PCILO STUDY OF NON-BONDING INTERACTIONS

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The PCILO method has been used for study of non-bonding interactions in the systems water–water and water–ethylene. The PCILO method is unable to account correctly for the intermolecular non-bonding interactions of the types lone electron pair — lone electron pair and lone electron pair–π bond. The potential energy curves, which should be strongly repulsive, are predicted as being attractive. The results obtained are discussed from the point of view of energy partitioning in terms of PCILO theory.

Due to their important role in chemistry and biology, hydrogen bonds were studied with the use of both semiempirical[1,2] and *ab initio* methods[2,3]. The semiempirical CNDO/2 method was used particularly for large hydrogen-bonded systems[1,4–6], but most calculations were carried out without complete geometry optimization. The CNDO/2 calculations[7–9] of simple hydrogen-bonded systems ($(H_2O)_2$, $CH_3OH\cdots HF$) with full geometry optimization showed that the global minima corresponded to $O\cdots O$ and $O\cdots F$ "bonds" (in the water dimer and methanol–HF system, respectively) and not to hydrogen bonds. Calculations by Gregory and Paddon–Row[10] showed that results of the INDO method are substantially worse than those of the CNDO/2. The existence of intermolecular interactions of the types lone electron pair–lone electron pair and lone electron pair–π bond which was predicted by these methods is quite contrary to both chemical experience and the more reliable *ab initio* calculations[7,10,11]. Similarly, the semiempirical PCILO method[12,13], adopting approximations of the CNDO/2 method for calculation of the integrals was used, in the past, successfully especially in studies of large intermolecular hydrogen bonded systems[14–18]. The PCILO calculations[19,20] of simple hydrogen-bonded complexes showed that combination of the CNDO/2 parametrization with perturbation theory and inclusion of restricted configuration interaction in the PCILO method can lead to a substantial improvement of the results for the hydrogen-bonded complexes as compared with the original CNDO/2 and INDO methods. However, in the PCILO calculations as well as in the CNDO/2 studies, the only optimized distances were predominantly $R_{X-H...Y}$ and r_{X-H} in $X—H\cdots Y$ bonds, non-bonding interactions of other types than hydrogen bonds being not yet studied in these complexes by the PCILO method.

This communication deals with a detailed study of the water–water and water–ethylene systems with full gometry optimization with the aim of finding whether or not the PCILO method (similar to the CNDO/2) fails in calculations of the non-bonding interactions of the types lone electron pair–lone electron pair and lone electron pair–π bond.

CALCULATION METHOD

The calculations of interaction energy and geometry of the systems water–water and water–ethylene were carried out by the PCILO method with optimization of geometry[21]. The geometry of the complexes studied was minimized in two ways: *a*) Optimization with respect to the $X \cdots Y$ distance (X, Y = C,O) (Fig. 1). *b*) Full geometry optimization of the whole system. The interaction energy E_{int} was defined as the difference between the total energy of the isolated molecules and that of the model complex:

$$E_{int} = (E_X + E_Y) - E_{X \ldots Y}, \quad (X, Y = C, O). \qquad (1)$$

The PCILO-optimized geometry of the monomers (Table I) served as the starting geometry. The lone electron pairs at oxygen atom were defined in the sp^3 hybridized form. For the sigma lone electron pairs we took the bond length equal to 0·1 nm. The calculations were carried out with a Siemens 4 004/150 computer in the Computer Centre, Comenius University, using the QCPE No 272 program[21].

TABLE I

The PCILO-optimized geometry of water and ethylene

Water	$R_{O-H} = 0{\cdot}1042$ nm;	$\sphericalangle HOH = 102{\cdot}46°$
Ethylene	$R_{C-H} = 0{\cdot}1123$ nm;	$\sphericalangle HCH = 112{\cdot}24°$
	$R_{C=C} = 0{\cdot}1322$ nm;	$\sphericalangle CCH = 123{\cdot}88°$

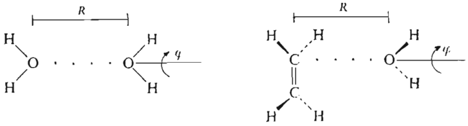

FIG. 1

The starting geometry of the water–water and water-ethylene systems

RESULTS AND DISCUSSION

Table II presents the PCILO results of the water–water and water–ethylene systems, the interaction energy of the dimers being obtained by varying the $R_{O...O}$ and $R_{O...C}$ distances. Variation of the φ angle showed in both the cases that the complexes with $\varphi = 90°$ are more stable. In all the cases studied we found attractive potential curves as function of the $R_{O...Y}$ distances ($Y = C, O$) (Fig. 2), hence the PCILO method (in contrast to experimental evidence and to the *ab initio* calculations of water dimer[7,11]) presumes the existence of stable complexes involving "bonds" of the types lone electron pair–lone electron pair or lone electron pair–π bond. Spoorling and Snook[22] studied the hydrogen-bonded water dimer by the PCILO method. They found that the open dimer is the most stable one, the calculated interaction energies being 18·41 and 23·44 kJ mol^{-1} for the experimental and the optimized geometries of the monomers, respectively. Comparison of these results with the interaction energy

TABLE II

The PCILO equilibrium geometry and interaction energy of the water–water and water–ethylene dimers (Fig. 1)

Dimer	$R_{O...Y}$, nm ($Y = C, O$)	φ(°)	E_{int} kJ mol^{-1}
I water–water	0·165	0	33·56
II water–water	0·162	90	36·17
III water–ethylene	0·190	0	35·80
IV water–ethylene	0·184	90	45·81

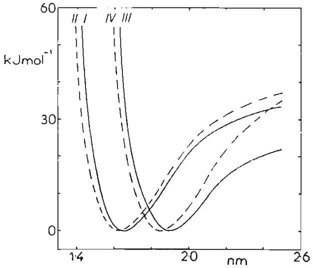

FIG. 2

The PCILO potential curves for the complexes *I* to *IV* (Table II) of the water–water and water–ethylene systems — dependence on the $R_{O...Y}$ ($Y = C, O$) distances found by us for the water dimer (where there exists the O···O interaction but no hydrogen bond interaction) shows that the complex calculated by us is the most stable one. Hence the existence of this complex must be ascribed to failure of the PCILO method in studies of the intermolecular interactions of the type lone electron pair–lone electron pair. Similarly, the PCILO results for the water–ethylene dimer (Table II) predict the existence of a considerably stable dimer with the "bond" of the type lone electron pair–π bond, the dimer with the angle $\varphi = 90°$ being more stable. Again the existence of this complex can be ascribed to incapability of the PCILO method to evaluate correctly the intermolecular interactions of the type lone electron pair–π bond.

Fig. 3 gives the PCILO geometry of fully optimized complexes *II* and *IV* (Table II), the geometry arrangement of the dimers showing a change and decrease of total energy, which results in further stabilization of these systems.

An explanation of origin of these interactions can be given by the energy partitioning. The total interaction energy E_{int} in the PCILO formalism can be described[12] as follows:

$$E_{\text{int}} = \Delta E_0 + \Delta E_2 + \Delta E_3 \,, \tag{2}$$

where ΔE_i means contribution of the i-th order to the interaction energy. The contribution of the second order (ΔE_2) can be divided further into:

$$\Delta E_2 = \Delta m_1 + \Delta m_2 + \Delta d_1 + \Delta d_2 \,, \tag{3}$$

where Δm_1, Δm_2, Δd_1, and Δd_2 stand for polarization energy, delocalization energy, intrabond correlation energy, and interbond correlation energy, respectively. Table III gives the individual contributions to the interaction energy in the water dimer. Out of the contributions of the third order, those are only given which contribute significantly to the interaction energy. ΔE_0 is negative *i.e.* destabilizing. The contribution of the second order (ΔE_2) is positive (*i.e.* stabilizing), the main contribution being

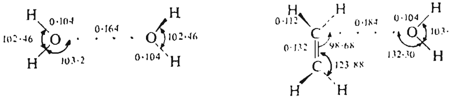

FIG. 3

The PCILO optimized geometry of the *II* system water–water and *IV* system water–ethylene (the angles and distances are given in degrees and nm, respectively) that of the delocalization energy Δm_2, but the total interaction energy $\Delta E_{int} = \Delta E_0 + \Delta E_2$ is negative (*i.e.* destabilizing) for the optimum O···O distance. The main stabilizing contribution is the ΔE_3 term of the perturbation expansion which is large and positive (in contrast to the hydrogen-bonded O—H···O water dimer[22]), the most significant interaction being delocalization-delocalization, Δdd.

From Table III it follows that the failure of the PCILO method in proper evaluation of non-bonding interaction in the water dimer is due, first of all, to the delocalization energy, which is large and stabilizing. The overestimation of the delocalization energy can be ascribed to the CNDO/2 parametrization of the PCILO method. Another possible source of error is the fact that lone electron pairs have no corresponding antibonding orbitals in the PCILO formalism, hence the lone electron pairs are inevitably defined worse than the bonding electron pairs. Moreover the PCILO method uses the minimum basis and only for valence electrons. The calculations of intermolecular interaction energies in the minimal basis are known[23] to lead to the so called superposition error of the basis set. Lipinski and Chojnacki[24] recently studied effect of the error of superposition of basis set on calculation of the interaction energies in terms of the CNDO/INDO methods. They showed that the determined effect of the error of superposition of the basis set enables explanation of the previously found erroneous structures[7–10,25] of dimers of water and ethylene.

In conclusion it must be noted that the calculations of intermolecular complexes by the PCILO method with full geometry optimization need considerable caution, because the energy hypersurface involves not only the minima corresponding to the

TABLE III

The PCILO partitioning of interaction energy for the *II* water dimer

Contribution to interaction energy, kJ mol^{-1}	$R_{O...O} = 0{\cdot}162$ nm
The zero order energy, ΔE_0	−102·970
Polarization energy, Δm_1	0
Delocalization energy, Δm_2	93·388
Intrabond correlation energy, Δd_1	1·732
Interbond correlation energy, Δd_2	5·432
The second order energy, ΔE_2	100·552
$\Delta E_0 + \Delta E_2$	−2·418
1 bond—2 bond correlation interaction, Δb_2	−2·304
Delocalization-delocalization interaction, Δdd	44·060
2 bond—2 bond correlation interaction, Δb_3	−3·168
The third order energy, ΔE_3	38·588
$\Delta E_0 + \Delta E_2 + \Delta E_3$	36·17

complexes in accordance with experimental experience and with *ab initio* calculations but also such minima which correspond to unrealistic structures. The existence of such structures must be ascribed to the failure of the PCILO method in correct evaluation of the non-bonding interactions of the types lone electron pair–lone electron pair and lone electron pair–π bond. To remove this imperfection of the PCILO method, it is necessary (as in the CNDO/INDO methods[24]) to evaluate the error caused by superposition of the basis set or to apply an extended basis for atomic orbitals of valence electrons.

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