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Full vs. constrain geometry optimization in the open–closed method in estimating the energy of intramolecular charge-inverted hydrogen bonds

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ABSTRACT

We investigate several variants of the open–closed method to estimate the energy of the intramolecular charge-inverted hydrogen bond in model systems. We show that, depending on whether the geometry of the reference open system is partially or fully optimized, the estimated value of the energy may be from a wide range. It seems that the most reasonable reference system should have geometry parameters optimized but with the simultaneous freezing of those geometry parameters whose relaxation may lead to the significant change in the bonding pattern. Results obtained by means of two other estimating methods are studied. Reasonable estimates of energy values can be obtained only if full geometry optimizations of the molecules being components of the isodesmic reaction do not lead to any significant difference in the bonding pattern comparing with that of the interaction-bonded system. All calculations were performed using the B3LYP/aug-cc-pVTZ approximation.

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1. Introduction

As opposed to the energy of the intermolecular hydrogen bond, the energy of the *intra*molecular hydrogen bond [1] cannot be defined in a strictly quantum mechanical way, since any attempt of extracting the energy of the intramolecular hydrogen bond from the total energy of the intramolecularly hydrogen-bonded system gives a high degree of discretion of the system chosen as a reference [2–4]. Nevertheless, some additive schemes to 'isolate' the energy of the intramolecular hydrogen bond from the total energy of a given molecule can be proposed [2–42]. They, however, strongly depend on the reference system chosen in such an approximate procedure.

One of the most popular [1–22] estimation schemes is based on the comparison of the total energy of the hydrogen-bonded (the so-called chelate or closed) form with the total energy of an open system obtained after the rotation of either the proton-donor or the proton-acceptor group leading to breaking the hydrogen bond [6,7]. Estimations based on the open form obtained either in the former or in the latter case lead, in general, to different values of the energy of the intramolecular hydrogen bond, since different references are used in both variants [3]. But even after the decision, which of these open forms is to be used in the estimation scheme, there is still the issue whether or not the geometry of the open sys-

tem should be fully optimized [3,5]. It seems that this problem is not often investigated and only in few papers some approach to this issue is proposed [3–7]. Most likely Schuster was the first who suggested [6] to use the open form with "the least changes in molecular geometry besides a cleavage of the H-bond". Then he pointed that (the open reference system) "need not be a local minimum of the energy surface" [7] and that this procedure "seems to be more appropriate", that the full geometry optimization of the open reference form, "in cases where it can be applied, because it does not mix a large energy of isomerization into the H-bond energy" [7]. Although, this comment seems to suggest that a 'real' hydrogen bond energy can be attributed to the *intra*molecular hydrogen bond, Schuster points that any splitting of the change in total energy into pure isomerization and H-bond energy is artificial [7].

If one tries to extract the energy of the intramolecular hydrogen bond from the total energy of the hydrogen-bonded (closed) system and assumes this energy as being the difference between the energy of the hydrogen-bonded system (E_c in Fig. 1) and the energy of the fictitious system having all geometry parameters exactly the same as in the hydrogen-bonded system (E_c^f in Fig. 1), but with the hydrogen bond being 'excluded', then the conservation of values of all geometry parameters and performing single point energy calculation for the open reference system ($E_o^{f,c}$ in Fig. 1) is more justified rather than performing the full geometry optimization. This situation is shown on the left hand side of Fig. 1.

On the other hand, however, the acceptance of this model seems to be questionable, since the geometry of the hydrogen-bonded system is related with the existence of the hydrogen bond.

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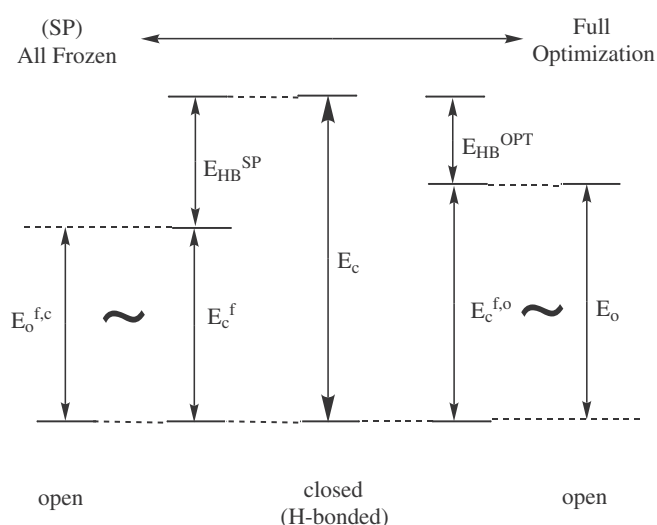
Fig. 1. Two models of the partition of the total energy of the hydrogen-bonded system (E_c) to the energy of the intramolecular hydrogen bond and the energy of some fictitious system obtained after the "exclusion" of this hydrogen bond.

It is clear if one considers geometry changes that arise during the open form→closed form step. The formation of the intramolecular hydrogen bond on passing from any open system to the closed one is inseparably related to the continuous change of the geometry of the open system to that of the hydrogen-bonded system. This geometry change is an integral effect accompanying the intramolecular hydrogen bond formation and should be investigated in this way. Thus, from this point of view, the preservation of values of all geometry parameters as they are in the closed hydrogen-bonded form and keeping them frozen in the open reference form (i.e., performing the energy single point calculation for the open form) is equivalent with the conservation of 'the information' about the hydrogen bond, since the presence of the hydrogen bond in the closed form is marked in conserved values of geometric parameters in the open reference system. Thus, it seems that performing the *full* geometry optimization of the reference open system is more justified from this point of view. The full geometry optimization of the open reference system is nowadays treated rather as a standard procedure in the open–closed method [21]. This of course corresponds to a different partition scheme of the total energy of the closed form as depicted on the right hand side of Fig. 1. Since $|E_o| > |E_o^{f,c}|$ then E_{HB}^{OPT} should be smaller than E_{HB}^{SP} (see Fig. 1).

Nevertheless another problem arises here. Namely, the full geometry optimization of the reference system may lead to structures where some new important interactions (whatever attractive or repulsive) are present even though they are not present in the closed hydrogen-bonded form [2–4,16–18]. Also the geometry of the fully optimized reference system may significantly vary from that of the hydrogen-bonded form. This may be manifested, for example, by significantly different values of bond distances, plane or dihedral angles. For example, Buemi et al. [3] rebuked the use of the most extended enol and enethiol tautomers of thiomalondialdehyde as reference structures [2] since the framework of the double bonds (trans) seems to be too different from that of the closed form (cis).

Thus, it seems that the most reasonable option of proceeding in the estimation of the energy of the intramolecular hydrogen bond (using the open–closed method) is performing the *constrain* (i.e., *partial*) geometry optimization of the reference system. To the best of our knowledge the issue of performing the constrain geometry optimization of the reference system was not investigated earlier in the literature. In this paper we propose keeping unchanged and frozen only those geometry parameters whose optimization

could lead to some significantly different entities, i.e., possessing significantly different arrangements of atoms, bonding or non-bonding interactions, etc. than in the hydrogen-bonded system. It seems that freezing dihedral angles that govern the positions of proton-donor and proton-acceptor atoms should be essential here, since it may prevent deflections of proton-donor and/or proton-acceptor groups leading to such significantly different entities. Although such a procedure may seem to be somewhat artificial, it is aimed against the possibility of obtaining a reference structure with important new interactions that could lead to unreliably small or high value of the hydrogen bond energy if these angles were not frozen during the geometry optimization procedure. Of course, although this procedure is safer than the full geometry optimization, it does not need to be used in all cases. For example, if we expect that the full geometry optimization will not lead to any new important interactions (whatever repulsive or attractive) then the full geometry optimization may be performed.

It should be mentioned that in general the term 'open' reference system can also be widened to 'open' systems which not necessarily are obtained after the rotation of either the proton-donor or the proton-acceptor group [2–5,8,9], however, this may lead to a different pattern of bonding that brings about the less reliability of this approach [3]. If this widen definition of the 'open' reference system is accepted then the ortho-para approach [5,24], where one compares energies of para- and hydrogen-bonded ortho-substituted forms of a molecule, may also be understood as a particular case of the open–closed method.

Very recently [43] we have introduced a term "charge-inverted hydrogen bond" that refers to a bonding between negatively charged H of the $X^{\delta+}$—$H^{\delta-}$ unit and electron deficient $\supset Y$[1] replacing $\subset Y$ of the usual hydrogen-bonded system, i.e., $\supset Y$ being an atom with lone-pair vacancy. Then a particular case of this interaction, the intramolecular charge-inverted hydrogen bond (IMCIHB) of the $Si^{\delta+}$—$H^{\delta-} \cdots \supset Al$ type, was investigated in several model systems [44]. This paper is the further study of these systems which are now used to investigate the issue of the acceptance of a given model of the geometry optimization, i.e., full or constrain, of the reference system in the open–closed method. We have estimated values of the energy of IMCIHBs using seven different variants of the open–closed method. They are based on comparing the energy of the closed system with the energy of the open system obtained after either the energy single point calculation or either the constrain or full optimization of its geometry. These methods are described in the Methodology section in more detail. Results obtained be means of these variants of the open–closed method are also compared with those obtained if other popular estimation procedures are used. Particular interest is given to the method where so-called isodesmic/homodesmic reactions are used [22–24,37,45–47].

2. Methodology

All calculations concerning systems with the IMCIHB and their references have been performed using the B3LYP/aug-cc-pVTZ level of theory [48–53] by means of Gaussian 03 set of codes [54]. For the geometry fully optimized systems the frequency analysis was used to verify that the optimized geometries correspond to the ground state stationary points. No imaginary frequencies were found. The analysis of the electron density distribution has been done by means of Xaim program [55].

To estimate the energy of the IMCIHB in investigated systems we have used seven variants of the open–closed method. In the first variant, the reference system had values of all geometry parameters exactly the same as in the $H^{\delta-} \cdots \supset Al$ interaction-bonded system

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[1] Symbol $\supset$ denotes the electron lone-pair vacancy on the proton-acceptor atom.

and only the energy single point calculation was performed for the reference system. This variant hereafter will be denoted as SP. In variants B and BA we only performed optimization of bond distances or of bond distances and plane angles, respectlively, while all the other geometry parameters have been taken from the closed system and kept frozen during the procedure of the geometry optimization. In the variant denoted as SiAlH2-f we have kept frozen only values of dihedral angles that govern the positions of the Si atom and of the –AlH$_2$ group in respect to the skeleton of the reference system. In the variant SiH2-f only dihedral angles describing the positions of the Si atom and of both hydrogen atoms of the –AlH$_2$ group have been frozen during the geometry optimization, while in the variant denoted as H2-f only dihedral angles of both hydrogen atoms of the –AlH$_2$ group have been frozen. Finally, we have also estimated the energy of the IMCIHB by performing the full geometry optimization of the open reference system. This scheme will be hereafter denoted as OPT.

3. Full vs. constrain geometry optimization

Recently we have shown [43,44] that negatively charged hydrogen atom of the $X^{\delta+}$—$H^{\delta-}$ unit may interact with an atom possessing the electron lone-pair vacancy leading to the inter- [43] or intramolecular [44] charge-inverted hydrogen bond (denoted as CIHB and IMCIHB, respectively). An example of the interaction of this kind may be the $Si^{\delta+}$—$H^{\delta-}\cdots\supset Al$ IMCIHB investigated recently [44] in several systems forming five-, six-, and seven-membered *quasi*-rings. These systems are shown in Fig. 2. For the simplicity, these systems are given numerical labels as follows: (**1**) H$_3$Si—CH$_2$—CH$_2$—AlH$_2$, (**2**) H$_3$Si—CH$_2$—CH$_2$—CH$_2$—AlH$_2$, (**3**) H$_3$Si—CH=CH—CH$_2$—AlH$_2$, (**4**) H$_3$Si—CH$_2$—CH=CH—AlH$_2$, (**5**) H$_3$Si—CH=CH=CH=CH—AlH$_2$, (**6**) H$_3$Si—CH=CH—CH$_2$—CH$_2$—AlH$_2$, (**7**) H$_3$Si—CH$_2$—CH=CH—CH$_2$—AlH$_2$, (**8**) H$_3$Si—CH$_2$—CH$_2$—CH$_2$—CH$_2$—AlH$_2$.

It is seen from Fig. 2 that in the case of all investigated systems one of the hydrogen atoms of the –SiH$_3$ group is pointing towards the lone-pair vacancy of the Al atom and systems acquire closed structure with H$\cdots$Al distances being about 2 Å. This indicates the presence of the intramolecular charge-inverted hydrogen bond.

One of the most popular approaches used for the estimation of the energy of the intramolecular hydrogen bond is the method based on the comparison of energies of closed and open (being a reference) systems [1–22]. Most often the open form is assumed as being obtained after the rotation of either the proton-donor or the proton-acceptor group (see Fig. 3). However, in the more general grasp of the closed-open method, also some other 'open' forms can be applied [2–5,8,9].

The energy of the open reference form has been obtained using several variants of the closed-open method as described in detail in the Methodology section. To mention briefly, these variants are based on either (single point calculations in the case of variant SP) the full or the partial geometry optimization of the reference system, where values of geometry parameters being not optimized (if any) have been taken from the closed system possessing the IMCIHB of the $Si^{\delta+}$—$H^{\delta-}\cdots\supset Al$ type (see Fig. 2). Values of energies of IMCIHBs in investigated systems estimated within these variants are shown in Table 1.

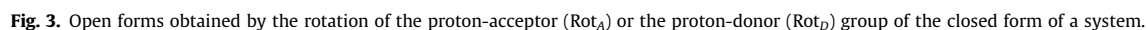For systems **1** and **8** we have investigated reference open forms where hydrogen atoms in positions **a** or **b** were replaced by the –SiH$_3$ group. Also for system **1** the –AlH$_2$ group was substituted to either the position **c** or **d** (see Fig. 2). Note that positions **b** and **d** are worse-fitted to the substitution of the –SiH$_3$ and –AlH$_2$ groups, respectively, than positions **a** and **c** since the substitution to positions **b** and **d** leads to the situation where the –SiH$_3$ or –AlH$_2$ group, respectively, protrudes out of the molecular skeleton. Thus, estimations based on these reference structures lead to higher values of energies of the IMCIHB in the closed form in comparison with their counterparts obtained if substitutions into positions **a** or **c** took place (see Table 1).

Values of energies obtained by means of diverse estimation methods, shown in Table 1, are in agreement with the degree of 'flexibility' of a given reference system during the calculation of its energy. This is schematically shown in Fig. 4. In agreement with the partition scheme accepted for the estimation of the energy of the IMCIHB in the closed form (see also Fig. 1) the gradual increase of the number of geometrical parameters that are allowed to relax during the geometry optimization of the reference system leads to the lowering of the energy value of IMCIHB.

In general, the geometry full optimization may lead to a reference system that is even more stable than the hydrogen-bonded closed form (these systems are given $E_{o,i}^{OPT}$ and $E_{o,j}^{OPT}$ energies in Fig. 4). This may happen, for example, if the reference system obtained after the geometry full optimization has some strongly stabilizing interactions that are not present in the closed form. This situation is schematically shown on the right hand side of Fig. 4. Since, in this case, the estimated value of the energy of the intramolecular hydrogen bond in the closed form can be considerably low or even can have opposite sign, such references should not be obviously assumed as proper. Similarly, the geometry full optimization of the open reference form may also lead to a structure possessing some significant locally repulsive interaction (these systems are given $E_{o,p}^{OPT}$ and $E_{o,q}^{OPT}$ energies in Fig. 4) being not present in the hydrogen-bonded closed form and leading to the increase of the estimated value of the IMCIHB energy ($\Delta E_p > \Delta E_1$, see Fig. 4). Such reference systems also should not be treated as proper
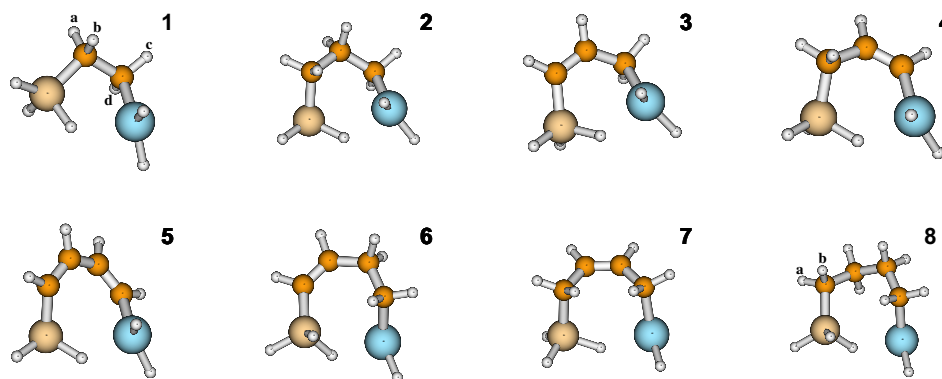
Fig. 2. Systems with the intramolecular charge-inverted hydrogen bond of the Si—H$\cdots\supset$Al type. Systems are given numerical labels as follows: (**1**) H$_3$Si—CH$_2$—CH$_2$—AlH$_2$, (**2**) H$_3$Si—CH$_2$—CH$_2$—CH$_2$—AlH$_2$, (**3**) H$_3$Si—CH=CH—CH$_2$—AlH$_2$, (**4**) H$_3$Si—CH$_2$—CH=CH—AlH$_2$, (**5**) H$_3$Si—CH=CH=CH=CH—AlH$_2$, (**6**) H$_3$Si—CH=CH—CH$_2$—CH$_2$—AlH$_2$, (**7**) H$_3$Si—CH$_2$—CH=CH—CH$_2$—AlH$_2$, (**8**) H$_3$Si—CH$_2$—CH$_2$—CH$_2$—CH$_2$—AlH$_2$. Geometry optimizations have been performed using the B3LYP/aug-cc-pVTZ level of theory.

Fig. 3. Open forms obtained by the rotation of the proton-acceptor (Rot_A) or the proton-donor (Rot_D) group of the closed form of a system.

Table 1
Estimated energy values (in kcal/mol) of IMCIHBs of the Si—H$\cdots \supset$Al type. Results obtained at the B3LYP/aug-cc-pVTZ level of theory.

System	Rotated group	SP	B	BA	SiAlH2-f	SiH2-f	H2-f	OPT[e]
1	—SiH$_3$[a]	−5.21	−4.82	−3.59	−1.71	−1.61	−1.44	−0.76
	—SiH$_3$[b]	−9.43	−8.71	−4.43	−2.81	−2.80	−2.79	
	—AlH$_2$[c]	−4.66	−4.24	−3.07	−1.76	−1.63	−1.44	
	—AlH$_2$[d]	−9.14	−8.50	−5.09	−2.84	−2.82	−2.79	
2	—SiH$_3$	−5.31	−4.88	−4.41	−3.36	−1.50	−0.99	−1.08
	—AlH$_2$	−7.01	−6.61	−5.79	−4.41	−3.24	−1.75	
3	—SiH$_3$	−8.13	−7.59	−7.05	−5.00	−2.75	−2.73	$\pi\cdots \supset$Al
	—AlH$_2$	−14.40	−11.84	−10.36	−8.97	0.00[f]	0.00[f]	
4	—SiH$_3$	−13.89	−12.85	−11.01	−5.63	−5.63	−2.31	$p_\pi \to \supset$Al
	—AlH$_2$	−6.74	−5.66	−4.81	−3.99	−3.79	−1.68	
5	—SiH$_3$	−5.23	−4.75	−3.93	−2.46	−2.42	−2.42	$p_\pi \to \supset$Al
	—AlH$_2$	−8.09	−7.37	−6.27	−4.85	−4.73	−4.72	
6	—SiH$_3$	−6.04	−5.03	−3.47	−1.41	−1.40	−1.40	−4.97/ −0.75
	—AlH$_2$	−10.61	−10.05	−8.44	−6.23	−6.19	−6.19	
7	—SiH$_3$	−7.95	−7.56	−7.09	−6.49	−6.07	−4.35	$\pi\cdots \supset$Al
	—AlH$_2$	−10.77	−10.12	−9.15	−8.24	−5.23	−4.69	
8	—SiH$_3$[a]	−5.93	−5.69	−4.88	−2.08	−1.40	−1.08	−2.51/ −0.54
	—SiH$_3$[b]	−7.57	−7.16	−6.50	−3.16	−2.48	−1.98	
	—AlH$_2$	−7.43	−7.11	−6.16	−3.49	−3.30	−3.29	

[a] Substitution to **a** position (see Fig. 2).
[b] Substitution to **b** position (see Fig. 2).
[c] Substitution to **c** position (see Fig. 2).
[d] Substitution to **d** position (see Fig. 2).
[e] The possible multitude of results obtained for systems **6** and **8** originates from the existence of several reference systems.
[f] Geometry optimization led to the closed form.

Fig. 4. Relative relations between values of energies of IMCIHBs obtained by means of diverse variants of the open–closed method.
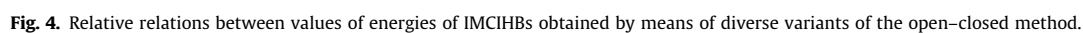
references in the open–closed method. Obtaining unreliable high value of the intramolecular hydrogen bond energy may indicate the presence of a significant locally repulsive interaction, while, on the contrary, the unreliable low value may indicate the presence of highly stabilizing interaction, e.g. an intramolecular hydrogen bond (new). The fact that the open reference system obtained after the full geometry optimization may possess such an important interaction and thus is not a proper reference system may also be obtained by means of the analysis of values of geometrical parameters, interatomic distances in particular. One can also predict that the open form may have either stabilizing or destabilizing interaction(s) and thus is the proper or improper reference system on the basis of the structural formula of the potential open reference system. This would avoid the useless full geometry optimization in this case.

From the data shown in Table 1 it is seen that the estimation method based on the reference system obtained by the rotation of the –AlH$_2$ group leads, in general, to higher values of the energy of IMCIHB in the closed form than in the case when the reference open system is obtained by the rotation of the –SiH$_3$ group instead. One may also notice that, at least, the partial optimization of dihedral angles has significant influence to the estimated value of the energy of IMCIHB.

In fact, in the case of the intramolecular hydrogen bond, the discussion about which estimation scheme gives better or worse values of energies is deprived of grounds, since they all are just based on the assumption of the additivity of bond energies. However such an approach is not justified by quantum mechanics and thus all attempts to 'calculate' the energy of the intramolecular hydrogen bond should be seen as an effort of defining undefinable. Indefiniteness of the energy of the intramolecular hydrogen bond should be emphasized since it seems to be not fully recognized. If we wish to introduce a property which is to be called the energy of the *intra*molecular hydrogen bond and which is to describe the local stabilization due to the X—H⋯Y interaction then it seems that the only marker of the 'quality' of its value is the "common sense". Since, in general, this value should be similar to the value of the intermolecular hydrogen bond energy [2,4,7] if only both interactions are of the same type and they are characterized by similar structure of the X—H⋯Y bridge (particularly similar value of the H⋯Y separation distance). Estimated value should also undergo various dependences, e.g. on the H⋯Y distance or on the value of the electron density in the bond critical point [56] of this interaction [57–71].

Recently [44] we have stated that IMCIHBs in systems **5** and **6** most likely should be the strongest in the investigated group of molecules. This statement was rooted in the shortest H⋯Al distance (1.96 Å) and in both the largest value of the electron density and of its Laplacian in the bond critical point of the H⋯Al interaction (ρ(BCP) = 0.0275 a.u. and $\nabla^2\rho$(BCP) = 0.0728 a.u., respectively). Only somewhat weaker IMCIHB should most likely be found in system **3** where values of the H⋯Al distance and of both ρ(BCP) and $\nabla^2\rho$(BCP) are 2.00 Å, 0.0260 a.u., and 0.0586 a.u., respectively [44]. Contrary, the IMCIHB in system **1** was supposed to be the weakest, since the IMCIHB in this molecule is characterized by significantly the longest H⋯Al distance (2.21 Å) and the smallest values of both ρ(BCP) (0.0196 a.u.) and $\nabla^2\rho$(BCP) (0.0254 a.u.). This was explained by strong strain forces arising during the five *quasi*-ring formation [44]. It is interesting to analyse whether or not these statements can found confirmation from the estimation values of energies of IMCIHBs listed in Table 1.

If one considers variant SP, then a rather significant discrepancy is seen depending on whether the reference open system was obtained after the rotation of the –SiH$_3$ or the –AlH$_2$ group. Indeed, high energy values of IMCIHBs have been obtained for systems **3** and **6** if the reference system was obtained by the rotation of the

–AlH$_2$ group, but this is also valid for the system **7** (−10.77 kcal/mol) for which values of the H⋯Al distance and of ρ(BCP) and of its Laplacian were found [44] to be 2.03 Å, 0.0229 a.u., and 0.0500 a.u., respectively. Contrary, if the open reference form was obtained by the rotation of the –SiH$_3$ group instead, then all estimated energy values for these systems are much lower and, moreover, the largest energy value is obtained for the system **4** (see Table 1). Freezing all dihedral angles of the reference form during the geometry optimization still leads to high energy values for systems **3** and **7** (and also for systems **4** and **6** if the open form was obtained after the rotation of either the –SiH$_3$ or the –AlH$_2$ group, respectively). Still, however, energy values of the IMCIHB in system **5** are not among dominant. They, however, are considerably high if one investigates for example variant H2-f, where all geometry parameters but dihedral angles of both hydrogen atoms of the -AlH$_2$ group were optimized. Nevertheless, this value (−4.72 kcal/mol) is similar to that of the system **7** (−4.69 kcal/mol) in which the IMCIHB was postulated [44] to be not so strong as in the system **5**.

This analysis shows that any relations between estimated values of energies of IMCIHBs and either the H⋯Al distance or the electron density value are not convincing and strongly depend on the model accepted to estimate the energy of the IMCIHB in investigated group of systems. This finding should rather be treated as a warning that, in fact, almost any value of the energy of the *intra*molecular hydrogen bond can be obtained, depending on the model accepted in the open–closed method, i.e., on the reference open system.

Even more vague situation is encountered if one performs the geometry full optimization of the open reference form (see the last column of Table 1). In the case of diverse open forms of systems **3**, **4**, **5**, and **7** the geometry full optimization leads to systems where the –AlH$_2$ group either interacts with the formally double bond of the -CH=CH—CH$_2$- unit (references of systems **3** and **7**) or becomes coplanar with the -CH = CH- unit (references of systems **4** and **5**) and participates in the $p_\pi \rightarrow \supset$Al coupling. Both these types of 'new' interactions significantly lower the energy of the open reference form. Thus estimations based on such reference systems should not be accepted as proper and thus they are neglected in Table 1. Some reference open forms for the rest of investigated systems are shown in Fig. 5. Also estimated values of energies (in kcal/mol) of IMCIHBs in their counterpart closed forms are given.

For systems **1** and **2** the presented energy values (-0.76 kcal/mol and −1.08 kcal/mol, respectively) are lower that those obtained from other schemes, in agreement with the general relation among diverse variants of the open–closed method (see Fig. 4). Estimated energy values for systems **6** and **8** can be a good example showing that the result may considerably depend on the reference open system. If one accepts system **8a** as the reference, then the energy of the IMCIHB in system **8** is estimated to be −2.51 kcal/mol. One can, however, obtain also energies of −0.54 kcal/mol or even + 0.82 kcal/mol! In the latter case, the positive energy results from the large stability of the most extended form of system **8**.

Diversity of different cases that may occur if the reference open form is fully optimized should be a warning and says that the variant of the open–closed method where the open form is fully optimized should be used with a great care. This variant should only be treated as a reasonable choice if the open form is as much similar to the closed form as possible, i.e., its geometry optimization does not lead to any 'new' important interactions (whatever attractive or repulsive) or to the significant change of the molecular skeleton. The presence of some 'new' strongly attractive interactions will lead to the significant lowering of the estimated value of the energy of the intramolecular hydrogen bond in the closed form or it may even lead to the change of its sign. Thus the energy value obtained from the open–closed method should be rather treated
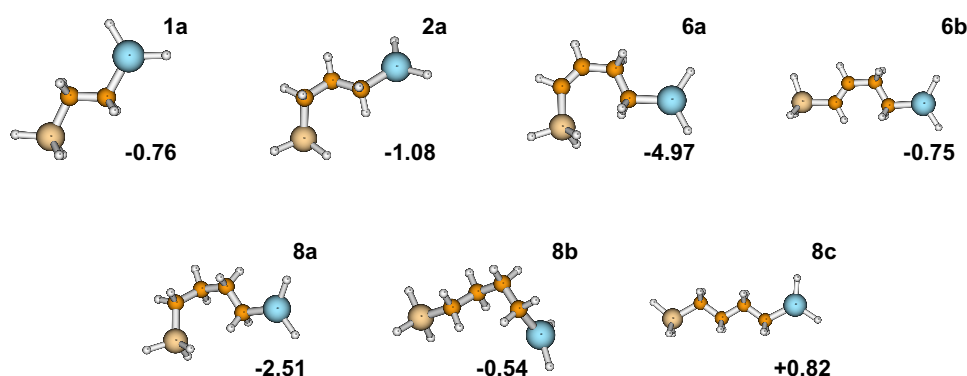
Fig. 5. Fully optimized reference open systems used in estimations of the energy of IMCIHB in the counterpart closed form (see Fig. 2). Estimated energy values (in kcal/mol) are also given near each reference. Geometry optimizations have been performed using the B3LYP/aug-cc-pVTZ level of theory.

as the energy difference between closed and open forms and hardly should be accepted as the energy of the intramolecular hydrogen bond in the closed form [22].

It is interesting to use other estimating procedures for IMCIHBs investigated here. We have used two additional methods. One of those utilizes so-called isodesmic/homodesmic reactions [45–47], which are "transformations in which the numbers of bonds of each formal type are conserved and only the relationships among the bonds are altered" [47]. The other approach uses the well-known formula by Espinosa [60]: $E_{HB}^V = \frac{1}{2} V_{BCP}$, where V_{BCP} is the density of the electron potential energy calculated in the bond critical point of the interaction [56].

The concept of isodesmic reactions [45–47] is generally considered to provide a useful tool for the estimation of intramolecular interaction energies [5,22–24,37]. However, the reliability of this method is based on several assumptions whose validity is at least uncertain. The most fundamental is the assumption that the total molecular energy can be partitioned into energies of chemically recognizable fragments. Moreover, these energies are assumed to be transferable between different molecules which involve similar chemical units. Once some partition scheme and the transferability of the fragment energies are accepted, the method of isodesmic reactions requires several other assumptions which do not seem to have been fully recognized and analyzed. For example there is a question whether or not the structures of molecules (II), (III), and (IV) (see Fig. 6) should be (fully) optimized [37]. In fact the full geometry optimization leads, in general, to different values of geometrical parameters of the same structural unit in relevant molecules. The other approach is to compute energies of (II), (III), and (IV) with the simultaneous conservation of values of relevant geometric parameters as they are in the fully optimized molecule (I). This procedure is in line with Molecular Tailoring Approach which is recommended in the case of systems possessing larger number of intramolecular hydrogen bonds [36–39]. In this case one can then perform optimizations of distances of only those bonds which are not present in (I). These are marked by the wavy bond line in Fig. 6. The former approach will be denoted hereafter as $E_{HB}^{iso,opt}$, while the latter as $E_{HB}^{iso,f}$.

Comparing both sides of isodesmic reactions which were used for the present study (see Fig. 6) one can see that they do not take into account IMCIHBs which are present in investigated molecules (**1**–(**8**) (systems denoted as (I) in Fig. 6). Thus the energy of IMCIHB can be evaluated as $E_{IMCIHB}^{iso} = E^{opt}(I) - E(I) < 0$, where $E(I) = E(III) + E(IV) - E(II)$ and $E^{opt}(I)$ corresponds to the fully optimized system (I). Results obtained by means of methods $E_{HB}^{iso,opt}$ and $E_{HB}^{iso,f}$ are shown in Table 2. They are completed with their counterparts obtained by means of Espinosa's formula $E_{HB}^V = \frac{1}{2} V_{BCP}$,

which makes use of the value of the density of the potential electron energy calculated in the bond critical point of the $H^{\delta-} \cdots \supset Al$ interaction in investigated systems.

First of all, a large difference between values of $E_{HB}^{iso,opt}$ and $E_{HB}^{iso,f}$ for all investigated molecules is noticeable (see columns 2 and 3 in Table 2). If one calls the energy value obtained for the $H_3SiH\cdots AlH_3$ dimer which is equal to -3.4 kcal/mol (-3.3 kcal/mol if BSSE-correction is used) [43] then energy values obtained by means of $E_{HB}^{iso,f}$ (as well as E_{HB}^V) approach seem to be too large. Contrary, $E_{HB}^{iso,opt}$ values obtained for systems (**3**),(**4**), and (**7**) are too low (also in a smaller extent for system (**5**)). They, however, result from the improper 'reference' system used in the isodesmic reaction. Namely, in these cases, the full geometry optimization of molecules denoted as (IV) being a component of relevant isodesmic reactions (see Fig. 6) leads to structures where the –AlH$_2$ group either interacts with the formally C=C double bond of either the -CH=CH–CH$_2$ unit in forms (IV) of molecules (**3**) and (**7**) or of the H$_2$C=CH- unit in the case of the form (IV) of (**5**) or becomes coplanar with the -CH=CH-unit as in the case of form (IV) of (**4**) and participates in the $p_\pi \to \supset Al$ coupling. All these interactions which, in fact, where also obtained in the fully optimized references of systems (**3**), (**4**), (**5**), and (**7**) in the estimation method OPT (see the last column in Table 1) significantly lower the energy of component molecule (IV) and, as a consequence, lead to unreliable value of IMCIHB energy if the $E_{HB}^{iso,opt}$ method is used.

Interestingly enough, this estimation procedure leads to reliable values of $E_{HB}^{iso,opt}$ in the case of other systems. Values obtained for (**6**) and (**8**) (-3.29 kcal/mol and -3.00 kcal/mol, respectively) are only somewhat lower than the value of -3.4 kcal/mol found for the $H_3SiH\cdots \supset Al$ dimer [43]. Results obtained by means of the $E_{HB}^{iso,opt}$ approach show that the full optimization of systems used in the homodesmic reaction can be used only in those cases, where any significant changes in the bonding pattern are *not* obtained. If this condition is satisfied then the use of homodesmic reaction may lead to a reasonable value of energy. Meaningfully lower values of $E_{HB}^{iso,opt}$ found for systems (**1**) and (**2**) reflect the larger effect of strain forces in these systems. The likely weakest IMCIHB present in molecule (**1**) is also seen if one considers $E_{HB}^{iso,f}$ values. In the case of (**1**), $E_{HB}^{iso,f} = -5.38$ kcal/mol whilst for the rest of molecules investigated in this study one obtains energies between -6.3 kcal/mol and -7.4 kcal/mol. Only for system (**3**) a significantly greater value of -9.44 kcal/mol is obtained. It should be noted that this is the method $E_{HB}^{iso,opt}$ instead of $E_{HB}^{iso,f}$ which is more in line with the OPT variant (or other were only few geometry parameters are frozen, e.g. H2-f, see Table 1) of the open–closed approach and the supermolecular approach used for calculating the energy value of the intermolecular hydrogen bond (interaction in general), where the
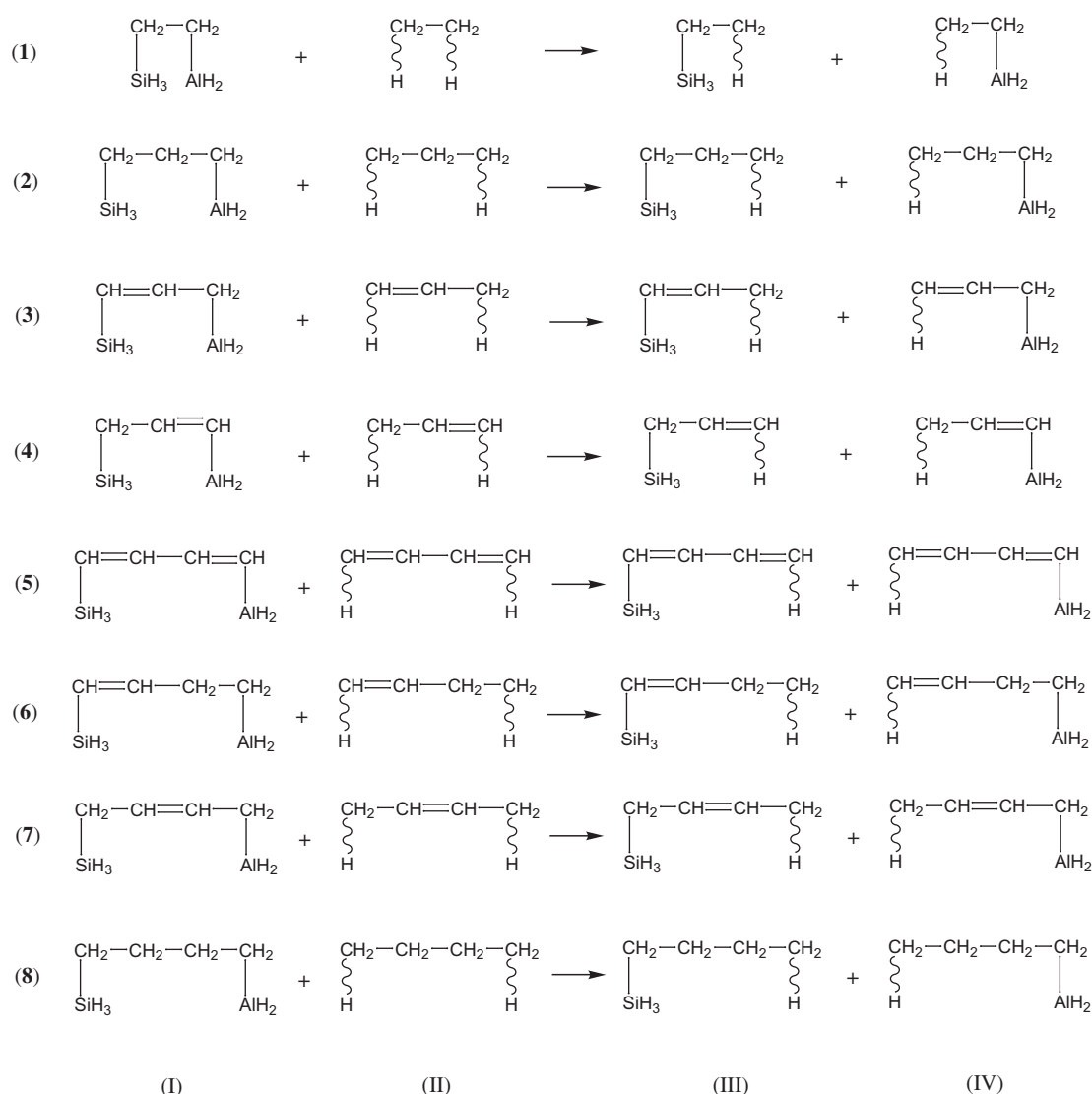
Fig. 6. Homodesmic reactions used for the estimation of energy values of IMCIHBs in systems (**1**)–(**8**) (see Fig. 2).

Table 2
Estimated energy values (in kcal/mol) of IMCIHBs of the Si—H⋯⊃Al type obtained by means of homodesmic reactions and Espinosa's formula (see text). Results obtained at the B3LYP/aug-cc-pVTZ level of theory.

System	$E_{HB}^{iso,opt}$	$E_{HB}^{iso,f}$	E_{HB}^{V}
1	−1.03	−5.38	−3.78
2	−1.41	−6.72	−6.00
3	−1.35	−9.44	−7.10
4	−0.14	−6.52	−6.25
5	−2.12	−6.41	−8.01
6	−3.29	−7.38	−7.99
7	−1.41	−6.87	−5.97
8	−3.00	−6.31	−6.27

full geometry optimization is performed. Thus $E_{HB}^{iso,opt}$ values instead of $E_{HB}^{iso,f}$ seem to be more 'proper' for comparing with either the value of −3.3 kcal/mol obtained for the H₃SiH⋯AlH₃ dimer [43] or the values obtained by the properly used open–closed method.

Energy values obtained by means of Espinosa's formula [60] are in agreement with the order of strengths of IMCIHBs postulated recently [44] on the basis of the $H^{\delta-}\cdots\supset Al$ distance value and of both the value of the electron density and its Laplacian in the bond critical point of these IMCIHBs. In fact, it is not an unexpected result

since V_{BCP} correlates with the interaction distance as well as with the value of the electron density in the bond critical point of this interaction [66,70,71]. As already mentioned, IMCIHBs in (**5**) and (**6**) were postulated to be the strongest within the investigated group of systems, the IMCIHB in (**3**) should most likely be only somewhat weaker, whilst the IMCIHB in (**1**) should be the weakest [44].

Unfortunately, although valuable in general, the Rotation Barriers Method [3,26] is useless in estimating the energies of IMCIHBs in investigated systems. This results from the fact that the rotation of the –SiH₃ group around the Si—C bond would lead to interactions with other hydrogen atoms of the –SiH₃ group and the rotation of the ⊃AlH₂- group around the C—Al bond would lead, on the other hand, to the proximity of two hydrogen atoms, one from –SiH₃, the other from –AlH₂. Moreover, in some reference structures one would obtain an unwanted conjugation of the $p_\pi \to \supset Al$ type.

Unreliably high values obtained particularly in methods where either none or poor geometry relaxation of the reference form is allowed or the full geometry optimization of the open reference form leads to a system with the new significantly repulsive interaction [2–5,16–18] may be the source of some speculations about the higher strength of intramolecular hydrogen bonds in comparison with intermolecular hydrogen bonds [2,4].

4. Conclusions

We show that, depending on the variant of the open–closed method accepted in the estimation procedure, i.e., on whether the geometry of the open reference system is fully or only partially optimized, one can obtain energy values from a rather wide range. This finding casts a shadow on the open–closed method and shows that it should be used with a great care, particularly if the geometry of the open form is to be fully optimized. The presence of some 'new' repulsive interactions will significantly increase the estimated value of the energy of the intramolecular hydrogen bond, while the presence of some 'new' attractive interactions (e.g. new hydrogen bonds) may significantly lower this value or even may cause the reversal of its sign. Similar result may also be obtained if the open reference form accepts extended stable structure.

Thus, to avoid the possibility of obtaining structures which could possess significant new interaction, either attractive or repulsive, we propose performing the *constrain* (i.e., *partial*) geometry optimization of the reference open system, where all, but those dihedral angles, whose optimization could lead to such relevant structures, geometry parameters are optimized. It seems that this freezing of geometrical parameters in particular should concern those dihedral angles which describe positions of the proton-donor or the proton-acceptor groups of the X—H···Y interaction with respect to the skeleton of the reference molecule.

In similar manner we show that the full geometry optimization of molecules used as components of homodesmic reactions may lead to unreliable estimates of the energy of the intramolecular hydrogen bond if only the full geometry optimization of at least one component molecule leads to the significant change in the bonding pattern as compared to that of the hydrogen- (more generally interaction-) bonded system. If this is not the case then reliable values can be obtained. Depending on the procedure accepted while the homodesmic reaction is used one may also obtain energies from a wide range. Energy values which are obtained by means of homodesmic reaction where geometrical parameters of component molecules are retained as in the parent molecule seem to be less proper if compared with those obtained by means of other methods where full optimization is performed, including E_{HB} of the intermolecular hydrogen bond of the same type.

If the IMCIHB energy is estimated by means of Espinosa's formula then the predicted order of IMCIHB strengths is obtained, however, it is rather to be expected since this prediction was done on the basis of the interaction distance and either the value of the electron density or its Laplacian in the bond critical point of this interaction, all properties correlating with the density of the potential electron energy included in Espinosa's formula.

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