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

Ajit J. Thakkar *

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

A B S T R A C T

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.

© 2013 Elsevier B.V. All rights reserved.

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 π-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 π-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

* Fax: +1 506 453 4981.
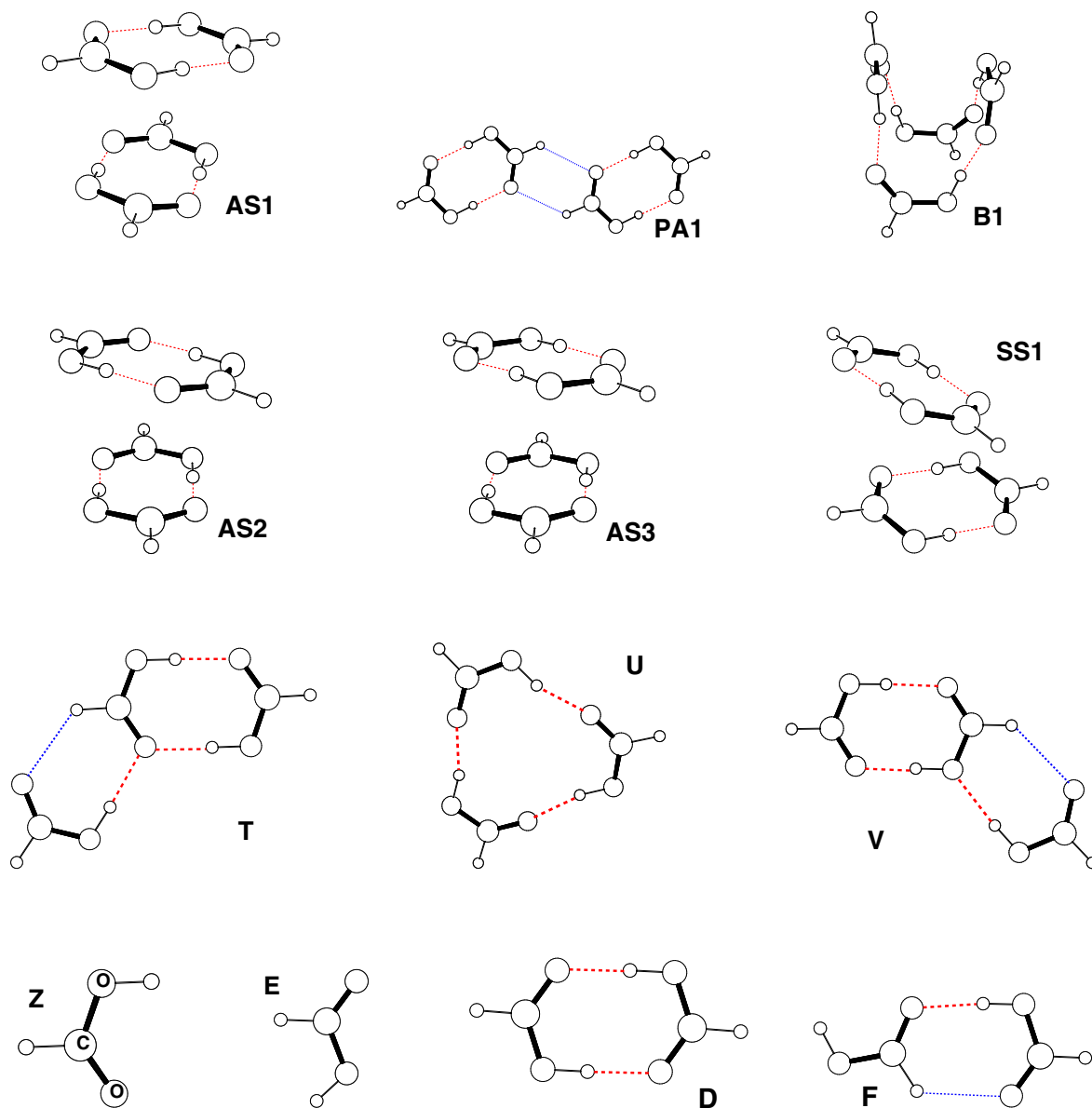 E-mail address: ajit@unb.ca

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 π-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 π-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.