.
- Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652. doi:10.1063/1.464913.
- Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623–11627. doi:10.1021/j100096a001.
- Klimeš, J.; Michealides, A. J. *Chem. Phys. Lett.* **2012**, 137, 120901. doi:10.1063/1.4754130.
- Torres, E.; DiLabio, G. A. J. *Phys. Chem. Lett.* **2012**, 3, 1738–1744. doi:10.1021/jz300554y.
- Roy, A. K.; Thakkar, A. J. *Chem. Phys.* **2005**, 312, 119–126. doi:10.1016/j.chemphys.2004.11.030.
- Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*, 2nd ed.; Wiley: New York, **2004**; ISBN: 978-0-470-09182-1.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, N.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburgh, PA, **2003**; Available from <http://www.gaussian.com>.