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## Small clusters of formic acid: Tests and applications of density functional theory with dispersion-correcting potentials

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## ABSTRACT

Dispersion-correcting potentials were proposed as a means to overcome the difficulties that conventional density functionals have in dealing correctly with noncovalent interactions. The procedure is tested and found to be quite successful for low-energy formic acid trimers and tetramers. It is then applied to reexamine formic acid pentamers.

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## 1. Introduction

Density functional theory (DFT) is the most widely used electronic structure method and has had a great deal of success. However, conventional DFT approximations fail when dispersion interactions are important. Many approaches to overcome these deficiencies have been proposed; for an overview, see Ref. [1]. Recently, Torres and DiLabio [2] developed dispersion-correcting potentials (DCP) for use with the hybrid B3LYP functional [3–5]. Their effective potentials for the H, C, N, and O atoms were demonstrated to predict accurate binding energies for dimers in the S22 [6,7], S66 [8], and HSG-A [7] benchmark databases. The DCP method is quite promising since it requires only modest basis sets.

The primary purpose of this short Letter is to test the B3LYP-DCP procedure [2] on the energy ordering of low-lying formic acid trimers and tetramers. The trimers are a relatively easy test because uncorrected B3LYP agrees reasonably well with the second-order Møller–Plesset (MP2) method in this case [9]. On the other hand, the tetramers constitute a much more stringent test because  $\pi$ -stacking interactions are important and uncorrected B3LYP fails [10]. Since the B3LYP-DCP method performs creditably in both these cases, it is then applied to reevaluate an old B3LYP study [11] of formic acid pentamers for which  $\pi$ -stacking could be important.

## 2. Results and discussion

Every structure newly reported in this work was obtained by energy minimization at the B3LYP-DCP/6-31+G(2d,2p) level. The basis set selected is the one recommended by Torres and DiLabio [2] for use with their effective potentials. The version of their potentials used was the one designed to subsume the effects of

counterpoise corrections. For the sake of readability, calculations at this level are referred to as simply DCP calculations. In each case, the energy-minimized structure was retained only if a subsequent harmonic vibrational frequency computation indicated that a local minimum had been obtained. All DFT calculations were done with GAUSSIAN03 [12].

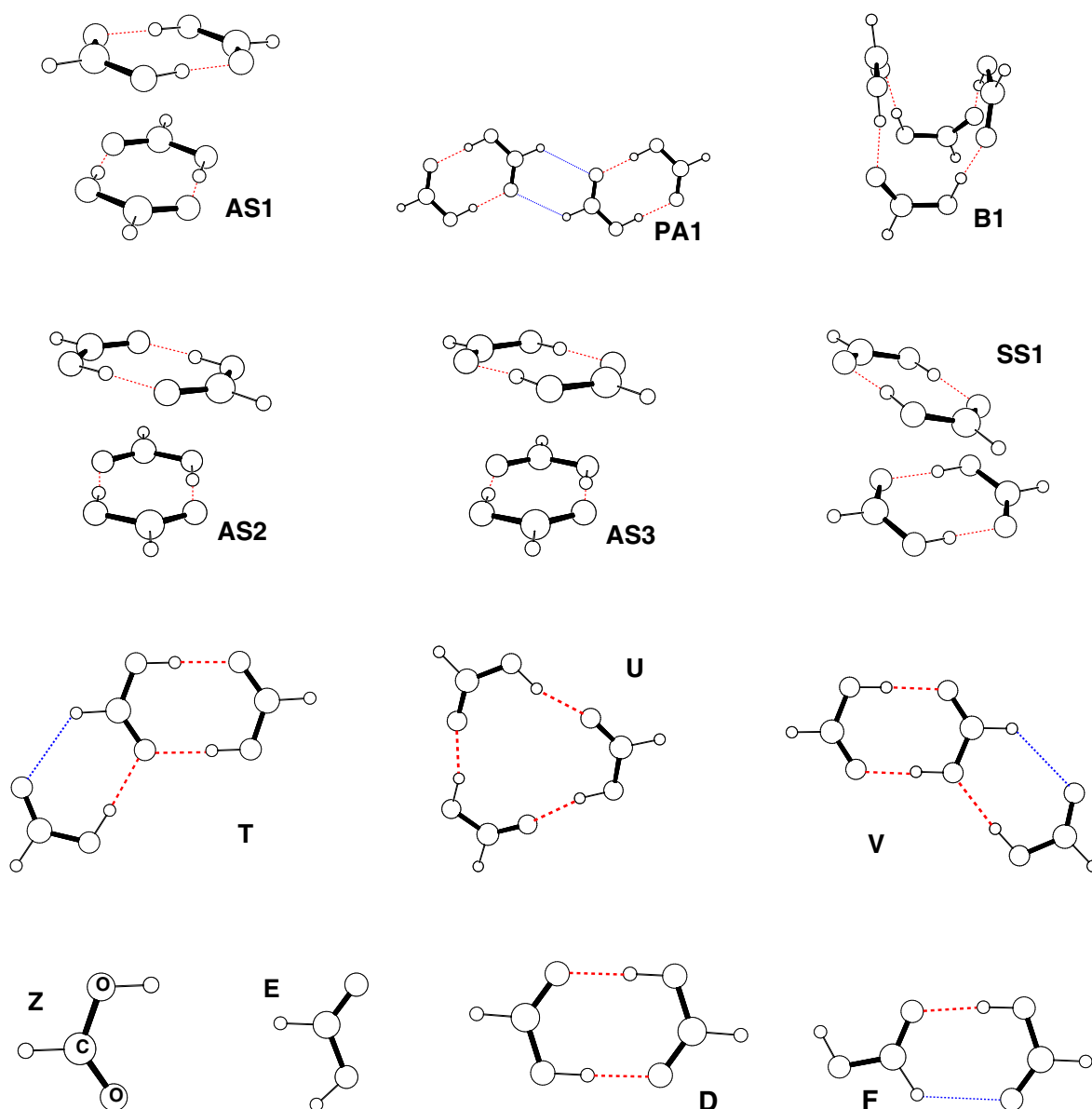
Smaller clusters are often recognizable units of larger clusters. Hence, as an aid to the discussion below, the most stable isomers of the formic acid monomer and dimer are shown in Figure 1. The lowest-energy Z monomer is more stable than the E form by about 4 kcal/mol as indicated by both experiment [13] and theory [14]. The lowest-energy D dimer has been known for decades [15,16]. The F dimer is the next most stable; see, for example, Refs. [17–19].

## 2.1. Tests on trimers and tetramers

Consider the trimers first. Local minima corresponding to the 13 most stable trimers [9] were found on the DCP potential energy surface. The order of the four lowest-energy isomers is exactly the same as that found earlier [9] by DFT calculations with four different hybrid functionals and large basis sets, and by MP2/cc-pVDZ calculations. The three lowest structures, denoted T, U, and V in this work, are shown in Figure 1. As in the previous work [9], the T and V trimers are planar complexes consisting of the D dimer H-bonded to the Z monomer in different ways, and the U trimer is cyclic. However, U is nonplanar at the DCP level whereas it was found to be planar in earlier work [9]. The DCP calculations indicate that the purely electronic energies of U and V, respectively, are 1.72 and 2.24 kcal/mol higher than that of T. The ten earlier calculations gave relative energies ranging between 0.80 and 2.55 kcal/mol for U and between 1.96 and 2.35 kcal/mol for V. Note that although the U trimer was a saddle point at the MP2/cc-pVDZ level [9], a local minimum was found at the MP2/cc-pVTZ level. The fourth trimer lies between 2.6 and 3.4 kcal/mol higher in energy

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**Figure 1.** The lowest-energy monomers, dimers, trimers, and tetramers of formic acid. O–H...O and C–H...O bonds are shown as (red) dashes and (blue) dots respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

than the T structure according to the current DCP calculations and all ten calculations of Ref. [9]. The next four trimers lie within 0.9 kcal/mol of each other and their DCP order differs from that of the earlier work [9]. The five trimers of highest energy lie at least 5 kcal/mol above T; the DCP method and the previous calculations [9] order them in the same way. Clearly, the DCP procedure is successful at predicting both the structures and relative energies for the lowest-lying trimers. A more quantitative assessment of the performance of the DCP method for formic acid trimers is not possible currently; it requires high level ab initio calculations for the low-lying trimers.

The tetramers of formic acid are a more stringent test of the DCP procedure because  $\pi$ -stacking is important. Conventional DFT calculations [20] led to the incorrect prediction that the lowest-energy tetramer was a planar association (PA1 in Figure 1) of two D dimers, and that the most stable stacked structure was 1.8 kcal/mol higher in energy. Subsequent high level ab initio calculations [10] established that the lowest-energy tetramer is the  $\pi$ -stacked

**Table 1**  
Relative energies (RE) and binding energies (BE) in kcal/mol for formic acid tetramers.

Isomer	RE		BE	
	DCP	Ref. [10]	DCP	Ref. [10]
AS2	0.00	0.00	38.58	35.16
AS3	0.31	0.26	38.27	34.90
SS1	0.60	0.46	37.98	34.70
AS1	0.83	0.69	37.75	34.47
PA1	1.05	0.84	37.53	34.32
B1	0.69	0.89	37.89	34.27
PA2	1.51	1.21	37.07	33.95
B2	0.82	1.50	37.76	33.66
PA3	2.02	1.67	36.56	33.49
SS2	1.61	1.81	36.97	33.35
CE	1.89	2.01	36.69	33.15

Isomer names are from Ref. [10]. 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 AS2 are  $-189.6106090 E_h$  and  $-758.5039169 E_h$ , respectively.

**Table 2**

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 pentamers at the DCP level.

Isomer	RE	BE	$A$	$B$	$C$	$\mu$
P1	0.00	49.23	654.2	372.8	353.9	1.23
P2	0.17	49.06	678.4	287.9	250.4	1.64
P3	0.64	48.59	631.3	378.0	315.0	1.73
P4	0.77	48.46	570.9	310.7	220.7	1.71
P5	0.92	48.31	658.7	375.6	344.2	1.62
P6	0.97	48.25	654.8	307.9	297.6	0.94
P7	1.21	48.02	508.7	361.6	251.3	1.92
P8	1.32	47.90	612.1	381.8	336.2	1.97
P9	1.35	47.88	591.6	314.6	234.2	2.27
P10	1.49	47.74	683.9	300.1	251.6	1.16
P11	1.58	47.65	613.4	388.1	318.5	1.89
P12	1.65	47.57	522.3	354.3	257.9	2.53
P13	1.77	47.46	680.5	310.8	281.5	1.02
P14	1.86	47.36	539.2	391.1	332.5	2.01
P15	1.86	47.36	589.3	388.5	320.6	1.82
P16	1.92	47.31	619.3	323.8	314.5	1.97
P17	1.92	47.30	444.9	274.3	169.7	2.44
P18	1.98	47.24	538.9	218.6	155.5	1.96

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 P1 are  $-189.6106090 E_h$  and  $-948.1314905 E_h$ , respectively.

structure shown as AS2 in Figure 1. Moreover, there are at least five local-minimum structures within 1 kcal/mol of the global minimum and three of these are  $\pi$ -stacks as seen in Figure 1. Energy minimizations at the DCP level were carried out for the 11 most stable tetramers [10]. Table 1 compares the DCP binding energies with the best available values [10]. The latter were obtained by combining coupled-cluster CCSD(T) energy corrections in the aug-cc-pVDZ basis set with MP2/cc-pVQZ structures and energies [10]. Table 1 shows that the DCP binding energies systematically overshoot the best values by amounts ranging from 3.1 to 4.1 kcal/mol which corresponds to errors in the 9–12% range. Cancellation of errors leads to much better DCP relative energies which agree with the reference values to better than 0.21 kcal/mol for the six lowest isomers. The DCP rank ordering is correct for the three

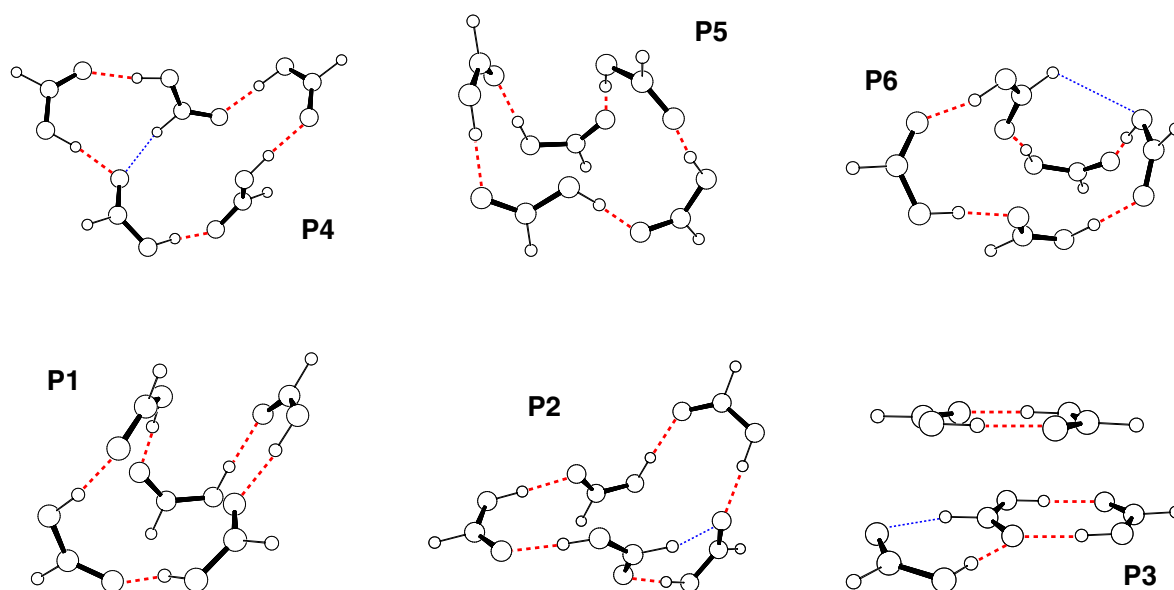
lowest-energy tetramers but becomes erroneous higher up the energy ladder.

## 2.2. Predictions for pentamers

The performance of the DCP procedure for the tetramers is good enough to suggest that the DCP method can be used to provide useful improvements over older uncorrected B3LYP calculations on the pentamers of formic acid [11]. All 43 pentamer structures obtained earlier [11] at the B3LYP/pc2 level were selected for study. Thirty other B3LYP/pc1 structures with relatively low MP2/cc-pVTZ single-point energies and containing motifs suggested by the more recent study of tetramers [10] were added to the starting set. These 73 initial pentamer structures were subjected to energy minimizations at the DCP level leading to 68 unique DCP local minima.

Properties of the most stable pentamer and 17 other local minimum structures which have energies no more than 2 kcal/mol above it are summarized in Table 2. The putative global minimum and the five pentamers that are separated from it by less than 1 kcal/mol are shown in Figure 2. The two most stable pentamers are nearly isoenergetic and consist of five  $Z$  monomers in a ring held together by five  $\text{OH}\cdots\text{O}$  hydrogen bonds. P1 is a book-like folded ring whereas P2 is a chair-like folded ring and has one  $\text{CH}\cdots\text{O}$  bond. P3 consists of a  $\pi$ -stack of a D dimer and a T trimer. P4, P5, and P6 shown in Figure 2 and seven other higher-energy structures in Table 2 are folded rings; some have one or more  $\text{CH}\cdots\text{O}$  bonds, three have one monomer in the  $E$  conformation, and P4 and P13 have two  $E$  monomers. Structures P8, P11, and P16 in Table 2 are  $\pi$ -stacks not unlike P3 shown in Figure 2. P18 is a planar association of a D dimer and a T trimer.

A planar ring P17 with two  $E$  monomers had been found to be the most stable by the earlier uncorrected B3LYP calculations [11]. After local optimization at the DCP level, P17 is seen from Table 2 to be 1.92 kcal/mol higher in energy than P1. The latter result highlights the strong influence of dispersion corrections on the pentamers. In contrast with the uncorrected B3LYP results [11] which suggested that some planar pentamer structures are low-lying in energy, very few of the 68 DCP minima are planar.



**Figure 2.** The lowest-energy pentamers of formic acid at the DCP level.  $\text{O-H}\cdots\text{O}$  and  $\text{C-H}\cdots\text{O}$  bonds are shown as (red) dashes and (blue) dots respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 3. Concluding remarks

The formic acid trimer calculations confirmed that the DCP method [2] does not introduce significant spurious effects in situations where dispersion corrections are not very important. Computations on the tetramers showed that the DCP procedure also does well when  $\pi$ -stacking is important; it correctly predicted the lowest-lying structures and their relative energies, and overshoot binding energies by only 9–12%.

The DCP predictions of formic acid pentamers are expected to be an improvement over the uncorrected B3LYP results reported previously [11]. Obviously, it would be useful to do higher-level ab initio calculations to verify the DCP predictions. Moreover, it would be interesting to compare the DCP predictions for the pentamers with other schemes for adding dispersion corrections to DFT. To facilitate such work, the Cartesian coordinates of the 18 pentamers listed in Table 2 are available as [Supplementary material](#).

Modest basis set requirements and its success with small formic acid clusters portend a useful role for the DCP method [2] in studies of other molecular clusters where both hydrogen-bonding and  $\pi$ -stacking are important. However, the DCP procedure does not introduce the correct  $1/R^6$  behavior at large distances and its utility could be quite limited for clusters, such as rare-gas clusters, dominated by dispersion effects.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.01.010>.

### References

- [1] J. Klimeš, A. Michealides, *J. Chem. Phys.* 137 (2012) 120901.
- [2] E. Torres, G.A. DiLabio, *J. Phys. Chem. Lett.* 3 (2012) 1738.
- [3] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [4] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.
- [5] R.H. Hertwig, W. Koch, *Chem. Phys. Lett.* 268 (1997) 345.
- [6] P. Jurečka, J. Šponer, J. Černý, P. Hobza, *Phys. Chem. Chem. Phys.* 8 (2006) 1985.
- [7] M.S. Marshall, L.A. Burns, C.D. Sherrill, *J. Chem. Phys.* 135 (2011) 194102.
- [8] J. Řezáč, K.E. Riley, P. Hobza, *J. Chem. Theory Comput.* 7 (2011) 2427.
- [9] A.K. Roy, A.J. Thakkar, *Chem. Phys. Lett.* 386 (2004) 162.
- [10] A. Karpfen, A.J. Thakkar, *J. Chem. Phys.* 124 (2006) 224313.
- [11] A.K. Roy, A.J. Thakkar, *Chem. Phys.* 312 (2005) 119.
- [12] M.J. Frisch et al., *GAUSSIAN03*, Revision B.05, Gaussian Inc., Pittsburgh, PA, 2003.
- [13] W.H. Hocking, *Z. Naturforsch.* 31A (1976) 1113.
- [14] A.G. Császár, W.D. Allen, H.F. Schaefer, *J. Chem. Phys.* 108 (1998) 9751.
- [15] J. Karle, L.O. Brockway, *J. Am. Chem. Soc.* 66 (1944) 574.
- [16] A. Almenningen, O. Bastiansen, T. Motzfeldt, *Acta Chem. Scand.* 24 (1970) 747.
- [17] L. Turi, *J. Phys. Chem.* 100 (1996) 11285.
- [18] J. Chocholoušová, J. Vacek, P. Hobza, *Phys. Chem. Chem. Phys.* 4 (2002) 2119.
- [19] R.M. Balabin, *J. Phys. Chem. A* 113 (2009) 4910.
- [20] A.K. Roy, A.J. Thakkar, *Chem. Phys. Lett.* 393 (2004) 347.