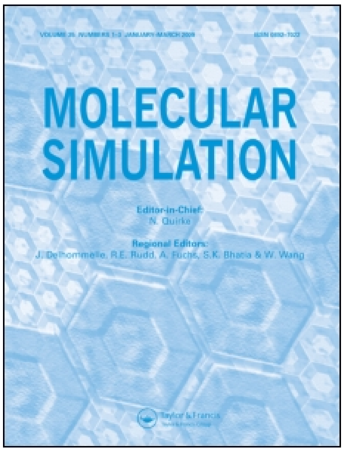

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

A study of dihydrogen bond interactions through three-centre bond and group indices

Fernando C. Rangel[a]; Adão L. B. Montel[a]; K. C. Mundim[a]
[a] Instituto de Química, Universidade de Brasília, Brasília, DF, Brazil

To cite this Article Rangel, Fernando C. , Montel, Adão L. B. and Mundim, K. C.(2009) 'A study of dihydrogen bond interactions through three-centre bond and group indices', Molecular Simulation, 35: 4, 342 — 348

To link to this Article: DOI: 10.1080/08927020802247065

URL: http://dx.doi.org/10.1080/08927020802247065

Molecular Simulation
Vol. 35, No. 4, April 2009, 342–348

A study of dihydrogen bond interactions through three-centre bond and group indices

Fernando C. Rangel*, Adão L.B. Montel and K.C. Mundim

Instituto de Química, Universidade de Brasília, Campus Darcy Ribeiro, 70919-970 Brasília, DF, Brazil

(*Received 10 March 2008; final version received 4 June 2008*)

We report here an investigation into the correlation between dihydrogen bond energies, three-centre bond indices and group indices in some dihydrogen-bonded dimers. This kind of bond is generated by interaction between proton-donator and proton-acceptor groups, $XH^{\sigma+} \ldots H'^{\sigma-}M$, where X is a more electronegative atom and M a less electronegative atom than hydrogen. The different electronegativities of the X atoms, as well the M atoms, would affect the correlations between $H^{\sigma+} \ldots H'^{\sigma-}$ distances and bond energies of these systems. In this work it will be shown that three-centre bond indices and group indices exhibit a better correlation with bond energies when compared to $H^{\sigma+} \ldots H'^{\sigma-}$ distances for this kind of system.

Keywords: three-centre bond indices; group indices; dihydrogen bond energy

1. Introduction

For chemists, the main support tool in the study of organic or inorganic systems is the concept of chemical bonding. Lewis' classic model was the main protagonist in the evolution of this concept. Today, some more complex cases such as multicentre bonds, which could not be described by Lewis' model, can be represented by multicentre bond indices [1]. Furthermore, some applications of bond indices in the study of molecular systems have been done [2–9]. The electronic description given by indices is not restricted to intramolecular interactions, but also includes intermolecular ones. So, intermolecular interactions such as hydrogen bonds, which have been intensely studied, can apparently be described through bond indices. This kind of interaction is of extreme relevance in the contributions that define the characteristics and properties of molecular systems such as protein conformations and the selectivity of catalysts, among innumerable others. The typical hydrogen bond [10–14] is an interaction involving a proton donator X and proton acceptor Y of kind $XH \ldots Y$. However, since the 1950s, some interactions of the $XH \ldots \pi$-electrons kind have become known [15–19]. This interaction is weaker than expected for conventional hydrogen bonds because π-electrons are less basic than the lone electronic pair. In the same way, it was imagined that a sigma-type bonding would not behave as a very effective proton-acceptor site. However, in the last 10 years, a new kind of hydrogen bond has been studied, which is called a dihydrogen bond [20,21]. This kind of bonding can be represented as $YXH^{\sigma+} \ldots H'^{\sigma-}M$, where Y is an atom or group of atoms bonded to X. X is more electronegative and M less electronegative than the hydrogen atom. Dihydrogen bonded systems have been the subject of much attention lately [22–27].

In this work, a relationship will be presented between dihydrogen bond energies, three-centre bond indices and group indices in some molecular systems. It will be shown that bond energies have a better correlation with these indices, particularly the indices which represent three-centre four-electron (3c-4e) bonds ($I_{\mathrm{CHH'}}$ and $I_{\mathrm{XHH'}}$), than with $H \ldots H'$ distances.

2. Bond indices

Bond indices were first proposed heuristically by Wiberg [28], for two centres, as follows:

$$W_{AB} = \sum_{\substack{a \in A \\ b \in B}} P_{ab}^2, \tag{1}$$

where A and B are atomic centres. The Wiberg indices always have positive values close to 1–3 for single, double and triple bonds, respectively.

It was later shown by Armstron and Perkins [29] that these indices are generated from following relationship

$$Tr(P^2) = 2N, \tag{2}$$

where P is the first order density matrix and N is the number of electrons. In this way, the representation of

---

*Corresponding author. Email: rangelfc@unb.br

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020802247065
http://www.informaworld.com

bond indices to closed-shell systems is given below:

$$P^k = 2^{k-1}P. \tag{3}$$

In a system with k atoms the bond indices can be obtained from the trace of the left side of Equation (3), that is,

$$I_{AB\ldots K}(RHF) = \sum_{a}^{A}\sum_{b}^{B}\ldots\sum_{k}^{K} P_{ab}P_{bc}\ldots P_{ka}. \tag{4}$$

From this definition, the total number of electrons in the molecular system is given by the sum of all bond indices, i.e.

$$2^{k-1}\sum_{A}\sum_{B}\ldots\sum_{K} I_{AB\ldots K} = N. \tag{5}$$

It is important to highlight that the sign of the bond indices, representing multicentre bonds, can be either positive or negative. It is different from bond indices' values of two centres, which generate only positive values. In the case of three-centre bond indices, positive values are attributed to three-centre two-electron (3c-2e) contributions while negatives ones could evidence 3c-4e contributions [30–33].

The valence of an atom can be defined as the sum of all two-centre bond indices between this atom and all others of the system under consideration. So, the atomic valence is defined as follows:

$$\mathrm{V}_A = \sum_{B\neq A} I_{AB}. \tag{6}$$

The concept of valence was generalised for atomic group valence by Mundim et al. [34–36], using Grassmann algebra. In this case it can be represented by the following equation,

$$\mathrm{V}_G = \sum_{\substack{A\in G\\ B\notin G}} I_{AB}. \tag{7}$$

This definition enables us to evaluate how much two atomic groups are bonded through molecular electronic distribution. In the case of two atomic groups ($G1$ and $G2$), the group valence and the bond order between these groups are numerically equivalent, that is,

$$\mathrm{V}_G \equiv I_{G1G2} = \sum_{\substack{A\in G1\\ B\in G2}} I_{AB}. \tag{8}$$

Through these generalisations we can identify and quantify multicentre chemical bonds as well as atomic group interactions.

3. Methods

In this work, a series of calculations for dihydrogen bond energies were carried out for different molecular systems. This energy has been correlated with H...H distances, three-centre bond indices and group indices. All geometry optimisations and bond energies were calculated at MP2/6-311++G** level using Gaussian 03 electronic structure package [37]. The three-centre bond indices and group indices were generated through Löwdin population analysis at the HF/6-31G level using the q-Hartree–Fock code generated in our Lab.

4. Results and discussion

4.1 Dihydrogen bond energy and three-centre bond indices

The correlation between interaction energy and $\mathrm{H}^{\sigma+}\ldots\mathrm{H}'^{\sigma}$ distances in dihydrogen systems does not seem to apply when interaction energies for different atoms X (C, O, N, F) and M (Li, Na, Be), $\mathrm{YXH}^{\sigma+}\ldots\mathrm{H}'^{\sigma-}\mathrm{M}$, are compared, as seen in Tables 1 and 2.

Figure 1 shows a monotonic decrease in bond energy as a function of increase distances H...H′. This decrease was expected because the hydrogen-bonding force depends on shared electronic densities, as well as on electrostatic interactions between chemical species.

Figure 2 shows that the bond energy also has good exponential correlation with three-centre bond indices $I_{\mathrm{CHH}'}$ ($R^2 = 0.998$) and with three-centre bond indices $I_{\mathrm{HH}'\mathrm{Li}}$ ($R^2 = 0.997$), where R is the correlation coefficient. A similar study was made by Alkorta et al. It was found an exponential correlation between charge variation and DHB (dihydrogen bonded) distances in analogous systems [38]. In this kind of system, the three-centre bond indices would be utilised as a measure of bond forces as well as H...H′ distances. Additionally, it gives information about electronic description of the systems under study.

The sum of bond indices $I_{\mathrm{CHH}'}$ and $I_{\mathrm{HH}'\mathrm{Li}}$ also maintains a good correlation, $R^2 = 0.994$, with dihydrogen bond energy, as seen in Figure 3.

This result suggests that in these systems 3c-4e and 3c-2e contributions are electronically self-compensated.

In the case of dihydrogen bonds involving more electronegative atoms directly bonded to hydrogen

Table 1. Distances for $r_{\mathrm{H'H}}$, three-centre bond indices $I_{\mathrm{CHH}'}$, three-centre bond indices $I_{\mathrm{HH'M}}$ and dihydrogen bond energies BE.

Molecular systems	$r_{\mathrm{HH}'}$ (Å)	I_{XHH}	$I_{\mathrm{HH'Li}}$	BE (kcal/mol)
HCCH--H′Li	2.0486	−0.0063	0.0169	−4.2
FCCH--H′Li	2.0166	−0.0069	0.0183	−4.5
ClCCH--H′Li	2.0018	−0.0073	0.0192	−4.7
NCH--H′Li	1.8233	−0.0125	0.0285	−8.2
NCCCH--H′Li	1.8719	−0.0105	0.0266	−7.6
$\mathrm{H_3CCCH}$--H′Li	2.1081	−0.0054	0.0147	−3.2
$\mathrm{H_3SiCCH}$--H′Li	2.0123	−0.0070	0.0187	−4.6
$\mathrm{(LiNCH)^+}$--H′Li	1.3463	−0.0450	0.0838	−26.0
$\mathrm{(NaNCH)^+}$--H′Li	1.4584	−0.0346	0.0666	−22.7

Table 2. Distances for $r_{HH'}$, three-centre bond indices $I_{XHH'}$, three-centre bond indices $I_{HH'M}$, dihydrogen bond energies BE and two-centre bond indices $I_{HH'}$.

Molecular systems	$r_{HH'}$ (Å)	$I_{XHH'}$	$I_{MHH'}$	BE (kcal/mol)	$I_{HH'}$
FH--H′Li	1.396	− 0.0224	0.0780	− 13.4	0.1026
FH--H′Na	1.370	− 0.0282	0.0950	− 14.6	0.1425
FH--H′BeH	1.704	− 0.0051	0.0320	− 3.3	0.0381
HOH--H′Li	1.502	− 0.0088	0.0293	− 7.3	0.0307
HOH--H′Na	1.491	− 0.0402	0.0876	− 16.2	0.1113
CNH--H′Li	1.489	− 0.0232	0.0601	− 13.6	0.0753
CNH--H′Na	1.446	− 0.0314	0.0777	− 15.1	0.1128
CNH--H′BeH	1.819	− 0.0052	0.0227	− 3.3	0.0262

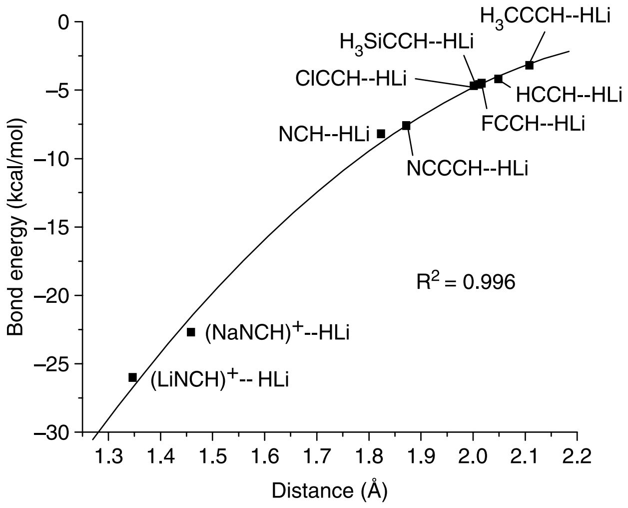

Figure 1. Relationship between dihydrogen bond energies (in kcal/mol) and interatomic distances (in Å).

(X...H′) a displacement of charge to H...H′ bond and respective increase in bond energies would result.

In the considered molecular systems there is apparently no correlation between H...H′ distance and dihydrogen bond energy when different atoms of high electronegativity are bonded to hydrogen atoms, as shown in Figure 4.

Figure 5 shows two different exponential curves, one of which is with dimers containing oxygen and nitrogen atoms, while the other has dimers containing fluorine. These curves show that a higher electronic density exists in HH′M centres from dimers with fluorine atoms than from dimers with oxygen and nitrogen atoms. It can be associated with the high electronegativity of fluorine atoms, which result in a high polarisation of the F—H bond. This polarisation brings a charge transference to the H...H′-interaction that would induce an increase in electronic density at this site. It can easily be observed in Table 2, for dimers with the same metallic hydrides, the electronic density in H...H′-bonded dimers containing fluorine is higher than in others.

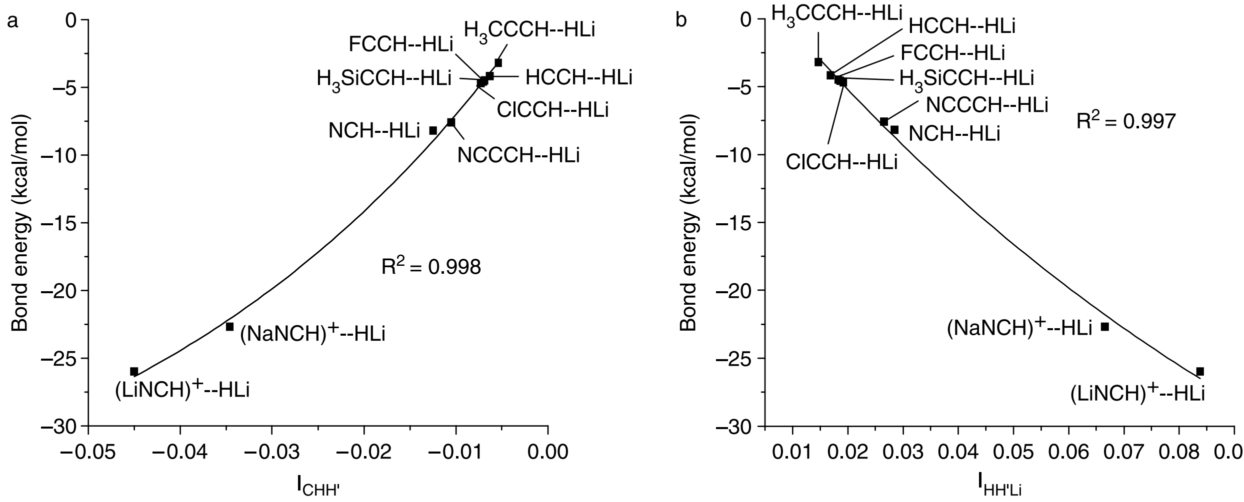

Figure 2. (a) Relationship between dihydrogen bond energies (in kcal/mol) and three-centre bond indices $I_{XHH'}$ and (b) relationship between dihydrogen bond energies (in kcal/mol) and three-centre bond indices $I_{HH'M}$.

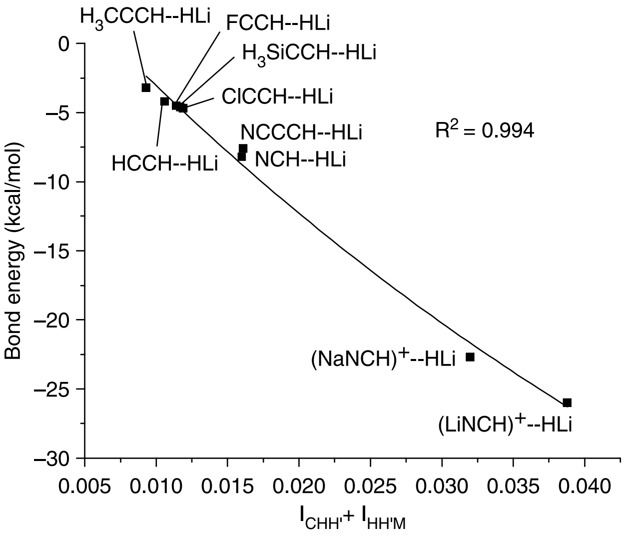

Figure 3. Relationship between dihydrogen bond energies (in kcal/mol) and the sum of three-centre bond indices $I_{CHH'}$ and $I_{HH'Li}$.

In respect to three-centre bond indices, $I_{XHH'}$, there is a good correlation between these indices and the dihydrogen bond energies, as shown in Figure 6.

This result is very important because three-centre bond indices, $I_{XHH'}$, measure contributions of the 3c-4e kind. This suggests that the stabilisation of dihydrogen chemical bonds occurs in terms of 3c-4e contributions. In other words, a good correlation between dihydrogen bond energies and the three-centre bond indices $I_{XHH'}$, shows that the contributions described by these three-centre bond indices are predominant in dihydrogen bonds.

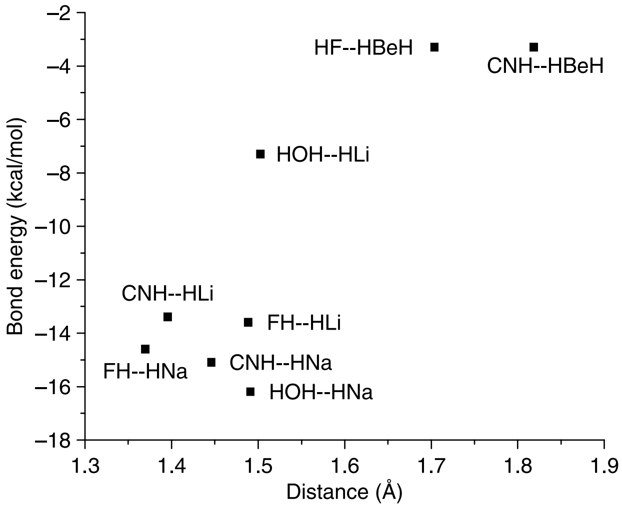

Figure 4. Relationship between dihydrogen bond energies (in kcal/mol) and the interatomic distances H—H′ for a system containing high electronegative atoms directly bonded to hydrogen.

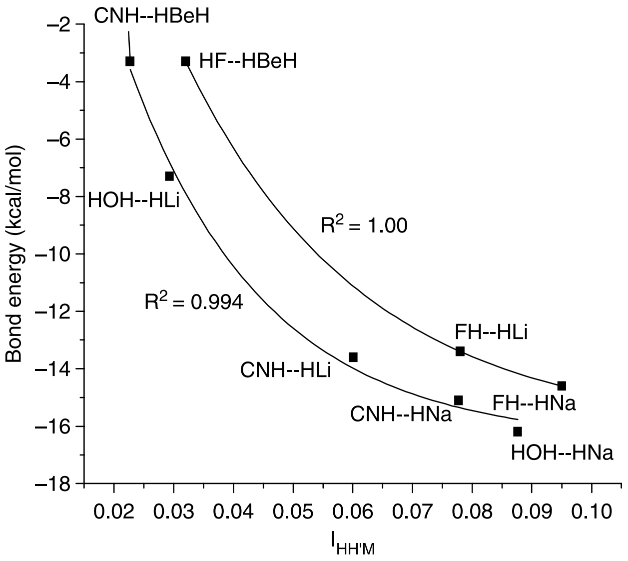

Figure 5. Relationship between dihydrogen bond energies (in kcal/mol) and three-centre bond indices $I_{HH'M}$ to system containing high-electronegative atoms directly bonded to hydrogen.

4.2 *Relationship between dihydrogen bond energy and group indices for some molecular systems*

In this section, the correlation between the $I_{HH'}$ and I_{G1G2} indices and dihydrogen bond energy in some systems will be discussed, as shown in Tables 3 and 4. The indices $I_{HH'}$ represent the bond order between hydrogen atoms involved in the interaction. Group indices, I_{G1G2}, represent the bond order between $G1$ and $G2$ groups, which contain molecules and metallic hydrides, respectively.

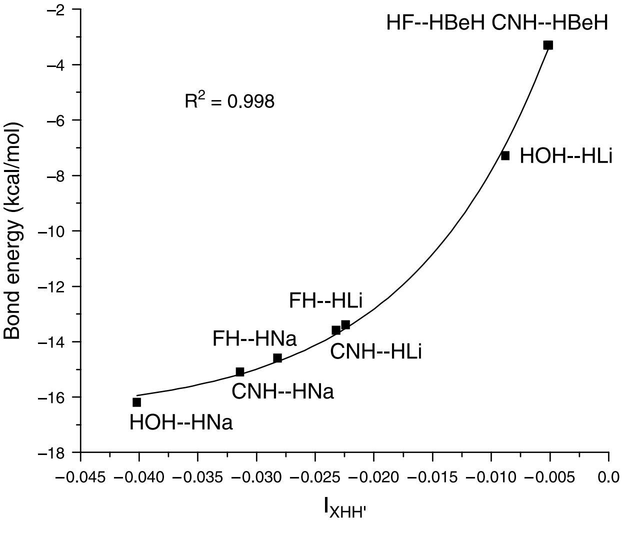

Figure 6. Relationship between dihydrogen bond energies (in kcal/mol) and three-centre bond indices $I_{XHH'}$ for a system containing high-electronegative atoms directly bonded to hydrogen.

Table 3. Two-centre indices $I_{HH'}$, group indices I_{G1G2} and dihydrogen bond energies BE.

Systems (*G*1--*G*2)	$I_{HH'}$	$I_{G1G2'}$	BE (Kcal/mol)
HCCH--H′Li	0.0173	0.0681	−4.2
FCCH--H′Li	0.0188	0.0729	−4.5
ClCCH--H′Li	0.0199	0.0758	−4.7
NCH--H′Li	0.0314	0.1124	−8.2
NCCCH--H′Li	0.0288	0.1010	−7.6
H3CCCH--H′Li	0.0147	0.0602	−3.2
H_3SiCCH--H′Li	0.0193	0.0737	−4.6
$(LiNCH)^+$--H′Li	0.1219	0.3309	−26.0
$(NaNCH)^+$--H′Li	0.0897	0.2599	−22.7

Table 4. Two-centre bond indices $I_{HH'}$, group indices I_{G1G2} and dihydrogen bond energies BE.

Systems (*G*1--*G*2)	$I_{HH'}$	$I_{G1G2'}$	BE (kcal/mol)
FH--H′Li	0.1026	0.2366	−13.4
FH--H′Na	0.1425	0.2970	−14.6
HF--H′BeH	0.0381	0.0921	−3.3
HOH--H′Li	0.0307	0.0967	−7.3
HOH--H′Na	0.1113	0.7082	−16.2
CNH--H′Li	0.0753	0.2108	−13.6
CNH--H′Na	0.1128	0.2784	−15.1
CNH--H′BeH	0.0262	0.0672	−3.3

In the case of interactions in molecular systems such as $YCH^{\sigma+} \ldots H'^{\sigma-}Li$ (see Table 3) there is a good correlation between bond energies and bond indices $I_{HH'}$ (see Figure 7). This shows that the perturbation caused by group Y to proton-donator group CH is accompanied by changing the electronic density in an H … H′ interaction in the dimers.

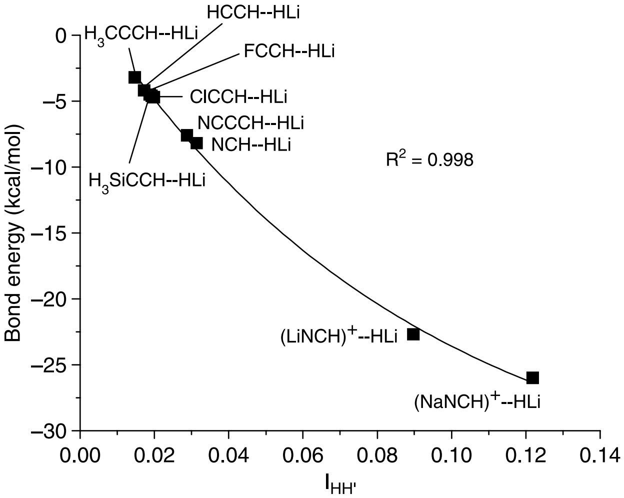

Figure 7. Relationship between dihydrogen bond energies (in kcal/mol) and two-centre bond indices $I_{HH'}$.

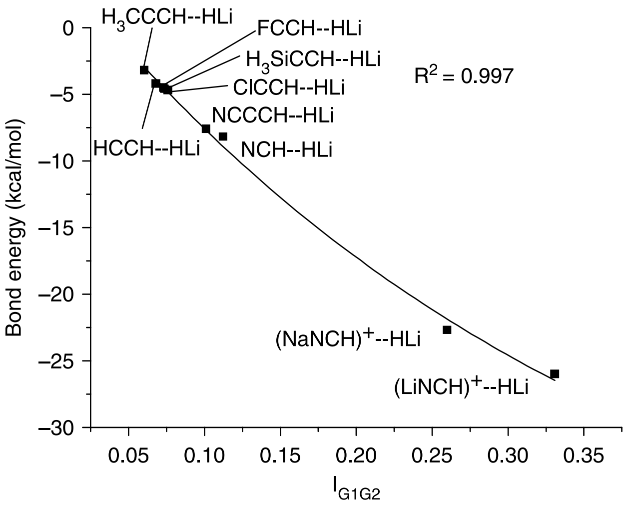

Figure 8. Relationship between dihydrogen bond energies (in kcal/mol) and group indices.

For the same molecular systems, $YCH^{\sigma+} \ldots H'^{\sigma-}Li$, the group indices I_{G1G2}, which measure all the shared contributions by groups *G*1 and *G*2 in the charge density, also present a good correlation with bond energies with $R^2 = 0.997$, as shown in Figure 8.

This suggests that the main contribution to the force of these interactions is between proton-donator CH and proton-acceptor H′Li groups. In other words, interactions between proton acceptor H′Li and Y are less important.

It was observed that in the case of systems containing more electronegative atoms, as seen in Table 4, the analysis of the bonding force cannot be done based only on sharing of the charge density between hydrogen atoms involved in the interaction H … H′, see Figure 9.

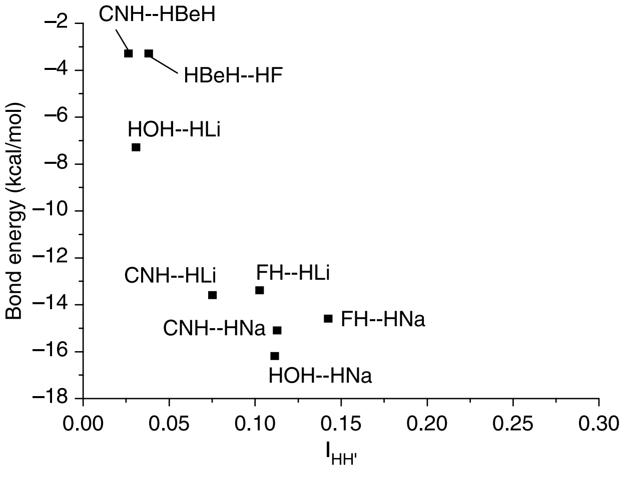

Figure 9. Relationship between dihydrogen bond energies (in kcal/mol) and two-centre bond indices $I_{HH'}$ for a system containing high-electronegative atoms directly bonded to hydrogen.

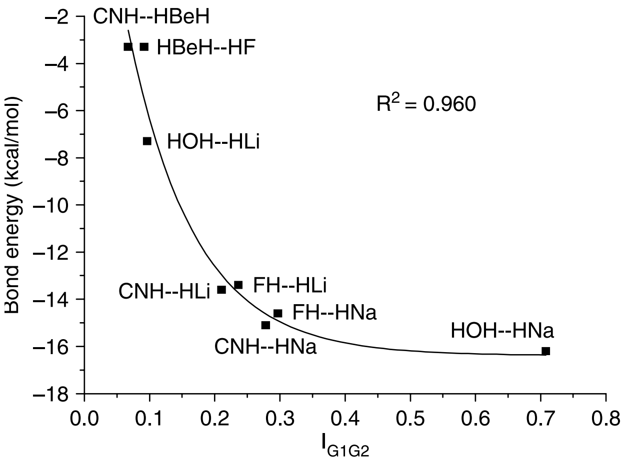

Figure 10. Relationship between dihydrogen bond energies (in kcal/mol) and group indices I_{G1G2} for a system containing high electronegative atoms directly bonded to hydrogen.

A better approximation would be the utilisation of group indices in the description of these interactions. These indices have the advantage of taking into account some shared contributions to the charge density, of adjacent atoms to hydrogen one, which were not computed in two-centre bond indices $I_{\mathrm{HH'}}$.

It can be observed from Figures 9 and 10 that when some shared contributions to the charge density are taken in account, represented through group indices, there is an approximation of the values on the curve. It is more evident in the case of the HOH…H′Na system. Furthermore, it is important to point out that a better correlation can be attained in separating systems containing fluorine from those which have oxygen and nitrogen atoms. Again, this displacement can be attributed to an eventual increase in electronic density at the bond H…H′, which is occasioned by the high electronegativity of the fluorine atom.

5. Conclusions

In all systems studied, the three-centre bond indices presented a better correlation with dihydrogen bond energy when compared with the H…H′ distances. The best results were obtained through the 3c-4e indices (I_{XHH}). This suggests that the stabilisation of dihydrogen chemical bonds occurs in terms of 3c-4e contributions. In other words, a good correlation between dihydrogen bond energies and the three-centre bond indices, $I_{\mathrm{XHH'}}$, appears to be associated with the 3c-4e nature of the dihydrogen bonds.

The sum of bond indices $I_{\mathrm{CHH'}}$ and $I_{\mathrm{HH'Li}}$ also maintains a good correlation, $R^2 = 0.994$, with dihydrogen bond energy.

The group indices, I_{G1G2}, presented a better description of dimers interactions than considering only the H…H′ bond order.

Acknowledgements

The authors are grateful for support granted to this work by the Brazilian Agency Foundations CNPq and CAPES.

References

[1] M. Giambiagi, M.S. de Giambiagi, and K.C. Mundim, *Definition of a multicenter bond index*, Struct. Chem. 1 (1990), pp. 423–427.
[2] F.C. Rangel, *Uma Abordagem Sobre os Índices de Ligação e sua Aplicação no Estudo das Ligações Dihidrogênio*, M.Sc. diss., Universidade de Brasília, Brazil, 2006.
[3] M.S. de Giambiagi and P. Bultinck, *Bond indices in dihydrogen bonds*, J. Braz. Chem. Soc. 19 (2008), pp. 263–267.
[4] T. Kar, R. Ponec, and A.B. Sannigrahi, *Electronic structure, stability, and nature of bonding of the complexes of C_2H_2 and C_2H_4 with H^+, Li^+, and Na^+ Ions. Extensive* ab initio *and density functional study*, J. Phys. Chem. A. 105 (2001), pp. 7737–7744.
[5] P. Bultinck, R. Ponec, and S. van Damme, *Multicenter bond indices as a new measure of aromaticity in polycyclic aromatic hydrocarbons*, J. Phys. Org. Chem. 18 (2005), pp. 706–718.
[6] R. Ponec, P. Bultinck, and A.G. Saliner, *Multicenter bond indices as a new means for the quantitative characterization of homoaromaticity*, J. Phys. Chem. 109 (2005), pp. 6606–6609.
[7] R. Ponec, G. Yuzhakov, and D.J. Tantillo, *Multicenter bonding in organic chemistry. Geometry sensitive 3c-2e Bonding in (C—H—C) fragments of organic cations*, J. Phys. Org. Chem. 69 (2004), pp. 2992–2996.
[8] M.S. de Giambiagi and M. Giambiagi, *Multicenter bond indices as a measure of aromaticity*, Phys. Chem. Chem. Phys. 2 (2000), pp. 3381–3392.
[9] M. Giambiagi, M.S. de Giambiagi, and M.D. Neto, *Crucial effect of hydration in a model for the antiepileptic vigabatrin and the prosthetic group interaction*, Phys. Chem. Chem. Phys. 3 (2001), pp. 5059–5062.
[10] M.L. Huggins, *Atomic structure*, Science 55 (1922), pp. 459–460.
[11] L. Pauling, *The nature of the chemical bond. Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules*, J. Am. Chem. Soc. 53 (1931), pp. 1367–1400.
[12] S. Scheiner, *Hydrogen Bonding. A Theoretical Perspective*, Oxford University Press, Oxford, 1997.
[13] G.A. Jeffrey, *An Introduction to Hydrogen Bond*, Oxford University Press, New York, 1997.
[14] G. Desiraju and T. Steiner, *The Weak Hydrogen Bond*, Oxford University Press, New York, 1999.
[15] M.L. Josien et al., *Le spectre infrarouge de l'acides bromhydrique eu iodhydrique en solution*, Bull. Soc. Chim. Fr (1955), pp. 1539–1543.
[16] M.L. Josien and G. Sourisseau, *Le spectre infrarouge de lacide chlorhydrique en solution – formation de complexes organiques*, Bull. Soc. Chim. Fr (1955), pp. 178–183.
[17] M. Oki and H. Iwamura, *Steric effects on O—H…(P1 interaction in 2-hydroxybiphenyl*, J. Am. Chem. Soc. 89 (1967), pp. 576–579.
[18] S. Suzuki, P.G. Green, R.E. Bumgarner, S. Dasgupta, W.A. Goddard III, and G.A. Blake, *Benzene forms hydrogen-bonds with water*, Science 257 (1992), pp. 942–945.
[19] K.S. Kim, *Comparison of the nature of π and conventional H-bonds: A theoretical investigation*, J. Mol. Struct. 615 (2002), pp. 227–238.
[20] A.L. Rheingold and T.F. Koetzle, *A new intermolecular interaction: unconventional hydrogen bonds with element-hydride bonds as proton acceptor*, Acc. Chem. Res. 29 (1996), pp. 348–354.
[21] K.N. Robertson, O. Knop, and T.S. Cameron, *C—H center dot center dot center dot H—C interactions in organoammonium tetraphenylborates: Another look at dihydrogen bonds*, Can. J. Chem./Rev. Can. Chim. 81 (2003), pp. 727–743.

[22] S.A. Kulkarni, *Dihydrogen bonding in main group elements: an* ab initio *study*, J. Phys. Chem. A 102 (1998), pp. 7704–7711.

[23] S.J. Grabowski, *High-level* ab initio *calculations of dihydrogen-bonded complexes*, J. Phys. Chem. A. 104 (2000), pp. 5551–5557.

[24] S.J. Grabowski, *Theoretical evidence for a new kind of intramolecular dihydrogen bond*, J. Chem. Phys. Lett. 327 (2000), pp. 203–208.

[25] J. Lundell and M. Petterson, *The dihydrogen-bonded complex* XeH_2–H_2O, Phys. Chem. Chem. Phys. 1 (1999), pp. 1691–1697.

[26] S. Berski, J. Lundell, and Z. Latajka, *A density functional study of the xenon dihydride–water complex*, J. Mol. Struct. 552 (2000), pp. 223–232.

[27] I. Alkorta, J. Elguero, O. Mó, M. Yáñez, and J.E. Del Bene, Ab initio *study of the structural, energetic, bonding, and IR spectroscopic properties of complexes with dihydrogen bonds*, J. Phys. Chem. A 106 (2002), pp. 9325–9330.

[28] K.A. Wiberg, *Application of the pople-santry-segal CNDO method to the cyclopropylcarbinyl and cyclobutyl cation and to bicyclobutane*, Tetrahedron 24 (1968), pp. 1083–1096.

[29] D.R. Armstron and P.G. Perkins, *Bond indices and valency*, J. Chem. Soc. Dalton Trans. 8 (1973), pp. 838–840.

[30] R.C. Bochicchio and R. Ponec, *On the physical meaning of bond indices from the population analysis of higher order densities*, J. Phys. Chem. A 102 (1998), pp. 7176–7180.

[31] R. Ponec and I. Mayer, *Investigation of some properties of multicenter bond indices*, J. Phys. Chem. A 101 (1997), pp. 1738–1741.

[32] A.B. Sannigrahi and T. Kar, *Three-center bond index*, Chem. Phys. Lett. 173 (1990), pp. 569–572.

[33] T. Kar and E.S. Marcos, *Three-center four-electron bonds and their indices*, Chem. Phys. Lett. 192 (1992), pp. 14–20.

[34] K.C. Mundim, *Anticommuting space – an alternative formulation of the wave function antisymmetry description*, J. Phys. 50(1) (1989), pp. 11–17.

[35] K.C. Mundim, M. Giambiagi, and M.S. de Giambiagi, *Molecular invariants – atomic group valence*, Nuovo Cimento – D 12 (1990), pp. 765–769.

[36] M. Giambiagi, M.S. de Giambiagi, and K.C. Mundim, *Group-group bond index for molecular-systems*, J. Chem. Soc. Faraday Trans. 88 (1992), pp. 2995–2999.

[37] M.J. Frisch, G.W. Truck, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr, T. Vreven, K.N. Kudin, J.C. Burant et al., GAUSSIAN 03, Revision C.02, Gaussian Inc., Pittsburgh, PA, 2004.

[38] I. Alkorta, K. Zborowski, and J. Elguero, *Theoretical study of dihydrogen bonds between* $(XH)_2 =$ *Li Na, BeH, and MgH, and weak hydrogen bond donors (HCN, HNC, and HCCH)*, J. Phys. Chem. A 110 (2006), pp. 10279–10286.