

Does the most stable formic acid tetramer have π stacking or C–H \cdots O interactions?

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(Received 22 March 2006; accepted 9 May 2006; published online 12 June 2006)

Density functional theory (DFT), Møller-Plesset (MP) perturbation theory, and coupled-cluster calculations are used to examine low-energy minima on the potential energy surface of the formic acid tetramer (HCOOH)₄. The potential energy surface is rather flat with respect to rotation of one of the dimers, relative to the other dimer in an aligned stack, about the axis passing through the inversion centers of the dimers. Our best calculations suggest that an aligned π - π stack of two dimers is very likely to be the global minimum but there are two other π - π stacks within 0.5 kcal/mol. Moreover, a fourth π - π stack, a planar association of two dimers held together by C–H \cdots O interactions, and a bowl structure all lie within 1 kcal/mol of the lowest-energy structure. © 2006 American Institute of Physics. [DOI: 10.1063/1.2209687]

I. INTRODUCTION

Formic acid is present in clouds and fog, and plays an important role in human metabolism. It is the first organic acid detected in interstellar ices. The *Z* (*trans*) and the less-stable *E* (*cis*) rotamers of formic acid are well known.^{1–6} The dimers of formic acid are prototypical models for multiple proton transfer reactions in which the constituents are held together by strong hydrogen bonds. It has been established experimentally that gas-phase formic acid forms a cyclic *C*_{2h} dimer^{1,7,8} *D*, shown in Fig. 1, which consists of two *Z* monomers held together by a pair of short and nearly linear O–H \cdots O bonds. Seven dimer structures were found by second-order, Møller-Plesset perturbation theory^{9,10} (MP2) calculations.^{11,12} The most stable one is the *C*_{2h} dimer of Fig. 1; it is separated by about 5 kcal/mol from the next most stable dimer structure.¹¹

The structures of small formic acid clusters have attracted considerable interest. Quantum chemical calculations have been used to characterize trimers,^{13,14} tetramers,^{13,15–18} and pentamers¹⁹ of formic acid. A theoretical study of the x-ray absorption spectra of small formic acid clusters has been reported.²⁰ Computational studies of hydrated clusters of formic acid, (HCOOH)_{*m*}(H₂O)_{*n*}, have been published for *m*=1 (Refs. 21 and 22) and *m*=2,3.²²

In the course of developing and testing an intermolecular pair potential for formic acid, Ramón and Ríos¹³ reported MP2 calculations of the interaction energies in three trimers and four tetramers of formic acid. They found that the most stable trimer had a structure in which a monomer was held to the *D* dimer by an O–H \cdots O hydrogen bond. Roy and Thakkar¹⁴ performed an extensive density functional theory

(DFT) study resulting in the identification of 33 local minima on the potential energy surface of the formic acid trimer. Their most stable trimer structure, shown in Fig. 1, appears to be very similar to that of Ramón and Ríos; it is planar and consists of the *D* dimer held to a monomer by an O–H \cdots O bond and a weak C–H \cdots O interaction. It was found¹⁴ to be about 1.15 kcal/mol lower in energy than a cyclic homodromic structure composed of three *Z* monomers.

By contrast, the case of the formic acid tetramer is less clear. Hartree-Fock (HF), MP2, and DFT calculations were first reported for formic acid tetramers by Stein and Sauer.¹⁵ They identified three stable structures: a cyclic homodromic structure with four *Z* monomers like CZ in Fig. 2, a π - π stacked structure similar to AS2 in Fig. 2, and a “butterfly” or “bowl” structure akin to B1 in Fig. 2. Their MP2 and DFT calculations both indicated that the butterfly structure was the lowest in energy. Next, the MP2 calculations of Ramón and Ríos¹³ on four structures, including those considered by Stein and Sauer, led them to suggest that a chain of two formic acid dimers like PA1 in Fig. 2 was the most stable tetramer.

Roy and Thakkar¹⁶ used DFT calculations with the hybrid B3LYP functional^{23,24} and large polarization-consistent (pc) basis sets^{25,26} to locate 75 local minima on the tetramer potential energy surface. Their structures included several of each of the types considered by Stein and Sauer, and by Ramón and Ríos. Roy and Thakkar’s lowest-energy structure, labeled F438 by them, appears to be the same as that of Ramón and Ríos. It is a planar association (PA) of two *D* dimers held together by two weak C–H \cdots O=C interactions; see structure PA1 in Fig. 2. They¹⁶ found two nearly degenerate structures about 0.4 kcal/mol higher in energy. One is a planar association (PA2) of *D* dimers held together by one C–H \cdots O=C and one C–H \cdots O–H interaction, and the other is a cyclic structure (CE) in which one of the monomers is in the *E* form, thereby making endocyclic C–H \cdots O

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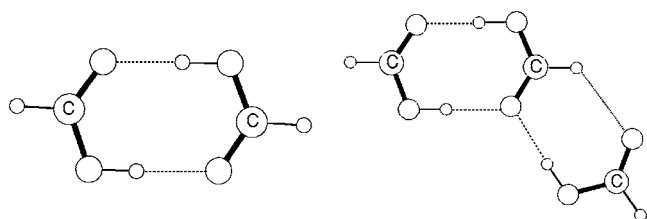


FIG. 1. The lowest-energy, gas-phase dimer and trimer structures.

linkages possible; see Fig. 2. Roy and Thakkar's lowest π - π stacked structures, labeled F456 and F448 by them, were about 1.8 and 2.0 kcal/mol higher in energy than the planar PA1 structure, and are shown as SS1 and SS2, respectively, in Fig. 2.

Noting that the B3LYP functional does not deal adequately with dispersion forces that are important in π - π interactions, Wang¹⁷ performed MP2 calculations and found a π - π stacked tetramer, possibly like AS1 in Fig. 2, to be lower in energy than the PA1 structure. He found that the relative stability of the PA1 and π - π tetramers is highly method dependent. Wang's finding that the π - π structure is the most stable also contradicted the conclusions of Stein and Sauer,¹⁵ and of Ramón and Ríos¹³ even though both the latter sets of authors had also used MP2 calculations. The differences among the three sets of MP2 calculations^{13,15,17} must be attributed to basis set effects. The older MP2 calculations^{13,15} used basis sets intermediate in size between double- and triple- ζ plus polarization. Wang's¹⁷ MP2 optimizations used a 6-31++G(*d,p*) basis set whereas his best single-point energies were based on a 6-311++G(3*df*,3*pd*) basis set.

Zhao and Truhlar¹⁸ pursued further the relative stability of the PA1 and two π - π stacked structures, labeled π_1 and π_2 by them and shown as AS1 and AS2 in Fig. 2. They used MP2/6-31+G(*d,p*) calculations to obtain the geometrical parameters of the structures, and then calculated single-point MP2 energies with the augmented correlation-consistent (cc) basis sets^{27,28} aug-cc-pVDZ and aug-cc-pVTZ. They extrapolated the MP2 energies to a complete basis set limit and calculated a higher-order correlation correction as the difference between coupled-cluster^{10,29-31} CCSD(T) and MP2 energies in a 6-31G*(0.25) basis set. They too found that the stacked tetramers are more stable than the PA1 structure.

Although Zhao and Truhlar's relative energies are most likely to be converged, they are based on geometries computed at a relatively modest MP2/6-31+G(*d,p*) level. Moreover, a close examination of their π - π structures shows that they are significantly different from Roy and Thakkar's F456 and F448 stacked structures. Zhao and Truhlar's π_1 and π_2 consist of parallel dimers with their inversion centers aligned. This is why we refer to these structures as aligned stacks (AS), and label them as AS1 and AS2, respectively, in Fig. 2. Roy and Thakkar have shifted stacks (SS); their F456, labeled SS1 in Fig. 2, has tilted dimers, and their F448, labeled SS2, has a lateral shift. Neither Wang¹⁷ nor Zhao and Truhlar¹⁸ examined any structures other than PA1 and π - π stacks. Among others, the bowl structure B1 of Stein and Sauer,¹⁵ and the CE and PA2 structures of Roy and Thakkar¹⁶ deserve further consideration. The purpose of this work is to report *ab initio* calculations designed to address these issues and come closer to deciding unequivocally the structure of the most stable formic acid tetramer.

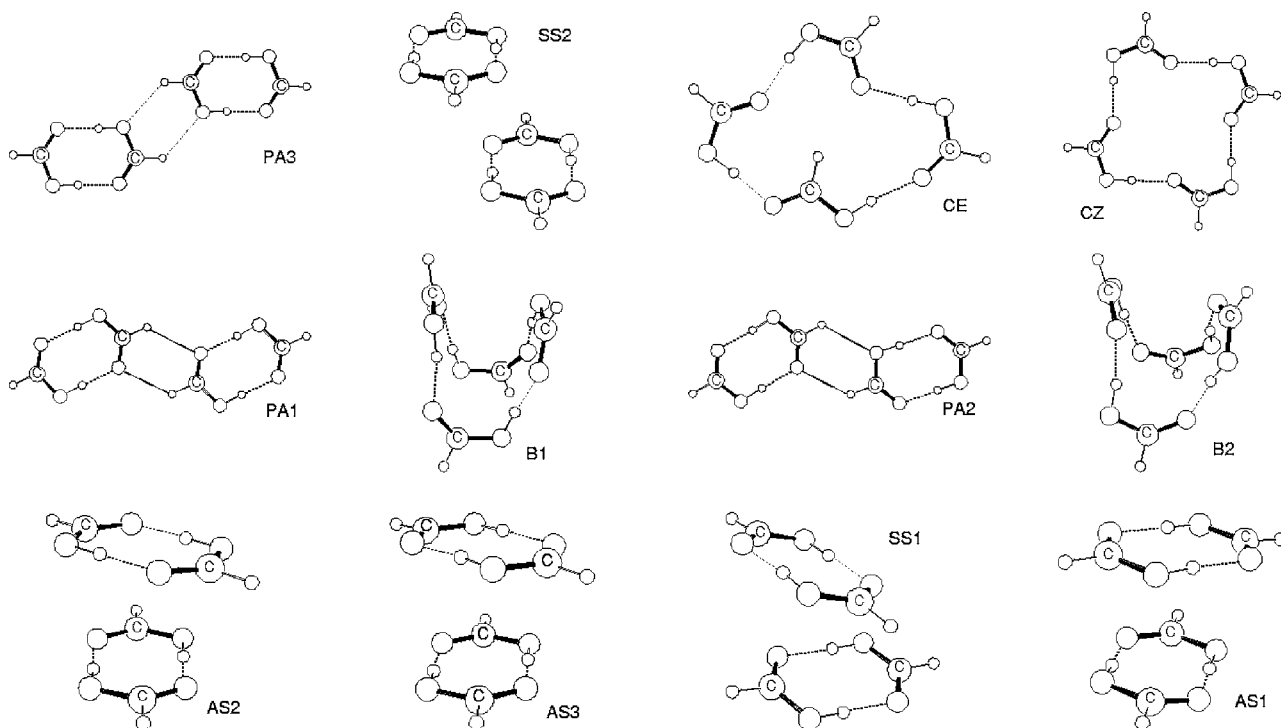


FIG. 2. Low-energy formic acid tetramer structures: aligned stacks (AS), shifted stacks (SS), planar associations (PA), bowls (B), and cycles (C). Thicker dashed (red) lines denote O-H...O bonds and thinner dotted (blue) lines denote C-H...O associations.

TABLE I. B3LYP and MP2 binding energies (kcal/mol) of formic acid tetramers with respect to four Z monomers. Counterpoise-corrected energies are indicated by cp. The symbols b1, b2, b3, and b4 denote the aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ basis sets, respectively.

		B3LYP			MP2				MP2(cp)			
	Symmetry	b1	b2	b3	b1	b2	b3	b4	b1	b2	b3	b4
AS2	D_2	32.55	34.80	31.24	40.29	39.76	39.40	38.08	31.35	31.47	34.84	34.52
AS3	C_2	32.31	34.59	31.02	40.23	39.72	39.28	37.96	31.24	31.44	34.72	34.42
SS1	C_2	32.21	34.75	31.24	40.36	39.69	39.33	37.90	31.22	31.32	34.69	34.35
AS1	D_2	31.95	34.30	30.63	39.99	39.59	39.01	37.71	31.00	31.29	34.47	34.18
B1	S_4	31.83	33.98	30.88	39.50	38.52	38.85	37.24	30.77	30.89	34.28	33.93
PA1	C_{2h}	34.23	36.23	32.97	37.47	38.41	37.67	36.88	31.09	31.35	33.90	33.86
PA2	C_s	33.85	35.77	32.59	37.13	37.96	37.29	36.47	30.76	31.15	33.55	33.55
B2	S_4	31.94	33.85	30.90	39.00	37.86	38.35	36.65	30.25	30.39	33.71	33.38
PA3	C_{2h}	33.40	35.26	32.16	36.71	37.47	36.86	36.02	30.36	30.87	33.14	33.17
SS2	C_i	32.07	34.34	30.93	38.33	38.30	37.67	36.52	29.89	30.44	33.33	33.15
CE	C_s	33.75	35.12	32.68	37.15	36.97	37.32	35.97	29.98	30.20	33.17	32.98
CZ	C_{4h}	30.21	31.69	29.67	32.88	32.98	33.34	32.21	26.97	27.64	29.77	29.70

II. COMPUTATIONAL SCHEME

Given the sensitivity of the relative energies of formic acid tetramers to the computational method used, an attempt to find the most stable tetramer can be both successful and credible only if all known low-energy structures are considered. Our selection of structures began with the computation of single-point MP2/cc-pVTZ and MP2/cc-pVQZ* energies at all 33 B3LYP/pc2 local minima found by Roy and Thakkar.¹⁶ The cc-pVQZ* basis set is a subset of the cc-pVQZ basis²⁷ obtained by removal of *f*-type functions on H and *g*-type functions on C and O atoms. Both MP2 energies found F456 (SS1 in the current notation) to be the lowest in energy. Moreover, one or both of the MP2 energies predicted PA1, PA2, B1, PA3, and CE (or F438, F464, F424, F459, and F403, respectively) to be within 1 kcal/mol of SS1. Hence, we selected these six structures, which also include all those predicted to lie within 1 kcal/mol of the lowest-energy structure by the B3LYP calculations of Roy and Thakkar.¹⁶ To these six structures, we added B2 (F420), which was the bowl-like structure of second-lowest energy, and the cyclic C_{4h} structure CZ of Stein and Sauer.¹⁵ Finally, we added four more π - π structures: SS2 (F448) from Roy and Thakkar,¹⁶ AS1 and AS2 from Zhao and Truhlar,¹⁸ and a promising new π stack that we found (AS3). All selected structures are shown in Fig. 2. This selection includes *all* the structures considered by Stein and Sauer,¹⁵ Ramón and Ríos,¹³ Wang,¹⁷ and Zhao and Truhlar,¹⁸ and a carefully selected subset of the structures of Roy and Thakkar.¹⁶

The 12 structures were then subjected to geometry optimization at the B3LYP/aug-cc-pVDZ, B3LYP/cc-pVTZ, B3LYP/aug-cc-pVTZ, MP2/aug-cc-pVDZ, and MP2/cc-pVTZ levels. Stationary points were verified to be local minima in all B3LYP cases but not for the MP2 cases where frequency calculations were not possible with the computer hardware at our disposal. MP2/aug-cc-pVTZ and MP2/cc-pVQZ energies were calculated at the MP2/cc-pVTZ geometries, and MP4/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ energies at the MP2/aug-cc-pVDZ geometries. Binding energies were computed correcting for basis set superposition error (BSSE) using the counterpoise procedure.³² All calcu-

lations were done with GAUSSIAN-03.³³ Coordinates of the MP2 geometries are available for download.³⁴

III. DFT AND MP2 RESULTS

We begin by considering our B3LYP and MP2 results. Table I lists binding energies, with respect to four Z monomers, computed with the B3LYP and MP2 methods and a variety of basis sets. It shows that the B3LYP method with correlation-consistent basis sets consistently predicts the planar PA1 structure to be the global minimum, in complete agreement with Roy and Thakkar¹⁶ who used the B3LYP method with polarization-consistent basis sets. However, the MP2 method consistently predicts a π - π stack to be the lowest-energy structure, in agreement with Wang,¹⁷ and Zhao and Truhlar.¹⁸ Since dispersion forces are important components of π - π interactions and the B3LYP method does not satisfactorily account for dispersion, the MP2 energies are likely to be more accurate than the B3LYP ones.

A comparison of the BSSE-corrected MP2 energies and their uncorrected counterparts in Table I shows that BSSE drops substantially for the calculations using the larger basis sets. For example, the BSSE for AS2 is 8.9 and 8.3 kcal/mol for the binding energies computed with the aug-cc-pVDZ and cc-pVTZ basis sets, respectively, but drops to 3.2 kcal/mol when the aug-cc-pVTZ and cc-pVQZ basis sets are used. In the latter cases, BSSE is less than 10% of the binding energy, and hence we can have confidence in the BSSE correction.

Extrapolation schemes are sometimes used to predict basis set limits or “complete-basis-set” (CBS) energies. In this work, we use extrapolations only to estimate the errors in our calculations. Our Hartree-Fock energies were extrapolated using a two-point exponential scheme³⁵ with $\alpha=1.54$, and our MP2 correlation energies were extrapolated using a two-point inverse-cube procedure.³⁶ The MP2/CBS binding energies predicted by extrapolating the aug-cc-pVDZ and aug-cc-pVTZ results differed from the MP2/aug-cc-pVTZ binding energies by an average of 0.42 kcal/mol and a maximum of 0.69 kcal/mol. The MP2 binding energies predicted by extrapolating the cc-pVTZ and cc-pVQZ results differed from

TABLE II. Binding energies (kcal/mol) of formic acid tetramers with respect to four Z monomers. Columns 2 to 6 are calculations with the aug-cc-pVDZ basis set. The correction terms are $\delta_M = \text{MP4} - \text{MP2}$ and $\delta_C = \text{CCSD(T)} - \text{MP2}$. The binding energy E_b in the last column is an estimate obtained by adding δ_C to the best MP2 result of Table I.

	MP2	MP4	CCSD(T)	δ_M	δ_C	E_b
AS2	40.29	41.30	40.93	1.00	0.64	35.16
AS3	40.23	41.18	40.71	0.95	0.48	34.90
SS1	40.36	41.26	40.71	0.90	0.35	34.70
AS1	39.99	40.88	40.29	0.89	0.29	34.47
PA1	37.47	37.93	37.93	0.45	0.46	34.32
B1	39.50	40.37	39.84	0.87	0.34	34.27
PA2	37.13	37.55	37.53	0.42	0.40	33.95
B2	39.00	39.82	39.29	0.82	0.28	33.66
PA3	36.71	37.09	37.03	0.38	0.32	33.49
SS2	38.33	39.11	38.52	0.78	0.20	33.35
CE	37.15	37.51	37.32	0.35	0.17	33.15
CZ	32.88	33.08	32.70	0.20	-0.17	29.53

the MP2/cc-pVQZ binding energies by an average of 0.35 kcal/mol and a maximum of 0.53 kcal/mol. In view of these findings, we consider the counterpoise-corrected MP2/cc-pVQZ binding energies given in the last column of Table I to be converged to better than ± 0.5 kcal/mol with respect to basis set enlargement and hence quite close to the MP2 limit.

The MP2 results suggest that the aligned π - π stack AS2 is the most tightly bound structure. However, AS3 is no more than 0.12 kcal/mol higher in energy than AS2, and two (SS1 and AS1) of the three other π - π stacks considered in this work are no more than 0.4 kcal/mol higher in energy than AS2. In light of the discussion of basis set effects in the previous paragraph, it is not possible to state unequivocally which of the low-lying π -stacks is the lowest-energy structure at the MP2 level. The small energy separations among the aligned stacks (AS2, AS3, and AS1) show that the potential energy surface of the formic acid tetramer is quite flat with respect to rotation of one of the dimers, relative to the other dimer in an aligned stack, about the axis passing through the inversion centers of the dimers. Moreover, the potential energy surface is also flat with respect to tilting one of the dimers in an aligned stack as indicated by the relatively low energy of the shifted stack SS1. On the other hand, a substantial lateral shift of one of the dimers as in SS2 is energetically unfavorable by 1.37 kcal/mol.

The planar associations PA1 and PA2, and the bowl-like structure B1 are also within 1 kcal/mol of the global minimum. The binding energies of the planar associations decrease in the order PA1, PA2, PA3, confirming the suggestion¹⁶ that C-H \cdots O=C linkages are stronger than C-H \cdots O-H interactions. To rationalize why the bowl B1 is more stable than B2, think of each bowl as a folded ring¹⁶ with the diagonally opposite monomers forming a π dimer. The monomer planes in these dimers are more nearly parallel in B1 than in B2, making the former the energetically preferred structure. The C_s cyclic structure CE with one monomer in the E conformation is 1.5 kcal/mol above the global minimum but, in agreement with Roy and Thakkar,¹⁶ it is

TABLE III. Zero-point vibrational corrections (δ_v) and corrected binding energies $E_b + \delta_v$ of formic acid tetramers with respect to four Z monomers. All quantities are in kcal/mol.

	δ_v	$E_b + \delta_v$
AS2	-3.91	31.25
AS3	-3.89	31.01
SS1	-3.89	30.81
AS1	-3.88	30.59
B1	-3.83	30.44
PA1	-4.13	30.19
PA2	-4.07	29.88
B2	-3.89	29.77
SS2	-3.78	29.57
PA3	-3.99	29.50
CE	-3.94	29.21
CZ	-3.49	26.04

significantly (3.3 kcal/mol) more stable than the C_{4h} cyclic structure CZ with all monomers in the Z conformation.

IV. HIGHER-ORDER EFFECTS

Next, we consider higher-order correlation effects using the aug-cc-pVDZ basis set. Table II lists binding energies computed at the MP2, MP4, and coupled-cluster CCSD(T) levels. The quantities of interest to us are the correction terms defined by $\delta_M = \text{MP4} - \text{MP2}$ and $\delta_C = \text{CCSD(T)} - \text{MP2}$. They are seen to be positive except for the high-energy cyclic structure CZ.

The two corrections are nearly equal to each other for the planar PA structures, but for all the other structures δ_M is larger than δ_C by factors ranging from 1.5 to 3.0. A detailed examination of the components of the MP4 and CCSD(T) energies shows that the differences arise primarily through the triple substitutions. The differences δ_M and δ_C have not been corrected for BSSE because they are small in magnitude and their counterpoise corrections are expected to be

TABLE IV. Binding energies (kcal/mol) of formic acid tetramers with respect to two dimers. Columns 2 to 6 are calculations with the aug-cc-pVDZ basis set. The correction terms are $\delta_M = \text{MP4} - \text{MP2}$ and $\delta_C = \text{CCSD(T)} - \text{MP2}$. MP2(cp) is a counterpoise-corrected binding energy in the cc-pVQZ basis set calculated at the MP2/cc-pVTZ geometry. The binding energy E_b in the last column is an estimate obtained by adding δ_C to MP2(cp).

	MP2	MP4	CCSD(T)	δ_M	δ_C	MP2(cp)	E_b
AS2	7.46	8.39	8.08	0.93	0.62	3.88	4.50
AS3	7.40	8.27	7.86	0.87	0.46	3.77	4.23
SS1	7.53	8.35	7.87	0.82	0.34	3.70	4.04
AS1	7.16	7.97	7.44	0.81	0.28	3.54	3.82
PA1	4.64	5.02	5.08	0.38	0.45	3.21	3.66
B1	6.67	7.46	6.99	0.79	0.33	3.29	3.62
PA2	4.30	4.64	4.68	0.34	0.38	2.90	3.28
B2	6.17	6.92	6.44	0.75	0.27	2.74	3.01
PA3	3.88	4.18	4.19	0.30	0.31	2.53	2.84
SS2	5.50	6.20	5.68	0.71	0.18	2.50	2.68
CE	4.32	4.60	4.48	0.28	0.15	2.34	2.49
CZ	0.04	0.17	-0.14	0.12	-0.19	-0.95	-1.14

even smaller. For example, for the three structures considered by Zhao and Truhlar,¹⁸ the counterpoise correction to δ_C varies from 0.02 to 0.09 kcal/mol.

Finally, the correction δ_C was added to our best MP2 binding energies given in the last column of Table I to obtain our best estimates of the binding energies E_b listed in Table II. The correction for higher-order correlation effects does not change the qualitative picture painted in the previous section. The only change in relative stabilities is that PA1 becomes slightly more stable than B1 but this is not significant because the two structures are separated by less than 0.1 kcal/mol. The higher-order correction increases the energy separation between the global minimum AS2 and the next lowest structure (AS3) to 0.26 kcal/mol.

Next, we consider the effects of zero-point vibrations. The highest level at which we were able to compute the zero-point energy (ZPE) was B3LYP/aug-cc-pVTZ. Moreover, the ZPE was obtained from harmonic frequencies even though some of the intermolecular vibrational modes are likely to be significantly anharmonic. Hence, our ZPE values should be regarded with a good deal of skepticism. The quantity of interest to us is the difference δ_v between the binding energies computed with and without ZPE corrections. The correction δ_v , computed at the B3LYP/aug-cc-pVTZ level, is listed in Table III together with our best estimate of ZPE-corrected binding energies obtained by adding δ_v to the binding energies listed in the last column of Table II.

The ZPE correction does not vary greatly for different structures of the formic acid tetramer. The correction is most different for the cyclic CZ structure. The only changes to the order of relative stability are that B1 and PA1 interchange places, as do SS2 and PA3.

The dimer forms a substantial fraction of a gas-phase sample of formic acid. Hence, it is also of interest to consider tetramer binding energies with respect to two dimers especially for the π stacks and PA structures. Calculations entirely analogous to those described above led to the binding energies summarized in Table IV. The binding energies with respect to two dimers are about an order of magnitude smaller than their counterparts with respect to four monomers. Unsurprisingly, the relative stability order is the same as when the reference is four monomers. The cyclic structure CZ with all monomers in the Z conformation is less stable than two dimers.

V. CONCLUSIONS

Our best *ab initio* calculations suggest that an aligned π - π stack of two dimers (AS2) is very likely to be the global minimum of the formic acid tetramer but there are two other π - π stacks within 0.5 kcal/mol. Moreover, a planar association of two dimers, a bowl structure, and yet another π - π stack all lie within 1 kcal/mol of the lowest-energy structure. Thus, π - π interactions prove stronger than C-H \cdots O interactions for formic acid tetramers. However, the energy differ-

ences are small, and it would be injudicious to generalize this conclusion to other systems.

The potential energy surface is rather flat with respect to rotation of one of the dimers, relative to the other dimer in an aligned stack, about the axis passing through the inversion centers of the dimers. A fuller examination of pertinent cuts through the potential energy surface seems warranted; the results might increase understanding of π - π interactions in general.

ACKNOWLEDGMENTS

The authors are grateful for an ample supply of computer time on the Linux clusters Schrödinger II and III at the University of Vienna. The authors thank Shamus Blair for assistance with the diagrams. One of the authors (A.J.T.) thanks the Natural Sciences and Engineering Research Council of Canada for continuing support.

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