# COUNTERPOISE-CORRECTED POTENTIAL ENERGY SURFACES OF SIMPLE HYDROGEN-BONDED SYSTEMS

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*Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.*

Geometric and energetic characteristics of various simple hydrogen-bonded complexes (water dimer, hydrogen fluoride dimer, formamide dimer, formic acid dimer, glycine dimer) have been studied by gradient optimization, which *a priori* eliminates the basis set superposition error (BSSE) by using the counterpoise (CP) method, as well as by the standard gradient optimization. Calculations were done at the Hartree–Fock, correlated MP2 and DFT levels with small- and medium-basis sets. The CP-corrected and standard PESs differ, depending on the theoretical level used. Larger differences were found if the correlation energy was included. Intermolecular distances from the CP-corrected PES are consistently longer, and the respective difference may be significant (≈0.1 Å). The stabilization energies obtained from the CP-corrected PES are always larger than those from the standard PES. Optimization at the standard PES might result in a wrong structure. For example, the "quasi-linear" structure of the $(HF)_2$ (global minimum) does not exist at the standard MP2/6-31G** and DFT/B3LYP/6-31G** PESs and it is found only when passing to the respective CP-corrected PESs.
**Key words:** Counterpoise correction; Potential energy surfaces; Hydrogen bonds; *Ab initio* calculations; Quantum chemistry.

Molecular clusters can be studied theoretically using variation or perturbation method. The former method determines the interaction energy as the difference between energy of supersystem and sum of energies of subsystems. In the perturbation method, an interaction energy is evaluated directly as a sum of various energy contributions (Coulombic, exchange-repulsion, induction, dispersion, ...). All these terms have clear physical meaning and, due to the basic principle of the method, the computation time is expected to be more favourable than that in the variation method. In fact, the opposite is true and perturbation method is nowadays used only rarely; vast majority of complex calculations is done using variation (supermolecular) method. This method is straightforward but the respective interaction energy is affected by a serious obstacle – the fact that different basis sets are used for evaluation of energies of supersystem and subsys-

tems. Supersystem, having larger basis set than subsystems, undergoes an artificial stabilization which is commonly referred to as basis set superposition error (BSSE). Boys and Bernardi[1] introduced in 1970 the function counterpoise (CP) method which eliminates the BSSE. The principle of the method is simple, subsystems are not treated in their own basis sets but in the basis sets of the whole complex. Enormous literature has been devoted to this subject and opinion about the use of CP method especially in the early years after its introduction was not unique. The importance of BSSE corrections and necessity of taking it completely into account was recognized by R. Zahradnik already in the seventies[2] and recommendation for consideration of the BSSE was included in his well-known review[3] on molecular interactions. Convincing arguments collected in Warsaw[4] and Utrecht[5] laboratories give definitive arguments supporting the original procedure of Boys and Bernardi[1] and the BSSE must be always eliminated.

In the case of single-point calculations, the situation is clear and interaction energy is corrected for the BSSE. Structure of larger clusters cannot be, however, evaluated using the point-by-point method and, instead, the gradient optimization is to be applied. Usually, the complex is optimized using standard supermolecular gradient optimization and only at the very end, *a posteriori*, the BSSE correction is added. This means that structure of a complex is optimized at standard potential energy surface (*i.e.*, without the CP corrections) and not at the theoretically more justified CP-corrected potential energy surface (PES). The final solution includes the use of BSSE-free techniques. For small complexes, an evidence was found[6–8] that proper consideration of CP corrections affects not only the interaction energy but also geometry and vibration frequencies. The problem of gradient optimization was not solved by introduction of "chemical Hamiltonian" (ref.[9]) which eliminates the BSSE from the very beginning since this method was not extended for the beyond-Hartree–Fock analytic gradient. Simon, Duran and Dannenberg[10] recently offered a straightforward and elegant solution. Their method allows to evaluate the gradient and Hessian of a complex at any *ab initio* level, using arbitrary *ab initio* code. The authors[10] applied the method to three H-bonded complexes (HF···HCN, HF···$H_2O$, HCCH···$H_2O$) and demonstrated that various complex properties obtained from CP-corrected PES differ from those obtained from a standard surface.

It is known that the BSSE also depends on the structure of a complex, and more compact structures are associated with larger BSSE than the "extended" ones. The multiminima PES determined by the standard and CP-corrected optimization can thus differ. Relative stabilization energies of various stationary points are more important for reactivity studies than the respective absolute values. Comparison of both multiminima surfaces is thus of topical importance.

The aim of the present paper is to compare geometries and interaction energies of various isomers of simple H-bonded systems at the CP-corrected and standard PESs using different *ab initio* theoretical levels with small- and medium-basis sets. The aim of the paper is not to make the benchmark calculations but merely to point out dif-

ferences between standard and CP-corrected PESs. It must be namely kept in mind that small- and medium-basis sets are used and will be used in near future for studies of extended molecular clusters like, *e.g.*, DNA base pairs. The benchmark calculations on CP-corrected PESs of small H-bonded systems using extended basis sets with consideration of anharmonicity are in progress[11,12].

## COMPUTATIONAL

The computational method used follows closely the procedure of Simon *et al.*[10]. Our code constructs CP-corrected interaction energies and its derivatives with respect to all internal coordinates by consecutive calls of the GAUSSIAN94 code[13] for the supermolecule and subsystems with and without "ghost" functions (Eqs 4 and 5 in ref.[10]). This information is used for geometry optimization. We used a combined algorithm: steepest descent with linear scaling if the gradient norm is large, followed by the DIIS (direct inversion in the iterative subspace) method of Pulay[14]. If the criteria of the optimization procedure are properly selected, the convergence is rapid. Typically, 10–15 gradient evaluations is needed to reach criteria of $10^{-5}$ hartree/bohr or hartree/rad for the systems studied. The present version of the code does not allow to use the dummy atoms as well as to evaluate Hessians and vibration frequencies.

Interaction energy was evaluated at the Hartree–Fock (HF), second-order Moller–Plesset (MP2) and Density Functional Theory (DFT) levels. All the correlation calculations were performed with frozen-core approximations, *i.e.*, the innermost electrons were not considered. The DFT calculations were performed with the Becke3LYP (B3LYP) functional containing gradient corrections to both exchange and correlations. Throughout the study, various split-valence basis sets were used: 6-31G, 6-31G*, 6-31G** and 6-311G(2d,p).

## RESULTS AND DISCUSSION

*$(H_2O)_2$.* Three stationary points exist at the PES of the water dimer (Fig. 1), the "quasi-linear" structure (*a*) represents the global minimum while the cyclic (*b*) and bifurcated (*c*) structures are saddle points. Geometric and energetic characteristics of those stationary points obtained from the CP-corrected and standard PESs are collected in Table I; calculations were performed at the MP2/6-31G** and B3LYP/6-31G** levels. Stabilization energies obtained from the CP-corrected PES are consistently larger than those obtained from the standard one; the largest difference was found for the global minimum – "quasi-linear" structure. The order of stability of various structures at both surfaces is the same, though the relative values of stabilization energy are larger at the CP-corrected PES. The cyclic structure corresponds to the stationary point only at both standard PESs; this structure was not found at the B3LYP CP-corrected PES. The intermolecular oxygen–oxygen distance obtained from the CP-corrected PES is again

systematically longer than that from the standard PES. This difference is largest for the bifurcated structure.

The global minimum, the "quasi-linear" structure, was additionally studied at various HF and MP2 levels and the respective geometric and energetic characteristics are summarized in Table II. Stabilization energies obtained from the CP-corrected PES are again systematically larger than those from the standard PES; these differences are at the MP2 level significantly larger. Also the intermolecular oxygen–oxygen distances

TABLE I
MP2/6-31G**- and B3LYP/6-31G**-optimized oxygen–oxygen distance (in Å) and stabilization energy (in kcal/mol) for various structures of the water dimer obtained from the CP-corrected and standard (in parantheses) PESs

| Dimer characteristics | Method | Structure | | |
|---|---|---|---|---|
| | | linear[a] | cyclic[b] | bifurcated[c] |
| $r$(O–O) | MP2 | 2.991 (2.913) | 2.811 (2.714) | 3.077 (2.926) |
| | B3LYP | 2.874 (2.900) | [d] (2.707) | 2.927 (2.890) |
| $\Delta E$ | MP2 | 5.07 (4.68) | 3.67 (3.62) | 3.34 (3.31) |
| | B3LYP | 5.18 (5.05) | [d] (3.46) | 3.23 (3.16) |

*Cf.* Fig. 1: [a] structure *a*, [b] structure *b*, [c] structure *c*. [d] Cyclic structure does not correspond to the stationary point at the CP-corrected PES.

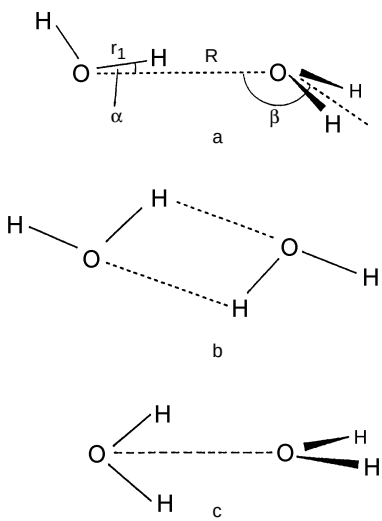



FIG. 1
Structures of the water dimer

from the CP-corrected surface are systematically longer than those from the standard PES. This difference is the smallest (0.001 Å) for the HF/6-31G level and largest (0.129 Å) for the MP2/6-311G(2d,p) one. Also the linearity of the H-bond (angle α) is affected by the inclusion of the BSSE; the CP-corrected surface is characterized by a considerably more linear H-bond. Differences in this angle are especially large at the correlated MP2 level. The nonplanarity of the proton acceptor molecule (angle β) is sensitive to the quality of the PES as well, and the standard PES is characterized by a systematically smaller angle β. This difference is again larger for correlated calculations.

The experimental intermolecular distance (2.946 Å, ref.[15]) is shorter than our best CP-corrected estimates from the correlated calculations. The experimental oxygen–oxygen distance is bracketed by MP2 values from both surfaces and higher-level calculations are required for quantitative comparison with experiment. From the data presented in Table II, it is, however, evident that standard PES (in comparison with the CP-corrected one) yields shorter intermolecular oxygen–oxygen distances, larger nonlinearity (angle α) and larger angle the proton-acceptor molecule includes with the O···O axis (angle β).

Recent theoretical studies on the water dimer[16,17] estimate stabilization energy around 5.0 kcal/mol and intermolecular distance around 2.9 Å. Evidently, our CP-corrected correlated stabilization energies reasonably agree while the CP-corrected distances are predicted to be longer by about 0.1 Å.

*$(HF)_2$*. Two stationary points are known to exist at the PES of this dimer, the "quasi-linear" and the cyclic one (Fig. 2, structures *a*, *b*). The former structure corresponds to the energy minimum while the latter is the transition structure separating two equivalent minima. For the reactivity studies, the energy difference between these two points provides an important information. As in the case of the previous complex, we tried to

TABLE II
Geometric (in Å and °) and energetic (in kcal/mol) characteristics of the "quasi-linear" structure of the water dimer obtained from the CP-corrected and standard (in parentheses) PESs at various theoretical levels

| Method[a] | $R$ | $r_1$ | α | β | $-\Delta E$ |
|---|---|---|---|---|---|
| HF/6-31G | 2.844 (2.843) | 0.957 (0.957) | 0.2 (0.3) | 150.1 (142.4) | 7.05 (7.05) |
| HF/6-31G* | 3.001 (2.971) | 0.952 (0.952) | 1.5 (5.2) | 121.7 (115.9) | 4.78 (4.70) |
| MP2/6-31G** | 2.991 (2.913) | 0.967 (0.967) | 2.7 (9.7) | 129.5 (99.1) | 5.07 (4.68) |
| MP2/6-311G(2d,p) | 3.025 (2.896) | 0.965 (0.967) | 2.0 (9.1) | 110.7 (101.6) | 4.61 (4.20) |

[a] Bond lengths and the valence angle of the isolated water molecule calculated in the sequence of used theoretical levels are: 0.950, 111.6; 0.947, 105.5; 0.992, 103.7; 0.961, 103.4, respectively.

determine the relative energies of these two structures, first at the MP2/6-31G** level (Table III). To our surprise, two different stationary points exist only at the CP-corrected PES and at the standard PES, there exists only one stationary point corresponding to the cyclic structure. From Table III, it is evident that DFT/B3LYP calculations yield exactly the same results. The quasi-linear structure is localized only at the CP-corrected PES. This means that the standard MP2 and DFT/B3LYP optimizations give qualitatively wrong structures. Geometric characteristics and interaction energies obtained at HF and MP2 levels with various basis sets are summarized in Table III. All global minima obtained at the HF level are consistent with the "quasi-linear" structure. The linearity (angle β) is consistently smaller at the CP-corrected surface. The same is true for the angle α which is consistently larger by about 20° at the CP-corrected PES. Passing to the correlated levels (standard PES) reduces the differences between both structures. At the MP2/6-31G** level, the "quasi-linear" structure disappears. Extending the basis set gives a slight improvement but the angle β is still too large and angle α too small. On the other hand, the CP-corrected angular geometric characteristics obtained at correlated levels agree nicely with experimental values[18] ($R$ = 2.72 ± 0.03 Å, α = 117 ± 6°, β = 10 ± 6°). As expected, the intermolecular distance $R$ is consistently larger at the CP-corrected PES. While the former value from MP2/6-311G(2d,p) calculations is larger than the experimental value, the latter is too short. Evidently, as in the previous case, basis sets used are too small for making any reliable comparison with experiments. Further, in order to find a trend in calculated results, the basis sets used should be improved in a systematic way. Finally, the proton-donor bond length (not shown) is at both surfaces longer than the proton-acceptor bond lengths, the differences at various levels being at both surfaces similar. Stabilization energies obtained from the CP-corrected PES are, as in all previous cases, larger than those from the standard PES. Our best CP-corrected estimate from the MP2/6-311G(2d,p) calculations (4.4 kcal/mol) agrees well with the experimental value (4.6 ± 0.2 kcal/mol) taken from ref.[17].

From the recent theoretical literature, we will mention only a study of Peterson and Dunning[19] using MP2 and CCSD(T) methods with extended aug-cc-pVQZ basis set.

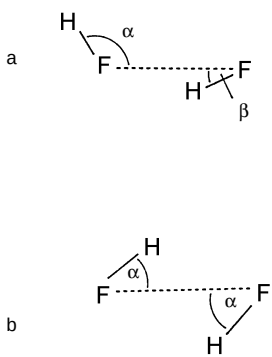



FIG. 2
Structures of the hydrogen fluoride dimer

TABLE III

Structural (in Å and °) and energetic (in kcal/mol) characteristics of the "quasi-linear" (Fig. 2, *a*) and cyclic (Fig. 2, *b*) structures of the $HF_2$ dimer obtained from the CP-corrected and standard PESs at various theoretical levels

| Level | PES | "Quasi-linear" | | | | Cyclic | | |
|---|---|---|---|---|---|---|---|---|
| | | R | α | β | $-\Delta E$ | *R* | α | $-\Delta E$ |
| HF/6-31G | CP-corrected | 2.740 | 143.1 | 3.7 | 6.26 | 2.704 | 59.9 | 3.86 |
| | standard | 2.706 | 125.1 | 8.5 | 6.26 | 2.571 | 55.9 | 3.56 |
| HF/6-31G* | CP-corrected | 2.798 | 117.7 | 6.9 | 4.54 | 2.738 | 55.3 | 3.18 |
| | standard | 2.709 | 96.7 | 17.0 | 4.27 | 2.596 | 51.8 | 2.92 |
| B3LYP/6-31G** | CP-corrected | 2.749 | 111.4 | 6.9 | 5.28 | 2.654 | 50.2 | 3.73 |
| | standard[a] | – | – | – | – | 2.492 | 46.4 | 3.27 |
| MP2/6-31G** | CP-corrected | 2.800 | 115.4 | 6.5 | 4.72 | 2.745 | 53.3 | 3.09 |
| | standard[a] | – | – | – | – | 2.539 | 48.3 | 2.49 |
| MP2/6-311G(2d,p) | CP-corrected | 2.820 | 116.3 | 6.6 | 4.40 | 2.741 | 52.9 | 3.04 |
| | standard | 2.682 | 91.9 | 17.5 | 3.97 | 2.599 | 49.3 | 2.78 |

[a] No "quasi-linear" structure obtained.

MP2 and CCSD(T) intermolecular distances *R* were found to be 2.737 and 2.732 Å, respectively. After correcting for the BSSE, slightly larger values resulted: 2.753 and 2.745 Å, respectively. Because the BSSE corrections were estimated by the point-by-point one-dimensional approach, their values should be taken with care. Corrected and uncorrected (in parentheses) stabilization energies obtained at MP2 and CCSD(T) levels[19] amount to 4.63 (4.38) and 4.72 (4.48) kcal/mol, respectively. Evidently, our MP2/6-311G(2d,p) stabilization energy obtained from the CP-corrected PES is close to both stabilization energies where the BSSE was added *a posteriori*, while the intermolecular distance obtained from the CP-corrected PES is longer.

At the highest theoretical level (MP2/6-311G(2d,p)), the energy difference between "quasi-linear" and cyclic structures amounts to 1.36 kcal/mol (CP-corrected PES). At the same theoretical level but at the standard PES, this energy difference becomes smaller (1.19 kcal/mol). Comparing uncorrected total energies of the complex, we found that the cyclic structure is by 0.029 kcal/mol more stable than the "quasi-linear" one. Only after correcting for the BSSE, the "quasi-linear" structure becomes more stable than the cyclic one. Evidently, evaluation of geometries and relative energies of various stationary points at the PES is a key problem and attention should be paid to proper consideration of the BSSE. Correct relative energies can be obtained only from the CP-corrected PES.

*Formamide dimer*. The PES of the formamide dimer (Fig. 3) contains four stationary points[20]. The cyclic structure of this dimer (Fig. 3, *a*) possesses two H-bonds and has a pattern similar to DNA base pairs which were studied in our laboratory intensively in the past years[21]. The four structures were studied at the HF/6-31G* level and their geometric and energetic characteristics are summarized in Table IV. The order of stability of various structures is at both surfaces retained, structure *a* (Fig. 3) being dominantly the most stable one. If, however, the relative energies are considered, we found some differences. First, local minimum (Fig. 3, structure *c*) is located 3.2 kcal/mol

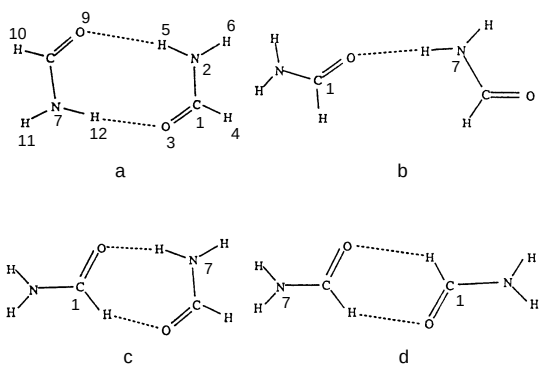



FIG. 3
Structures of the formamide dimer

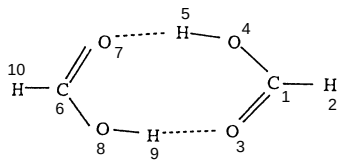
above the global minimum at the standard PES. This value increases to 4.4 kcal/mol at the CP-corrected PES; extending the basis sets and taking more correlation energy into account further increases this difference. The most stable structure (Fig. 3, *a*) was studied at three different levels and the respective results are given in Table V. As with the previous complexes, stabilization energies from the CP-corrected PES are systematically larger than those from the standard PES. Also intermolecular distances are systematically longer at the former surface. The largest difference in stabilization energy and intermolecular distance was found at the MP2/6-31G** level.

*Formic acid dimer*. Cyclic structure of this dimer (Fig. 4, *a*) with two C=O···H–O H-bonds is very stable. By simultaneous transfer of two protons, it passes through a transition structure (Fig. 4, *b*) to the other energy minimum. The transition structure is characterized by symmetrical position of both hydrogens between the respective oxygens. We tried to optimize both stationary points at the CP-corrected surface but we failed with the transition structure. The respective algorithms require assigning all the atoms to the first or second subsystem. During the following optimization, both protons

TABLE IV
HF/6-31G* optimized C1–N7 distance (in Å) and stabilization energy (in kcal/mol) for various structures of the formamide dimer (Fig. 3) obtained from the CP-corrected and standard (in parentheses) PESs

| | Structure | | | |
|---|---|---|---|---|
| | *a* | *b* | *c* | *d* |
| *r*(C1–N7) | 3.774 (3.740) | 4.209 (4.101) | 3.551 (3.521) | 4.892 (4.845) |
| Δ*E* | 11.14 (11.10) | 5.68 (5.63) | 7.49 (7.46) | 3.79 (3.76) |

a

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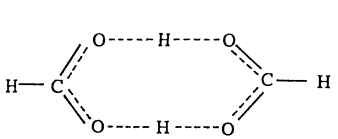


FIG. 4
Structures of the formic acid dimer

TABLE V
Geometric (in Å and °) and energetic (in kcal/mol) characteristics of the cyclic structure of the formamide dimer (Fig. 3, structure *a*) obtained from the CP-corrected and standard PESs at various theoretical levels

| Level | PES | $R_{29}$ | $r_{25}$ | $r_{89}$ | $\alpha_{259}$ | $\alpha_{125}$ | $-\Delta E$ |
|---|---|---|---|---|---|---|---|
| HF/6-31G | CP-corrected | 2.931 | 1.005 | 1.233 | 167.4 | 120.1 | 14.03 |
| | standard | 2.911 | 1.007 | 1.234 | 168.0 | 120.2 | 14.01 |
| HF/6-31G* | CP-corrected | 3.016 | 1.005 | 1.204 | 170.5 | 125.4 | 11.14 |
| | standard | 2.995 | 1.005 | 1.205 | 171.5 | 125.6 | 11.10 |
| MP2/6-31G** | CP-corrected | 2.972 | 1.018 | 1.235 | 173.6 | 120.3 | 12.37 |
| | standard | 2.906 | 1.021 | 1.238 | 175.0 | 120.6 | 12.14 |

TABLE VI
Geometric (in Å and °) and energetic (in kcal/mol) characteristics of the cyclic structure of the formic acid dimer (Fig. 4) obtained from the CP-corrected and standard PESs at various theoretical levels

| Level | PES | $R_{16}$ | $r_{45}$ | $\alpha_{145}$ | $-\Delta E$ |
|---|---|---|---|---|---|
| HF/-31G** | CP-corrected | 3.933 | 0.961 | 111.0 | 13.05 |
| | standard | 3.900 | 0.963 | 111.3 | 13.02 |
| MP2/6-31G** | CP-corrected | 3.915 | 0.989 | 108.8 | 13.21 |
| | standard | 3.833 | 0.995 | 109.5 | 12.92 |

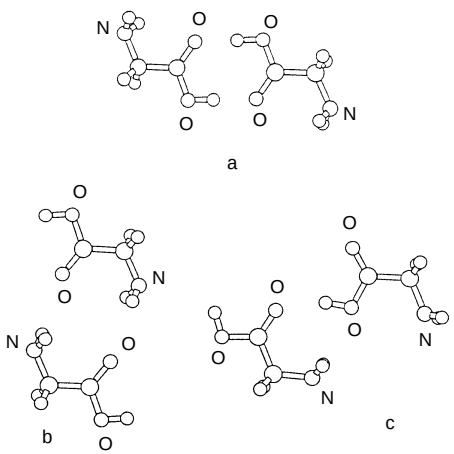


FIG. 5
Structures of the glycine dimer

migrate from the starting symmetrical position to the nonsymmetrical position characteristic of energy minimum. The presently used computational procedure thus does not allow to investigate such transition structures where some atoms are symmetrically shared by both subsystems.

Geometric and energetic characteristics of the energy minimum (Fig. 4, structure *a*) are summarized in Table VI; here we performed calculations only at the HF/6-31G** and MP2/6-31G** levels. From obtained values it is clear that also in this case, intermolecular distances from the CP-corrected PES are systematically longer. The respective difference is larger (≈0.08 Å) at the correlated level. Lengthening of the O–H bond upon formation of the H-bond is predicted at both PESs; this lengthening is smaller at the CP-corrected surface. This conclusion might be of importance since the elongation of the X–H bond upon formation of the X–H···Y H-bond is proportional to the observable red shift of the X–H stretching frequency.

*Glycine dimer*. The dimer is interesting since the isolated glycine possesses more stable isomers with energy difference below 3 kcal/mol. The PES of glycine dimer is thus very complex since dimers are formed not only between the same subsystem isomers but also between different isomers. Hence, the most stable structure of the dimer need not be formed from the most stable subsystem isomers, but by energetically higher-lying isomers. The energy loss resulting from the fact that the dimer is formed by higher isomers may be outweighed by the gain obtained from the dimer formation. HF/6-31G** stabilization energies (in kcal/mol) of three structures of the dimer (Fig. 5), obtained from the standard PES are the following: *a* 13.06, *b* 1.59, *c* 4.82. When passing to the CP-corrected PES, the change in absolute values of stabilization energies is marginal: *a* 13.07, *b* 1.65, *c* 4.83. Evidently in this case, the results from the CP-corrected and standard PESs are almost identical. Let us mention that while structures *a* and *b* are formed from isolated glycine molecules in their global minima, in the case of structure *c*, two different isomers participate. Nevertheless, the global minimum *a* remains clearly the most stable.

## CONCLUSION

*a*) CP-corrected and standard PESs of simple H-bonded complexes differ. The differences depend on the theoretical level and basis set used, and usually are larger at the correlated level. Intermolecular distances from the CP-corrected PES are systematically longer than those from the standard PES; the difference may be large (≈0.1 Å). Also the intermolecular angles from the two surfaces differ considerably. Stabilization energies obtained from the CP-corrected PES are always larger than the stabilization energies calculated in a usual way (*i.e.*, *a posteriori* corrected for the BSSE).

*b*) Stability order of various isomers of a molecular complex determined at both surfaces are mostly similar. The relative energies determined at both surfaces may, however, differ.

*c*) Optimization at the standard PES may sotimes lead to a wrong structure of a cluster, with respect to optimization at the rigorously CP-corrected PES. This conclusion is warning and gives a clear evidence about the necessity of using only the CP-corrected gradient optimization.

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