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A SIMPLE SEMIEMPIRICAL APPROXIMATION FOR BOND ENERGY

by

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ABSTRACT

A simple semiempirical expression for bond energy, related with a generalized bond index, is proposed and applied within the IEH framework. The correlation with experimental data is good for the intermolecular bond energy of base pairs of nucleic acids and other hydrogen bonded systems. The intramolecular bond energies for a sample of molecules containing typical bonds and for hydrides are discussed. The results are compared with those obtained by other methods.

Key-words: Bond energy; Bond index.

1. Introduction

The chemical bond is usually described, when this is done in terms of MO's, through the first-order reduced density matrix. The McWeeny-Mulliken population analysis [1] assumes that this matrix contains most of the chemically significant information. The introduction of bond indices generalizing the Wiberg ones [2] is an alternative to the Mulliken population; they have been successfully applied to different types of molecules [3,4] and have permitted to advance in the description of the hydrogen bond [5].

Both the electronic density and the total energy may be partitioned in different ways in order to derive chemical structural formulae [6]. Semiempirical estimations of bond energies based on energy partitions have been carried out to various levels of sophistication [7,8,9]. A completely different classical approach to bond energy through the principle of electronegativity equalization has been developed by Sanderson [10].

We propose here a crude definition for bond energy, related to bond indices. We apply it to inter and intramolecular bonds within the IEH approximation; the parameters involved are not subject to fitting. We compare our results with those of the approximations mentioned above.

We shall endorse the pragmatic attitude following which, in semiempirical methods, especially if applied to large systems, rough approximations are self-justified if they work. How much this is true, we shall see in the discussion.

2. Bond energy

The bond index I_{AB} between atoms A and B is defined as [2,3]:

$$I_{AB} = 4 \sum_{\substack{\underline{a} \in A \\ \underline{b} \in B}} \Pi_{\underline{b}}^{\underline{a}} \Pi_{\underline{a}}^{\underline{b}} \quad (1)$$

where

$$\Pi_{\underline{a}}^{\underline{b}} = \sum_{\underline{i}} x_{\underline{i}\underline{a}} x^{\underline{i}\underline{b}} \quad (2)$$

is the first-order density matrix for non-orthogonal bases, $x_{\underline{i}\underline{a}}$ ($x^{\underline{i}\underline{b}}$) being the covariant (contravariant) coefficient of the atomic orbital \underline{a} in the \underline{i} -th MO.

To each pair of atoms in a molecule we assign a semiempirical bond energy ϵ_{AB}

$$\epsilon_{AB} = 4 \sum_{\substack{\underline{a} \in A \\ \underline{b} \in B}} \Pi_{\underline{b}}^{\underline{a}} \Pi_{\underline{a}}^{\underline{b}} \beta_{\underline{ab}} \quad (3)$$

where $\beta_{\underline{ab}}$ is a parameter depending on orbitals \underline{a} and \underline{b} .

$$\beta_{\underline{ab}} = (\alpha_{\underline{a}} + \alpha_{\underline{b}})/k \quad (4)$$

$\alpha_{\underline{a}}$ is in turn the negative of the ionization potential of orbital \underline{a} . Through k we shall ensure that the ϵ_{AB} 's add up to the total electronic energy E

$$E = \sum_{A,B} \epsilon_{AB} \quad (5)$$

Note that this includes the one-center terms, allowing A to be equal to B. Due to (5) and to the idempotency of Π it can be easily shown, paralleled by the introduction of a weight

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in the bond index definition [3], that k must be

$$k = (2/E) \sum_{\underline{a}} \Pi_{\underline{a}} \alpha_{\underline{a}} \quad (6)$$

Formula (3) bears close resemblance to Fischer and Kollmar's [7] resonance energy. Indeed, the Fischer-Kollmar CNDO results show that their resonance energy accounts pretty well for a high percentage of the total bond energy.

Up to here, no requirement is imposed on E , which is thus not tied to any specific approximation. Of course, it would make no sense to apply such expressions within an ab initio treatment. We choose to calculate our examples with the IEH method [11], so that our ϵ_{AB} 's appear in all the tables as ϵ_{IEH} . On using this approximation for the energy, we are relying on the homogeneity property of the electronic energy [12], based in turn on approximate relationships between the MO eigenvalues and total Hartree-Fock energy for closed-shell molecular systems [13].

3. Results and discussion

We apply formula (3), where the parameters $\alpha_{\underline{a}}$ are taken from Ref. [14]. The correlation of the ϵ_{IEH} results with experimental ϵ_{exp} is analyzed through a least squares adjustment

$$\epsilon (\text{kcal/mol}) = a \epsilon_{IEH} (\text{eV}) + b \quad (7)$$

Theoretical ϵ (kcal/mol) are thus obtained for each group of molecules considered.

Table 1 shows the bond energies for some base pairs of nucleic acids. Geometry for the Watson-Crick pairs was taken from Ref.[15]; that for the C-C pair from Ref.[16] and for U-U and T-T we adopt the most probable theoretical configuration [17] with the sum of the van der Waals radii [18] as their intermolecular distances. We shall compare our results with those of Ref.[9], where the interactions between nucleic acids, both in hydrogen bonded and stacked configurations, are analyzed exhaustively. The different approximations listed in the Table are: A) multipole expansion of ab initio charge distribution with repulsion term computed as the sum of atom-atom terms; A') idem with repulsion terms computed as the sum of bond-bond terms; A'') same as A') with other van der Waals radii [9].

Our results show a very satisfactory agreement with the experimental ones, expressed through the value of the correlation coefficient, 0.977 (in formula (7) $a = -7.729$ and $b = 0.519$). They are similar to those of approximations A), A') and A''). The best results for the interaction energy of the A-T and G-C pairs, calculated through the extension of an exchange perturbation theory to larger molecular systems, are respectively -8.60 and -23.75 kcal/mol [19].

Our sequence of stabilities for the pairs in the table is:

G-C C-C A-U A-T T-T U-U

while the experimental in vacuo is [20]

G-C C-C A-U A-T U-U T-T

That is, our predictions disagree regarding T-T and U-U. The inversion occurs also in the three approximations A), A') and A"). This discrepancy is analyzed in Ref. [9] in the light of different experimental measurements. The relative stabilities of A-U and A-T, for which the theoretical values are very similar, depend also on the experimental conditions. On the other hand, there exists an uncertainty in the intermolecular H-bond distance [9], and the IEH electronic energy is sensitive to it.

In approximations A), A') and A") the interaction energy is expressed as the sum of four terms: the electrostatic, polarization, dispersion and repulsion components. Let us remark that our plain definition, which merely adds products of the first-order density matrix weighted by a semiempirical energy factor, correlates equally well with experiment.

Sanderson [10] proposed a classical (non quantum mechanical) approach to bond energy, based on the principle of electronegativity equalization. Two terms are supposed to contribute, one covalent and the other electrostatic. In the case of H-bond energies of systems smaller than the nucleic acid pairs, he neglects the covalent term and supposes that the energy of the protonic bridging is the sum of the electrostatic energies for each pair of oppositely charged ions separated by the bond length. The quantities obtained thus are reported in Table 2.

We have previously estimated the indices for bonds such as

CH...Y [21], which are not consistent with a purely electrostatic model, and we have seen that these bond indices show values similar to those of usual hydrogen bonds. We apply the present approximation to these systems with the H-bond distances of Ref.[10] and verify that agreement with experiment is good, the correlation coefficient being 0.965 ($a = 2.206$, $b = 2.114$).

Let us remark that in a recent semiempirical approach using the EH Hamiltonian for the evaluation of exchange repulsion and charge transfer energies, the intermolecular energy for several dimers has been calculated [22]; the binding energies obtained for H_2O and $HCOOH$ are respectively -5.4 and -9.8 kcal/mol. The energy decomposition analysis of Morokuma et al. has been applied in an ab initio calculation studying the origin of hydrogen bonding [23]; the interaction energies obtained for the HF , H_2O and NH_3 dimers are respectively -7.6, -7.8 and -4.1 kcal/mol. These can be compared with the results of Table 2.

We can then say that formula (3) shows the appropriate correlation with experiment for intermolecular H-bonding.

Table 3 compares our results with those obtained through a bond energy estimation based on the MNDO approximation [8] for ten typical bonds. Interatomic distances are taken from Ref.[24] and experimental bond energies are those reported in Ref.[8]. Figure 1, complementary of Table 3, shows experimental bond

energies as functions of ϵ_{AB} for both approximations.

As read in the Table, the correlation between ϵ_{IEH} and experimental results is satisfactory for each kind of bond, namely C...C, C...O, C...N but breaks down if considered as a whole; the same thing happens with the ϵ_{MNDO} definition. The in situ bond energy [25] presents only one anomaly, the C≡C bond energy: it is too low relative to the experimental one which, furthermore, puts it higher than the C≡N bond energy.

Our results for CC bonds in ethane-ethylene-acetylene obey the ratio 1:1.96:2.94, in good agreement with the experimental one of 1:1.80:2.46. For ϵ_{MNDO} the ratio is 1:1.64:2.30 and for $\epsilon_{in\ situ}$ 1:1.46:1.93. In a bond energy calculation which uses the Hellman-Feynman theorem [26] it is 1:2:2.90. The best agreement is obtained for CNDO, 1:1.7:2.4 [7]. Our C=O/C-O ratio is 2.10 (1.66 for Ref. [8], 1.97 for Ref.[25]) and the experimental one 2.19. As for C≡N/C-N, we obtain 2.88 against an experimental value of 2.86 (2.25 in Ref.[8], 2.68 in Ref.[25]).

The partition of ϵ_{IEH} in its σ and π contributions to CC bonds in C_2H_4 and C_2H_2 gives respectively (-12.26; -13.91 eV) for C_2H_4 and (-20.04; -28.02 eV) for C_2H_2 . The relation $\epsilon_{IEH}^{\pi}/\epsilon_{IEH}^{\sigma}$ is thus 1.76 and 2.40 for each compound. The CNDO ratios [7] are respectively 1.34 and 1.60, while empirical studies [10,p.19] report 1.50 and 1.75. Due to the boundary conditions imposed to the IEH bond index [2], the π contributions are possibly somewhat overestimated.

The correlation coefficients in Fig.1 for ϵ_{MNDO} and ϵ_{IEH} are 0.938 and 0.952 respectively. In the first one, the points more distant from the straight line correspond to the C-H, C-N and O-H bonds, while in the second one they correspond to C-N and C=O. The in situ bond energy [25] in Table 3 has a very good correlation coefficient of 0.984. The definition of this bond energy is a function of the resonance integral; in addition, it contains several semiempirical parameters depending on the two atoms involved in the bond, that permit an adjustment to experimental data. As mentioned in the introduction, we have applied our formula with no fitting of the parameters α_a .

Table 4 shows that the results of our definition succeed in reflecting very small differences in the CH distance passing from CH_4 to C_2H_2 , that is when hybridization changes from sp^3 to sp . The bond energy increase in this series is also found for the Fischer-Kollmar resonance energy term [7]. We verify once more that the resonance energy term [25] and our definition yield good relative estimatives for a given kind of bond.

Figure 2 shows the correlation between our IEH bond energy and the experimental one for some binary hydrogen compounds. Interatomic distances are taken from Ref.[24]. We test our formula for these small compounds, although they should obviously be treated with more rigorous approximations and we do not expect to obtain satisfactory results.

The correlation coefficient 0.912 of the least square adjust-

ment ($a = 5.000$, $b = 9.024$) is not satisfactory. The mean error (relative to experiment in the values obtained from the most probable straight line) is around 8%. The bond index definition of Eq. (1), and hence our bond energy definition, is not appropriate for bonds with an ionic character exceeding certain limits. It is seen in the Figure that hydrides seem to have a bound of -18 eV for the calculated ϵ_{IEH} ; thus, polar covalent bonds of experimental bond energies higher than 100 kcal/mol are not likely to be reproduced using definition (3). This is the case, for example, of the OH' bond as well as HF and HCl. These two are not reported in the Figure; their experimental values are respectively 135.6; 103.3 kcal/mol and the theoretical ones -17.34 ; -15.89 eV.

The BH' terminal bond in B_2H_6 neither correlates well with experiment. Here, it must be mentioned that the values used for BH' and BH'' are not truly experimental ones. The bond energies for BH' and BH'' calculated by Sanderson are 98.9 and 44.2 [10]; as they lead to his atomization energy of 572.0 kcal/mol, in excellent accord with the experimental one of 573.0 kcal/mol, we have taken them as "experimental" values. Furthermore, our results for this molecule involve a non-negligible B-B contribution, -6.59 eV, of the same order of magnitude as one of the bridging BH'' bonds, -7.82 eV; each BH' has a bond energy of -15.27 eV. The valence bond structures [15] also assume a B-B contribution. Our B-B bond index, 0.542 [3] agrees with these predictions better than a SINDO bond order one of 0.988 (sim-

ilar to the terminal BH' of 0.974) which is considered too large [28]. On the other hand, the transferability property expected for the calculated bond energy [7] is more or less obeyed by (NH,NH'), (PH,PH') and (BH,BH'). For all that precedes, it looks as if the value taken as experimental for BH' is too high.

If the values for water and diborane are eliminated from the Figure, the correlation coefficient improves to 0.954 and the mean error decreases to 4.9%.

Ref. [10] reports the atomization energy calculation of a wide group of binary hydrogen compounds. In some cases, when the net hydrogen charge is high, Sanderson introduces an empirical correction factor in order to fit experimental data. Using the group of our best results ($c=0.954$), his mean error is 3.8%.

4. Conclusions

- The bond energy definition proposed here gives IEH results in good correlation with experimental values for intermolecular H-bonds of nucleic acid pairs and also for those of other smaller systems.

- When calculating some typical bonds, a suitable correlation with experiment is attained within each kind of bond.

- In the binary hydrogen compounds considered, the bond energy exhibits a limiting value. For this reason, the correlation for the high experimental bond energies of the more ionic species is not satisfactory, while it improves for the less ionic species.

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Figure Captions

Fig. 1 - Correlation between MNDO bond energies (\bullet) of Ref. [8] and the present IEH bond energies (\blacksquare) with experimental ones. The straight lines obtained through least squares adjustment are respectively the full line and the broken line.

Fig. 2 - Least squares adjustment between our bond energy ϵ_{IEH} and the experimental bond energy ϵ_{exp} [10] for some binary hydrogen compounds. BH' and BH'' are intended for B_2H_6 , where H'' is the bridging hydrogen. PH' is in PH_3 , SiH' in SiH_4 , SH' in SH_2 , CH' in CH_4 , NH' in NH_3 and OH' in H_2O .

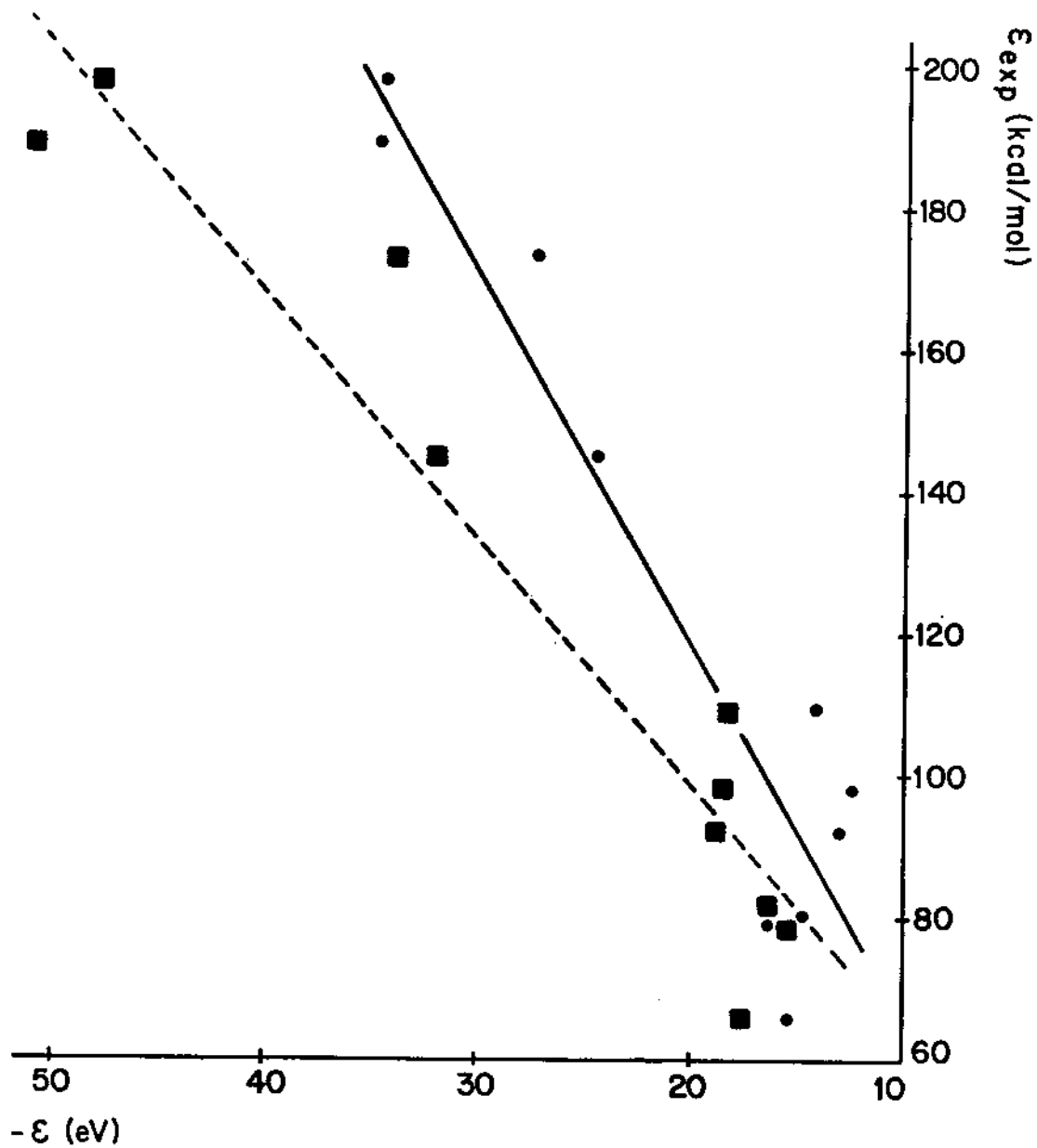


FIG.1

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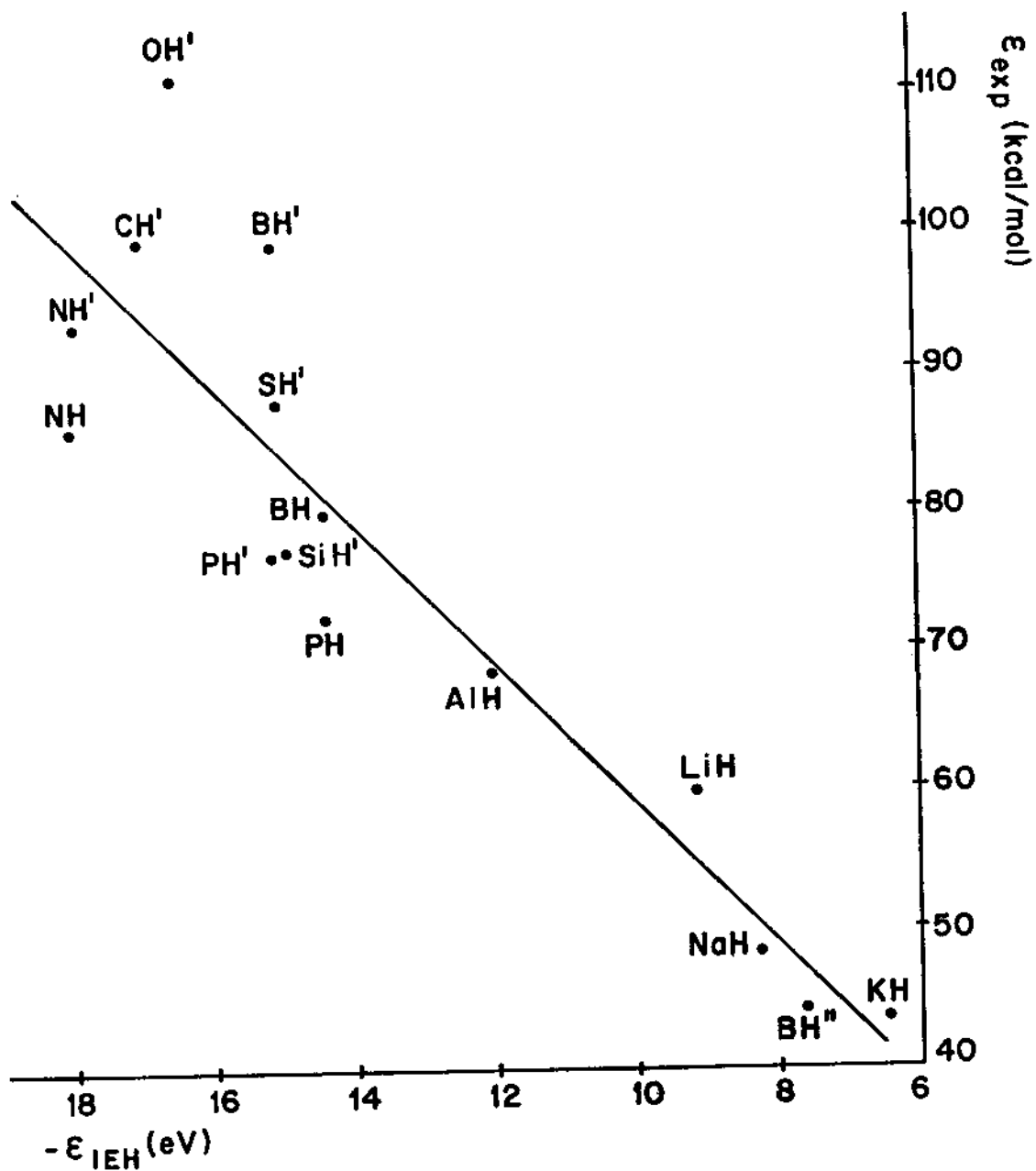


FIG.2

Table 1. Bond energies for base pairs of nucleic acids. ϵ in the fourth column is obtained from the straight line built through least squares adjustment, eq. (7).

Base pair	$-\epsilon_{IEH}$ (eV)	ϵ_{exp} [20] (kcal/mol)	$-\epsilon$ (kcal/mol)	$-\epsilon$ of Ref. [9]		
				A	A'	A''
A-U	1.65	14.5	13.3	13.2	12.4	11.4
U-U	1.13	9.5	9.2	9.2	9.0	9.4
A-T	1.63	13.0	13.1	12.9	12.0	11.0
T-T	1.18	9.0	9.6	9.5	9.6	10.1
G-C	2.56	21.0	20.3	23.7	22.5	21.5
C-C	2.19	16.0	17.4	19.9	18.1	17.3

Table 2. Other hydrogen bond energies (see Ref. [10], p. 115).
 ϵ in the fourth column is obtained from the straight line
 built through a least squares adjustment, eq. (7).

Molecule	$-\epsilon_{\text{IEH}}$ (eV)	ϵ_{exp} [10] (kcal/mol)	$-\epsilon$ (kcal/mol)	ϵ [10] (kcal/mol)
NH ₃	0.81	3.8	3.9	1.3
H ₂ O	1.30	5.0	5.0	5.5
HF	1.84	6.8	6.2	12.7
CH ₃ OH	1.96	6.0	6.4	5.6
HCOOH	2.28	7.1	7.1	6.7
CH ₃ COOH	2.24	7.0	7.1	5.6

Table 3. Comparison of the present IEH bond energies, MNDO [8] and in situ [25] ones for a sample of molecules containing typical bonds. (*) Reported in Ref. [8].

Molecule	Bond	$-\epsilon_{\text{IEH}}$ (eV)	$-\epsilon_{\text{MNDO}}$ (eV)	$\epsilon_{\text{in situ}}$ (kcal/mol)	ϵ_{exp} (kcal/mol) (*)
C_2H_6	C-C	16.36	14.91	88.2	80.5
C_2H_4	C=C	32.07	24.45	128.7	145
C_2H_2	C \equiv C	48.06	34.45	170.4	198
CH_3OH	C-O	16.25	16.39	84.4	79
CH_3CHO	C=O	34.12	27.29	166.0	173
CH_3NH_2	C-N	17.64	15.43	70.8	66
$\text{CH}_3\text{C}\equiv\text{N}$	C \equiv N	50.93	34.79	189.4	189
C_2H_6	C-H	16.86	12.43	98.5	98.2
CH_3NH_2	N-H	18.96	13.15	93.3	92.2
CH_3OH	O-H	18.35	14.24	109.5	109.4

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Table 4. Bond energies for the C-H bond in the series CH_4 , C_2H_6 , C_2H_4 , C_2H_2 . ϵ in the last column is obtained through least squares adjustment, eq. (7).

Molecule	CH distance [27] (\AA)	$-\epsilon_{\text{IEH}}$ (eV)	ϵ_{exp} (kcal/mol)	$-\epsilon$ (kcal/mol)
CH_4	1.094	16.90	~ 99.3 [27]	99.3
C_2H_6	1.099	16.86	98.2 [8]	98.6
C_2H_4	1.087	17.14	~ 106 [27]	105.3
C_2H_2	1.059	17.80	~ 121 [27]	121.2

References

- [1] R. McWeeny, J. Chem. Phys. 19(1951)1614;
R.S. Mulliken, J. Chem. Phys. 23(1955)1833.
- [2] M.Giambiagi, M.S. de Giambiagi, D.R. Grempel and C.D. Heymann, J. Chim. Phys. 72(1975)15.
- [3] M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, Z. Naturforsch. 39a(1984)1259.
- [4] I. Mayer and M. Révész, Inorg. Chim. Acta 77(1983)L205.
- [5] M. Giambiagi, M.S. de Giambiagi and W.B. Filho, Chem. Phys. Lett. 78(1981)541;
M.S. Giambiagi, M. Giambiagi and D.M.S. Esquivel, Z. Naturforsch. 38c(1983)621.
- [6] G. Corongiu and E. Clementi, Gazz. Chim. Ital. 108(1978)273.
- [7] H. Fischer and H. Kollmar, Theoret. Chim. Acta. 16(1971)163.
- [8] Chen Zhixing, J. Mol. Structure (THEOCHEM) 108(1984)139.
- [9] J. Langlet, P. Claverie, F. Caumon and J. C. Boeueve, Int. J. Quantum Chem. 19(1981)299.
- [10] R. T. Sanderson, Chemical bonds and bond energy (Academic Press, N. York, 1976).
- [11] Program from P. Dibout, QCPE 10(1973)256.
- [12] R.G. Parr and R. Gadre, J. Chem. Phys. 72(1980)3669;
E.S. Kryachko, Int. J. Quantum Chem. 22(1982)661.
- [13] K. Ruedenberg, J. Chem. Phys. 66(1977)375;
D. B. Boyd, J. Chem. Phys. 67(1977)1787 and Refs. therein.

- [14] J. Hinze and H.H. Jaffé, J. Am. Chem. Soc. 84(1962)540;
J. Hinze and H.H. Jaffé, Can. J. Chem. 41(1963)1315.
- [15] L. Pauling, The nature of the chemical bond(Cornell,
Ithaca, 1960) chaps. 8,10,12.
- [16] G. A. Jeffrey and Y. Kinoshita, Acta Cryst. 16(1963)20.
- [17] B. Pullman, P. Claverie and J. Caillet, Proc. Natl. Acad.
Sci. USA 55(1966)904.
- [18] A. Bondi, J. Phys. Chem. 68(1964)441.
- [19] W.A. Sokalski and H. Chojnacki, Int. J. Quantum Chem.
13(1978)679.
- [20] I.K. Yanson, A.B. Teplitsky and L.F. Sukhodub, Biopoly-
mers 18(1979)1149.
- [21] M.S. de Giambiagi, M. Giambiagi and C.A. Chamarelli, Nvo.
Cim. 3D(1984)522.
- [22] V.A. Zubkov, Theoret. Chim. Acta 66(1984)295.
- [23] H. Umeyana and K. Morokuma, J. Am. Chem. Soc. 99(1977)1316.
- [24] L.E. Sutton, Tables of interatomic distances(Chem. Soc.,
London, 1958).
- [25] Chen Zhixing, Theoret. Chim. Acta 66(1985)365.
- [26] S. Fliszar, Int. J. Quantum Chem. 26(1984)743.
- [27] P.J. Durrant and B. Durrant, Introduction to advanced
inorganic chemistry(Wiley, N. York, 1962).
- [28] K. Jug, J. Am. Chem. Soc. 99(1977)7800.