# π Bonding in Second and Third Row Molecules: Testing the Strength of Linus's Blanket**

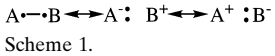
**John Morrison Galbraith,[a] Esti Blank,[a] Sason Shaik,*[a] and Philippe C. Hiberty*[b]**

**Abstract:** The flexibility of valence bond (VB) theory provides a new method of calculating π-bond energies in the double-bonded species $H_mA{=}BH_n$, where A, B = C, N, O, Si, P, S. This new method circumvents the problems usually associated with obtaining π-bond strengths by targeting only the π bond, while all other factors remain *constant.* In this manner, a clean separation between σ- and π effects can be achieved which highlights some expected trends in bond strength upon moving from left to right and up and down the Periodic Table. *Intra*-row π bonds conform to the classic statement by Pauling [L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, **1960**, 3rd edition] regarding the relationship of heteronuclear bond strengths to their homonuclear constituents whereas *inter*-row π bonds do not. This variance with Pauling's statement is shown to be due to the constraining effect of the underlying σ bonds which prevents optimal $p_\pi - p_\pi$ overlap. While Pauling's statement was based on the assumption that the resonance energy (RE) would be large for heteronuclear and small for homonuclear bonds, we have found large REs for *all* bonds studied herein; this leads to the conclusion that REs are dependent not only on the electronegativity difference but also the electronegativity sum of the constituent atoms. This situation where the bond is neither covalent nor ionic but originates in the covalent – ionic mixing has been termed charge shift (CS) bonding [S. Shaik, P. Maitre, G. Sini, P. C. Hiberty, *J. Am. Chem. Soc.* **1992**, *114*, 7861]. We have shown that CS bonding extends beyond single σ bonds in first row molecules, thus supporting the idea that CS-bonding is a ubiquitous bonding form.

**Keywords:** ab initio calculations · bond theory · charge shift bonds · π interactions · valence bond

## Introduction

The resurgence of interest in valence bond (VB) theory in recent years[1] has made the highly influential work of Linus Pauling in the development and advancement of VB theory[2] ever more relevant. One of the fundamental results of VB theory is the concept of resonance. The idea of the resonance between covalent and ionic structures in bond formation (Scheme 1) led Pauling to state that "the energy of an actual bond between unlike atoms is greater than (or equal to) a normal covalent bond between these atoms."[3] This has become a cornerstone of the chemical bond concept.



Scheme 1.

The first question that this statement raises is that of the definition of a "normal covalent bond." Pauling originally assumed that a normal covalent bond, A–B, would lie between A–A and B–B with A–A and B–B making equal contribution [Eq. (1a)]. This definition worked for a large number of single bonds but broke down in cases such as LiH, where the difference between

$$D_{A-B}(\text{a.m.}) = \tfrac{1}{2}(D_{A-A}+D_{B-B}) \quad (1a)$$

$$D_{A-B}(\text{g.m.}) = (D_{A-A}D_{B-B})^{1/2} \quad (1b)$$

homonuclear bond strengths was large, causing Pauling to change from the arithmetic mean to the geometric mean [Eq. (1b)] based on the product relation for the bond forming power between two unlike orbitals.[4] The amount that a heteronuclear bond was stronger than this average was believed to be due to the resonance of ionic electron configurations with the purely covalent configuration. The extent of this resonance depends on the stability of the ionic relative to the covalent configuration; a result of the ability of one component of the heteronuclear bond to attract electrons

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[**] The title makes reference to the blanket of Linus van Pelt of the comic strip "Peanuts" by George Schulz. Linus is the intellectual of the group and is always offering bits of wisdom to the rest of the peanuts gang. This in analogy to the highly intellectual Linus Pauling who gave so much wisdom to the chemical community.

Supporting information for this contribution is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author.

  0947-6539/00/0613-2425 $ 17.50+.50/0 

more than the other. This idea was the basis of Pauling's highly influential electronegativity scale.

Does this statement cover all bonds or is it limited to a select group of molecules? With this question in mind we have set out to determine to what extent or in which cases Pauling's famous statement extends to π bonds by systematically comparing the strengths of heteronuclear π bonds with the average strengths of the corresponding homonuclear π bonds. For this to be done, we will present a novel strategy that allows to compute the strength of a π bond in situ, that is without modifying the bond length or the strength of the underlying σ bond, as opposed to traditional estimations based on rotational barriers or hydrogenation energies. Although Pauling originally only considered single bonds and specified that these relations "do not apply to substances containing double or triple bonds,"[5] the in situ procedure allows the π bond to be considered as a separate entity and therefore possibly subject to the same relationships as single σ bonds. This procedure has also the advantage of being applicable to *any* double bond between atoms of the series (C, N, O, Si, P, S), unlike existing tabulations that lack O=O, S=S and S=O bonding energies. This completed set of coherent in situ π bond energies will, as a second objective of this study, make possible a systematic assessment of homonuclear and heteronuclear π bonds and the emergence of regular and logical tendencies of π-bonding energies across the Periodic-Table.

**Abstract in French:** *La flexibilité de la méthode de la liaison de valence est mise à profit pour étudier les caractéristiques des liaisons π dans les composés de type $H_mA{=}BH_n$ (A,B = C, N, O, Si, P, S). Cette méthode permet d'estimer l'énergie d'une liaison π sans rien changer au reste de la molécule, contrairement aux cycles thermodynamiques habituellement employés pour ces estimations. De cette manière, les effets dûs aux liaisons σ et π sont clairement distingués, mettant en évidence des tendances régulières d'énergies de liaison π de gauche à droite et de haut en bas du tableau périodique. Les liaisons π entre atomes de la même ligne du tableau obéissent à la règle de Pauling [L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, **1960**, 3ème ed.] selon laquelle la force d'une liaison hétéropolaire A–B est supérieure à la moyenne des forces des liaisons homopolaires A–A et B–B. En revanche, cette règle est mise en défaut si les atomes A et B appartiennent à des lignes différentes, à cause de la contrainte exercée par le squelette σ qui empêche les orbitales π d'interagir de façon optimale. Alors que la règle de Pauling était basée sur la supposition que l'énergie de résonance due au mélange des formes covalentes et ioniques est grande pour une liaison hétéropolaire et faible pour une liaison homopolaire, nos résultats mettent au contraire en évidence d'importantes énergies de résonance dans toutes les liaisons π étudiées. Ces énergies de résonance dépendent non seulement de la différence mais aussi de la somme des électronégativités des atomes A et B. Ce type de liaison, appelé «liaison par transfert de charge» et dont la force tient principalement à l'énergie de résonance associé au mélange covalent – ionique, est analogue a celui déjà mis en évidence dans les liaisons σ de certains atomes de la première ligne [S. Shaik, P. Maitre, G. Sini, P. C. Hiberty, J. Am. Chem. Soc. **1992**, 114, 7861].*

## Strategy and Methods

**Strategy**: The first step in testing the Pauling statement is to determine the energy of π bonds. However, this is not as straightforward as it may appear, due to the fact that wherever there is a π bond there is a σ bond as well, and the effects of these two different types of bond are not so easily separable. For example, the energy required to simply pull apart a double-bonded molecule would be the energy of the π- and σ bonds together. The π-bond energy can then be determined by subtracting the σ-bond energy which has to be determined from a source other than the initial calculation itself. This procedure can lead, at times, to unreasonable results due to the fact that a σ-single bond is not the same as the σ

**Abstract in Hebrew:**

תקציר: שיטת הקשר-הערכי (VB) מאפשרת לחשב אנרגיות קשר של קישרי π במולקולות הקשורות בקשרים כפולים מסוג $H_mA{=}BH_n$ כאשר A, B הם האטומים C,O,N,Si,P ו- S. השיטה עוקפת את הקשיים השגורים בחישוב חוזקי קשר π על ידי התמקדות במרכיב ה-π בעצמו כאשר כל הגורמים האחרים מקובעים. בצורה כזאת מושגת הפרדה נקיה בין אפקטי σ ו-π ומאירה בכך נטיות בחוזק הקשר כאשר נעים בטבלא המחזורית לאורך מחזור ובמורד המשפחה. הנטיות של קשרי π במחזור מציתות להצהרה של פאולינג [L.PAULING, The Nature of the Chemical Bond, Cornell University Press, Ithaca, **1960**, 3rd ed.] באשר ליחס בין חוזקי קשרים הטרו-נוקליארים ורכיביהם ההומו-נוקליארים. לעומת זאת הנטיות של קשרי π השייכים למחזורים שונים אינן תואמות את הצהרת פאולינג. הסטיה נובעת מהאילוץ של קשרי ה- σ אשר מונע חפיפה טובה של אורביטלי ה- p היוצרים את קשר ה- π . הצהרת פאולינג התבססה על ההנחה שאנרגית הרזוננס (בין הצורה היונית לקוולנטית) של קשרים הומו-נוקליארים היא זניחה, בעוד מימצאינו מראים שאנרגיות הרזוננס של כל קשרי ה- π הן גבוהות. יתרה מכך, נמצא שאנרגיות הרזוננס תלויות לא רק בהפרשי האלקטרו-שליליות של מרכיבי הקשר, אלא גם בסכום ערכי האלקטרו-שליליות. מצב זה, בו הקשר אינו קוולנטי ואינו יוני אלא נובע מערבוב הצורות היונית והקוולנטית, כונה קשר charge-shift (cs).

[S. Shaik, P. Maitre, G. Sini, P. C., Hiberty, J. Am. Chem. Soc. **1992**, *114*, 7861]

ממצאינו מראים שקשירת cs חורגת מתחום קישרי ה- σ ותחולתה כללית.

  0947-6539/00/0613-2426 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 13

component of a double bond. The experimental value[6] for the double bond in $H_2C{=}CH_2$, for example, is 173.3 kcal mol$^{-1}$ while the single bond in $H_3C{-}CH_3$ is 86.1 kcal mol$^{-1}$ resulting in a π-bond energy of 87.2 kcal mol$^{-1}$, that is 1.1 kcal mol$^{-1}$ *higher* than the C–C σ-bond energy. Another serious problem is related to the states of the fragments in the molecule and at infinite separation. Thus, for example, in $H_2Si{=}SiH_2$ the $SiH_2$ fragments assume a dominant character of the triplet[7] coupled to a singlet ground state disilene. As a result, the double bond in $H_2Si{=}SiH_2$ is weaker than the single Si–Si bond in $H_3Si{-}SiH_3$.[8]

There are presently two common ways of estimating π-bond energies; through rotational barriers or through some sort of thermochemical cycle. The idea behind rotational barriers is that when an $H_mA{=}BH_n$ molecule is rotated 90° to the biradical transition state, the π bond is broken while the σ bond remains intact. However, in addition to breaking the π bond there are other geometric changes associated with the rotation (length of the σ bond, changes in A–H and B–H bond lengths, pyramidalization of A and B atoms), and thereby the measured rotation barrier reflects relaxation effects in addition to the π bond. In addition, the 90° rotated species can have some hyperconjugation effects especially when A or B is an atom with lone pairs such as N or P. As a result, not *all* π-type interaction will be turned off upon rotation. Lastly, this procedure cannot be applied to molecules containing A=O or A=S because there are no hydrogens to rotate.

The method of thermochemical cycles suffers from similar problems of geometric changes and also requires some major approximations to be made somewhere in the cycle. In the following cycle used by Schmidt, Truong and Gordon [Eq. (2)],[9]

$$H_{m+1}A{-}BH_{n+1} \rightarrow H_m\dot{A}{-}BH_{n+1}+\dot{H} \qquad D(A{-}H) \qquad (2a)$$

$$H_m\dot{A}{-}BH_{n+1} \rightarrow H_m\dot{A}{-}\dot{B}H_n+\dot{H} \qquad D(B{-}H) \qquad (2b)$$

$$H_m\dot{A}{-}\dot{B}H_n \rightarrow H_mA{=}BH_n \qquad -D_\pi \qquad (2c)$$

$$2\dot{H} \rightarrow H_2 \qquad -D(H{-}H) \qquad (2d)$$

$$H_{m+1}A{-}BH_{n+1} \rightarrow H_mA{=}BH_n+H_2 \qquad \Delta H^\circ \qquad (2e)$$

$$D_\pi = D(A{-}H)+D(B{-}H)-\Delta H^\circ - D(H{-}H) \qquad (2f)$$

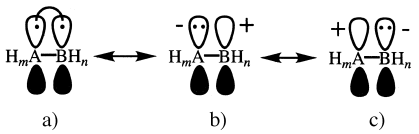
the problem lies with the $H_m\dot{A}{-}\dot{B}H_n$ biradical in Equation (2b). Experimentally, this species does not exist and further, it cannot be calculated by standard molecular orbital (MO) methods.[10] Therefore, the value of $D$(B–H) must be approximated in another way.

An indication of the problems associated with determining π-bond energies can be seen in the disagreement among values obtained with different methods. Gordon et al.[9] found π-bond energies by both rotation barriers and the previously discussed hydrogenation reaction for $H_mA{=}BH_n$ molecules, where A, B = C, N, O, Si, P, S. Estimates of π-bond energies obtained with the two methods differ by as much as 9 kcal mol$^{-1}$ in the case of HN=NH. Using isodesmic reactions, Schleyer and Kost[11] obtained π-bond energies for $H_mA{=}BH_n$ molecules, where A = C, Si and B = C, N, O, Si, P, S which were generally greater than those of Gordon et al.[9] by as much as 16 kcal mol$^{-1}$ for $H_2C{=}O$. Notable also is the disparity with the values of Kutzelnigg[12] which were obtained through evaluation of experimental thermodynamical data.

The present work exploits the features of VB theory and applies a new method for finding the π-bond energies in situ. Through this method, it is possible to determine the π-bond energy, while all other factors remain *constant* thus achieving a clean separation between σ and π effects. This method is applied to all molecules of the type $H_mA{=}BH_n$ where A, B = C, N, O, Si, P, S in order to test the extent of Pauling's statement as it applies to π bonds.

**Methods**: The $H_mA{=}BH_n$ two-electron π bonds can most simply be described as a resonance mixture of the three structures shown in Scheme 2; the covalent Heitler–London (HL) structure 2a (Scheme 2), hereafter referred to as $\Phi_{HL}$, and the ionic structures 2b and 2c (designated $\Phi_{A^-B^+}$ and $\Phi_{A^+B^-}$. The total wavefunction for the π bond then becomes:

$$\Psi(H_mA{=}BH_n) = c_1\Phi_{HL}+c_2\Phi_{A^-B^+}+c_3\Phi_{A^+B^-} \qquad (3)$$



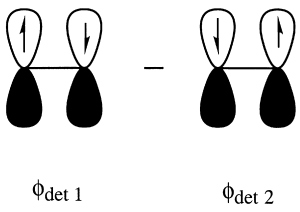

Scheme 2.

The computation of this VB wavefunction and the corresponding π-bond energy was accomplished using TURTLE[13] which is a general nonorthogonal CI program that simultaneously optimizes the VB coefficients [($c_1-c_3$, Eq. (3)] as well as the orbitals. This optimization procedure is based on the super-CI technique[14] which is related to the generalized Brillouin theorem.[15] In this manner the active (bonding) electrons are allowed to correlate while the inactive (nonbonding) space is described by a set of doubly occupied orbitals which adjust to the bond pair.

Hiberty and co-workers,[16] have found it advantageous to allow a unique set of orbitals for each VB structure. In this manner, each orbital can fluctuate in size and shape and adjust to the local charge and as a result, this method is called the "breathing-orbital" valence bond (BOVB) method. The BOVB method produces generally good dissociation energies due to the inclusion of some dynamic electron correlation effects associated with the breathing orbital degree of freedom.

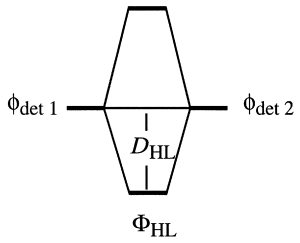
The problems associated with the determination of π-bond energies discussed above can be avoided using VB theory, by further dividing $\Phi_{HL}$ into its constituent determinants. The Heitler–London structure $\Phi_{HL}$ is made up of the negative combination of the two spin paired determinants ($\alpha\beta$,$\beta\alpha$ on

centers A and B, respectively) $\phi_{det1}$ and $\phi_{det2}$ depicted in Scheme 3. The energy stabilization due to spin pairing of the




Scheme 3.

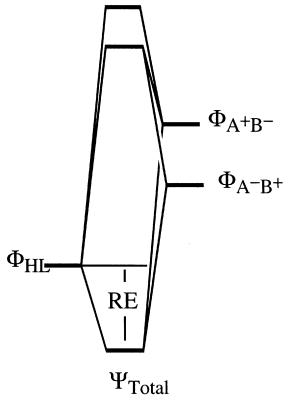
bonding electrons arises from the combination of these two determinants as depicted in Scheme 4. Now it is known in the case of single bonds (e.g. $H_2$) that the energy of each constituent determinant of the HL wave function is nearly equal to the energy of the separate fragments, and this for any internuclear distance from equilibrium geometry all the way to infinite distance.[17] It follows that the bonding energy of a single bond can be calculated as the energy gap between such a single determinant and the true ground state, both being taken at the equilibrium molecular geometry, without actually separating the fragments. Extending this technique to π bonds, one may define a reference non-bonding situation for the π electrons, simply by preventing the two single covalent determinants from mixing, all other factors remaining *constant*, thus obtaining a clean separation of σ and π effects. According to this procedure,[17] and as depicted in Scheme 4,




Scheme 4.

the Heitler–London bond energy $D_{HL}$ is the difference between the energy of $\Phi_{HL}$ alone, $E_{HL}$, and the energy of a single, spin-paired determinant, $E_{det}$. Similarly, the total π-bond energy $D_\pi$ is the difference between the total energy of the wavefunction in Equation (3), $E_T$ and $E_{det}$. The resonance energy RE is then the difference between $E_T$ and $E_{HL}$ corresponding to the energy lowering due to mixing $\Phi_{HL}$ with $\Phi_{A^-B^+}$ and $\Phi_{A^+B^-}$ as depicted in Scheme 5.

It is important to qualify the resonance energy (RE) quantity which, while not an observable, is a useful concept much like charge density. The definition of a purely covalent VB structure which serves as a reference to define the RE of the ground state depends on holding the active bonding orbitals strictly localized. In a finite basis set the RE concept is perfectly meaningful. However, since nothing prohibits the construction of a complete basis set entirely centered on one atom, an expansion of the basis set over and over could cause the covalent structure $\Phi_{HL}$, when calculated *alone*. This is




Scheme 5.

done in order to use the increasing flexibility of the basis set in order to resemble the ground state as much as possible and slowly converge to the generalized (GVB)[18] or spin-coupled (SC)[1d,e] valence bond solution which incorporates ionic configurations through small delocalization tails in the active orbitals.[19] It follows, therefore, that numerical values of covalent/ionic REs may well show basis set dependence and must be considered as indicative rather than accurate. As a simple test of this dependence, we have recalculated the π-bond energies for two molecules with extreme values of REs, $H_2C{=}CH_2$, and O=O, by adding a set of diffuse functions to the 6-311G* basis set. The RE value of $H_2C{=}CH_2$ increased by 0.2 kcal mol$^{-1}$ (from 29.7 kcal mol$^{-1}$ to 29.9 kcal mol$^{-1}$) while this of O=O increased by mere 0.1 kcal mol$^{-1}$ (from 55.6 kcal mol$^{-1}$ to 55.7 kcal mol$^{-1}$). The scant changes give a strong indication that the basis set dependence is not severe, at least in the range of the already quite extended basis set used in the present study.

It is important to add that all the trends which emerge from this study, which are based on the BOVB data, were also retrieved with the VBSCF method[13] in which a common set of orbitals are optimized for the three configurations in Scheme 5 (the VBSCF data are not shown to save space and avoid reiterating of all trends but are available as Supporting Information). Thus, it is the uniformity of trends that matters rather than the absolute values of the RE quantity. Such values can therefore be the basis of useful bonding concepts, provided they are calculated in a basis set of reasonable size, as used in the present study, and common to all molecules under study.[20]

There are two factors effecting $D_{HL}$; the Hamiltonian matrix element and the overlap between $\phi_{det1}$ and $\phi_{det2}$. It has been shown by Shaik[21] that it is useful to consider the reduced resonance integral $\beta$ [Eq. (4a)] when mixing VB determinants. In Equation (4a), $H_{12}$ is the off-diagonal matrix element and $S_{12}$ the overlap between $\phi_{det1}$ and $\phi_{det2}$, and $H_{11}$ is the self element of $\phi_{det1}$ (or $\phi_{det2}$).

$$\beta_{12} = (H_{12} - H_{11}S_{12}) \quad (4a)$$

$$\beta_{ab} = \beta_{12}/2S_{ab} \quad (4b)$$

However, the cumbersome language of determinants can easily be translated into the more familiar language of orbitals



0947-6539/00/0613-2428 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 13

as in Equation (4b) where $S_{ab}$ is the overlap and $\beta_{ab}$ the reduced resonance integral between the bonding orbitals (p orbitals in the present case) on atoms A and B.[21]

The weights of VB states were determined by the formula of Coulson–Chirgwin[22] [Eq. (5)], which is the VB analogue of the Mulliken population analysis.

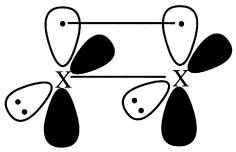
$$w_i = c_i^2 + \Sigma_j c_i c_j S_{ij} \quad (5)$$

All $H_mA{=}BH_n$ (A, B = C, N, O, Si, P, S) molecules except O=O, O=S and S=S were geometrically optimized by density functional theory (DFT)[23] using the B3LYP functional[24] along with the 6-311G[25] basis for first row atoms and the MacLean–Chandler[26] basis on second row atoms. A group of five pure angular momentum polarization functions was added to each basis set, resulting in a total basis set designated 6-311G*.

It should be noted that our in situ calculated $D_\pi$ bear some relationship with the *intrinsic* bonding energies calculated by Jacobsen and Ziegler.[27] In close analogy with our procedure, these authors define a reference non-bonding energy for the interacting fragments at the molecular equilibrium geometry in terms of Pauli repulsion and purely electrostatic interactions between the fragments which keep their local unmodified charge density.

Although some of the $H_mA{=}BH_n$ molecules investigated in this study (e.g. $Si_2H_2$) are *slightly* more stable in non-planar geometries, in order to retain the true π nature of the bonds so that comparisons across the Periodic Table could be made in a meaningful manner, all cases studied herein were constrained to lie in a single plane. Moreover, the π-bond energies calculated this way are representative of some real systems since, even if the planar form may not be the ground state of the pristine compound, studied here, some substituted species (e.g. disylenes) and constrained cases do exhibit planar geometries. As such, our π-bond energies are both useful and practical.

O=O, O=S and S=S are cylindrically symmetric triplets in their ground states and so geometry optimization required extra care in order to ensure a singlet state with a correct spatial and spin symmetry (a combination of MO determinants in which two electrons singlet paired occupy a single π bond). As a result, O=O, O=S and S=S were optimized using the complete active space self-consistent field (CASSCF) procedure.[28] The active space was chosen to include all six π electrons and all four π orbitals thus describing the $^1\Delta_g$ state ($^1\Delta$ state for O=S). The optimized geometries were then used for VB calculations. For VB calculations of O=O, O=S and S=S, two bonding electrons were artificially placed in one plane of the π manifold thus breaking cylindrical symmetry[29] as depicted in Scheme 6. While this state does not correspond to any physically observable state, it is consistent with the other π bonds studied herein. All DFT and CASSCF calculations were completed using the GAUSSIAN94[30] suite of programs.




X = O, S

Scheme 6.

## Results

The B3LYP/6-311G* optimized geometries are presented in Table 1 (detailed structural information is available as Supporting Information). Table 2 contains the π-bond energies of Gordon et al.[9] and Schleyer et al.[11] along with the computed and average [according to Eq. (1a)] BOVB values. Table 3 contains the orbital overlaps of the p AOs ($S_{ab}$) which make up the π bond (2p on second row atoms and 3p on third row atoms). In addition the average orbital overlap determined as $0.5(S_{aa}+S_{bb})$ [analogous to Eq. (1a)] is included for comparison. The $D_{HL}$ values are reported in Table 4 and the reduced resonance integrals, $\beta_{ab}$, are in Table 5. Table 6 contains the resonance energies (RE) and Table 7 VB weights of ionic configurations. All Tables are arranged as the lower triangle of a square matrix in order to highlight the trends as both atoms move from the left to right and up and down the Periodic Table (descending diagonal.) In all Tables and in the following discussion, the $H_mA{=}BH_n$ molecules are labelled as A=B, without inclusion of the implicit hydrogens.

## Discussion

**Bond lengths**: Table 1 shows that the A=B molecules can be divided into three distinct groups based on the bond length; group **1** where both A and B are second row atoms, group **2** where A is a second and B a third row atom, and group **3** where both A and B are third row atoms. This grouping follows logically from the increase in atomic radius as the principal quantum number increases. Thus, group **1** has the smallest average A=B distance (1.238 Å) followed by **2** (1.588 Å) and **3** (2.016 Å). This grouping is prevalent for all properties calculated herein and therefore all bonding features will be discussed by group.

Within all groups, the bond lengths decrease upon moving from left to right of the Periodic Table for both homo- and heteronuclear molecules as can be seen in Table 1 by moving from C=C to N=N to O=O (descending a diagonal). This is to be expected as the A=B bond lengths are dominated by the corresponding σ bonds which will shrink along with the atomic radius from left to right of the Periodic Table due to the increasing effective nuclear charge.

Table 1. Equilibrium A=B bond lengths (in Å) optimized at the B3LYP/6–311G* level for $H_nA{=}BH_m$ molecules (A, B = C, N, O, Si, P, S).[a]

| $r_{eq}$ (A–B) | | C | N | O | | Si | P | S |
|---|---|---|---|---|---|---|---|---|
| C | | 1.327 | | | | | | |
| N | **1** | 1.266 | 1.240 | | | | | |
| O | | 1.200 | 1.200 | 1.194 | | | | |
| Si | | 1.707 | 1.600 | 1.528 | | 2.139 | | |
| P | **2** | 1.670 | 1.587 | 1.493 | **3** | 2.081 | 2.044 | |
| S | | 1.615 | 1.579 | 1.512 | | 1.956 | 1.949 | 1.928 |

[a] Groups 1–3 are indicated in bold.

**π-Bonding energies**: Upon moving from left to right of the Periodic Table, the bond strength should increase because the effective nuclear charge increases and the atomic radius decreases. In σ bonds this trend is observed from Li–Li to

C–C but breaks down for N–N to F–F. This irregular behaviour of the σ bonds, termed the lone pair bond weakening effect (LPBWE),[31] is due to repulsions between lone pairs, on the late group atoms and the bond pair. Indeed, when the effects of LPBWE were removed, Sanderson[31d] observed the expected bond energy increase from Li to F. In the case of π bonds there will be no LPBWE due to the orthogonality of the lone pairs to the π-bond pair. Accordingly, the π bond strengths do increase as expected along a descending diagonal of each group in Table 2b. However, it is

Table 2. A=B π-bond energies in kcal mol$^{-1}$. a) Values according to Gordon[9] and (Schleyer[11]). b) BOVB bond energies calculated herein with average homonuclear π-bond energies according to Equation (1a) in parenthesis.[a]

| | | C | N | O | | Si | P | S |
|---|---|---|---|---|---|---|---|---|
| a) | | | | | | | | |
| C | | 65 (71) | | | | | | |
| N | **1** | 63 (81) | 60 | | | | | |
| O | | 77 (93) | 62 | – | | | | |
| Si | | 38 (36) | 36 (37) | 50 (56) | | 25 (24) | | |
| P | **2** | 43 (49) | 44 | 53 | **3** | 29 (30) | 34 | |
| S | | 52 (56) | 42 | – | | 50 (44) | 40 | – |
| b) | | | | | | | | |
| C | | 72.0 | | | | | | |
| N | **1** | 85.6 (81.4) | 90.7 | | | | | |
| O | | 105.0 (81.6) | 98.2 (90.9) | 91.1 | | | | |
| Si | | 47.1 (53.6) | 58.4 (62.9) | 79.0 (63.1) | | 35.1 | | |
| P | **2** | 52.6 (56.1) | 57.2 (65.5) | 65.9 (65.7) | **3** | 41.9 37.7) | 40.2 | |
| S | | 60.7 (59.0) | 59.9 (68.3) | 64.1 (68.5) | | 57.7(40.5) | 47.5 (43.1) | 45.9 |

[a] Groups 1–3 are indicated in bold.

interesting to note that O=O is only slightly larger than N=N (0.4 kcal mol$^{-1}$) possibly due to an *indirect* manifestation of the LPBWE. While the lone pairs on O=O cannot effect the π bond directly, they can weaken the σ bond leading to a greater O=O distance followed by a weaker π bond due to insufficient orbital overlap. This idea is supported by the O=O distance in Table 1 which is only marginally smaller than the N=N distance. Finally, the presented in situ π bond strengths are higher than the π-bond energies of Gordon et al.[9] and Schleyer et al.[11] in line with the intrinsic π-bond strengths of Jacobsen and Ziegler[27] for $C_2H_4$ and $SiCH_4$. In addition the regularity of trends exhibited by the in situ results is not observed by Gordon et al.[9] or Schleyer et al.[11] where there the separation of σ- and π effects is less clean (Table 2a).

A plot of the BOVB calculated $D_\pi$ versus the corresponding arithmetic mean values (Figure 1) shows that in some cases $D_\pi$ is larger than that of a "normal covalent bond" in accordance with the postulate of Pauling while in other cases it is not.[32] Closer examination of the $D_\pi$ values (Table 2b) reveals that all A=B molecules from groups **1** and **3** obey Pauling's statement while those in group **2** do not (C=S and O=Si are exceptions and will be discussed separately later). As stated above, Pauling's rule was developed for σ bonds which are free to optimize their lengths and overlaps. However, π bonds are buttressed and their lengths constrained by the σ frame. The π bonds are therefore not optimal. When the two components of the A=B bond are from the same row of the Periodic Table,

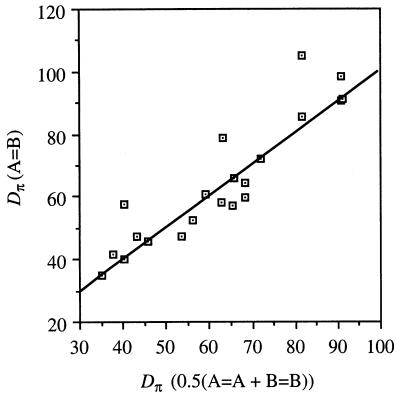



Figure 1. The degree of conformity of $H_mA{=}BH_n$ π-bond energies to the postulate of Pauling (Ref. [2]). The BOVB π-bond strength, $D_\pi$, is plotted against the $D_\pi$ arithmetic mean of its homonuclear constituents as in Equation (1a). Solid line indicates where $D_\pi$ is equal to the average. All values are in kcal mol$^{-1}$.

this buttressing effect is present to a similar extent in both homonuclear bonds and therefore carries over into the average. However, when A and B are from different rows, the σ constraint is sufficiently different from one row to the other leading to unequal contributions to the average and $D_\pi$ values which are smaller than the average.

The effect of σ constraints on the π overlap can be seen in Table 3 which contains the computed p AO overlap, $S_{ab}$, along with the average overlap and the difference between the two.

Table 3. Comparison of the orbital overlaps $S_{ab}$ to the average of the overlaps $S_{aa}$ and $S_{bb}$.[a]

| Group | A=B | $S_{ab}$ | 0.5 ($S_{aa}$+$S_{bb}$)[b] | Δ |
|---|---|---|---|---|
| | C=C | 0.402 | 0.402 | – |
| | N=N | 0.325 | 0.325 | – |
| **1** | O=O | 0.244 | 0.244 | – |
| | C=N | 0.376 | 0.364 | +0.003 |
| | N=O | 0.289 | 0.285 | +0.004 |
| | C=O | 0.336 | 0.323 | +0.013 |
| | Si=Si | 0.357 | 0.357 | – |
| | P=P | 0.294 | 0.294 | – |
| **3** | S=S | 0.244 | 0.244 | – |
| | Si=P | 0.324 | 0.326 | −0.002 |
| | P=S | 0.274 | 0.269 | +0.005 |
| | Si=S | 0.309 | 0.301 | +0.008 |
| | C=Si | 0.357 | 0.380 | −0.023 |
| | C=P | 0.337 | 0.348 | −0.011 |
| | C=S | 0.320 | 0.323 | −0.003 |
| | N=Si | 0.311 | 0.341 | −0.030 |
| **2** | N=P | 0.293 | 0.310 | −0.017 |
| | N=S | 0.265 | 0.285 | −0.020 |
| | O=Si | 0.270 | 0.301 | −0.031 |
| | O=P | 0.263 | 0.269 | −0.006 |
| | O=S | 0.230 | 0.244 | −0.014 |

[a] Groups 1–3 are indicated in bold. [b] Virtually the same results are obtained with the geometric mean values.

In **1** and **3** the A=B overlap is very close to the A=A/B=B average and generally slightly larger. However, in **2**, the $S_{ab}$ values are smaller than the average and differ significantly indicating that A=B is overstretched relative to A=A and B=B. As a result, approximating the normal heteronuclear bond as the average of homonuclear components is mean-



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ingless in group **2**. To test the σ constraints we performed $D_\pi$ calculations with shrunken A=B bond lengths. When this was done for group **2** test cases C=Si and C=P, the $D_\pi$ values went above the homonuclear average when $S_{ab}$ was slightly above the $S_{aa}/S_{bb}$ average. Thus, the σ-buttressing effect is the underlying reason behind Pauling's correct statement that the hetero-/homonuclear relations in σ bonds do not hold for multiple bonds. That this relation *does* hold for *intra* row π bonds is a fortuitous by-product of the similar buttressing effect within a row.

**Components of the π-bonding energies**: To understand the trends in the π-bond energies, we must consider the VB configuration mixing in some detail based on Equation (6).

$$D_\pi = D_{HL}+RE \quad (6)$$

It is useful to consider first the $D_{HL}$ values which are the bond energies due to the fundamental configuration (Scheme 4). Table 4 shows that within each group the portion of $D_\pi$ due to $\Phi_{HL}$, $D_{HL}$, clusters around a constant (45, 26 and 20 kcal mol$^{-1}$

Table 4. Portion of total π bond energy (in kcal mol$^{-1}$) due to the Heitler–London VB configuration, $\Phi_{HL}$.[a]

| $D_{HL}$ | | C | N | O | | Si | P | S |
|---|---|---|---|---|---|---|---|---|
| C | | 42.3 | | | | | | |
| N | **1** | 45.5 | 44.1 | | | | | |
| O | | 48.6 | 42.4 | 35.4 | | | | |
| Si | | 25.6 | 26.7 | 26.5 | | 19.5 | | |
| P | **2** | 27.3 | 27.2 | 28.8 | **3** | 19.9 | 18.8 | |
| S | | 28.8 | 25.3 | 23.5 | | 22.3 | 19.6 | 18.3 |

[a] Groups 1–3 are indicated in bold.

for groups **1**, **2** and **3**, respectively). The only exception to this generality is the O=O bond which is weaker than other members of group **1** possibly due to the indirect LPBWE as discussed above. This consistency is due to the contrasting effects of $\beta$ and S as seen in Tables 3 and 5. $\beta$ increases along a descending diagonal as would be expected from the increase in nuclear charge. On the other hand, S decreases due to a combination of the orbital shrinking, due to the greater effective nuclear charge, along with the constraints of the σ framework which prevents maximization of $p_\pi - p_\pi$ orbital overlap. As a result, $D_{HL}$ which is proportional to $\beta S$[21] remains constant within a group.

Within each group, the relative ordering of $D_{HL}$ values is determined by the interplay of bond length and the compactness of the $p_\pi$ bond orbitals. Upon moving from left to right in the Periodic Table, the smaller bond lengths result in larger $D_{HL}$. However, increased effective nuclear charge and electronegativity also leads to more compact bond orbitals and the resulting worse overlap gives a somewhat lower $D_{HL}$. This interplay which works in opposite directions results in a seemingly random order of $D_{HL}$ within a group. On going from C=C to C=N to N=N, for example the bond length steadily decreases while $D_{HL}$ goes from 42.3 to 45.5 to 44.1 kcal mol$^{-1}$. This up–down pattern is an outcome of the competition between bond length and the loss of overlap due to orbital compactness and σ constraints as can be witnessed when $D_{HL}$ values are determined for the above molecules at a fixed bond length ($r_{A=B} = 1.327$ Å, $D_{HL} = 42.3$, 38.1 and 32.5 kcal mol$^{-1}$ for C=C, C=N and N=N, respectively; $r_{A=B} = 1.266$ Å, $D_{HL} = 51.9$, 48.8 and 44.1 kcal mol$^{-1}$ for C=C, C=N and N=N, respectively). Thus, the very low $D_{HL}$ value of O=O in Table 4 (35.4 kcal mol$^{-1}$) could originate in the oxygen's orbital compactness as well as in indirect influence of the lone-pair bond weakening effect (LPBWE)[31] which further constrains the O–O bond to be too long to express the potential $D_{HL}$ of the π bond.

Table 5. Reduced resonance integrals, $\beta$ (in kcal mol$^{-1}$), as determined by Equations (4a) and (4b).[a]

| $\beta$ | | C | N | O | | Si | P | S |
|---|---|---|---|---|---|---|---|---|
| C | | – 61.2 | | | | | | |
| N | **1** | – 70.3 | – 74.9 | | | | | |
| O | | – 80.5 | – 79.4 | – 76.8 | | | | |
| Si | | – 40.2 | – 47.1 | – 52.6 | | – 30.8 | | |
| P | **2** | – 45.1 | – 50.3 | – 57.2 | **3** | – 33.9 | – 34.7 | |
| S | | – 49.7 | – 50.9 | – 53.7 | | – 39.5 | – 38.5 | – 39.3 |

[a] Groups 1–3 are indicated in bold.

When ionic structures are mixed into the HL structure, there is a substantial increase of the bond energy. Figure 2 shows the total π-bond energy in terms of $D_{HL}$ and the

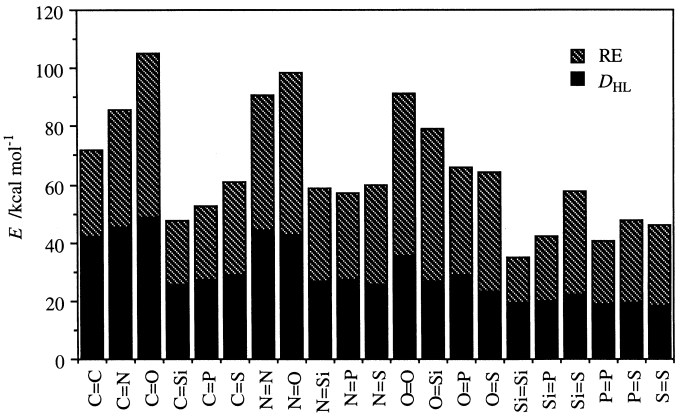


Figure 2. The contribution to the total π-bond energy from the Heitler–London configuration $D_{HL}$, and from the resonance energy, RE, due to covalent–ionic mixing. Energies in kcal mol$^{-1}$.

covalent–ionic resonance energy RE. It is evident that RE makes up a considerable part of $D_\pi$ in all cases. In groups **1** and **3** $RE_{A=B}$ is always larger than the average of $RE_{A=A}$ and $RE_{B=B}$ as seen in Table 6. Considering that Pauling thought

Table 6. Resonance energies (in kcal mol$^{-1}$) according to Scheme 5. Average of homonuclear resonance energies in parenthesis.[a]

| RE | | C | N | O | | Si | P | S |
|---|---|---|---|---|---|---|---|---|
| C | | 29.7 | | | | | | |
| N | **1** | 40.1 (38.5) | 46.6 | | | | | |
| O | | 56.4 (42.7) | 55.8 (51.2) | 55.7 | | | | |
| Si | | 21.6 (22.7) | 31.7 (31.1) | 52.5 (35.7) | | 15.6 | | |
| P | **2** | 25.3 (25.6) | 30.0 (34.0) | 37.1 (38.0) | **3** | 22.0 (18.5) | 21.4 | |
| S | | 31.9 (28.6) | 34.6 (37.1) | 40.6 (41.6) | | 35.4 (21.6) | 27.9 (24.5) | 27.5 |

[a] Groups 1–3 are indicated in bold.

the RE of homonuclear bonds would be negligible, the amount of $RE_{A=B}$ above the average of $RE_{A=A}$ and $RE_{B=B}$ is what Pauling called the "resonance" of ionic configurations and is the basis of the idea that a heteronuclear bond is stronger than its homonuclear components. The greater importance of ionic configurations in heteronuclear bonds can be seen in the larger total weights of $\Phi_{A^+B^-}$ and $\Phi_{A^-B^+}$ for hetero- versus homonuclear bonds in groups **1** and **3** (Table 7).

Table 7. Weights of ionic VB configurations ($\Phi_{A^-B^+}/\Phi_{A^+B^-}$).[a]

| A / B | | C | N | O | | Si | P | S |
|---|---|---|---|---|---|---|---|---|
| C | | 0.155/0.155 | | | | | | |
| N | **1** | 0.125/0.203 | 0.159/0.159 | | | | | |
| O | | 0.088/0.278 | 0.133/0.212 | 0.148/0.148 | | | | |
| Si | | 0.195/.101 | 0.329/0.064 | 0.406/0.041 | | 0.136/0.136 | | |
| P | **2** | 0.146/0.147 | 0.220/0.108 | 0.296/0.053 | **3** | 0.069/0.257 | 0.138/0.138 | |
| S | | 0.094/0.225 | 0.136/0.152 | 0.199/0.096 | | 0.039/0.400 | 0.081/0.230 | 0.137/0.137 |

[a] Groups 1–3 are indicated in bold.

The RE in group **2**, on the other hand is less than the average RE of homonuclear bonds again due to the σ constraints. Only Si=O and C=S, precisely the group **2** bonds which obey Pauling's rule, have REs greater than the homonuclear average.

As already mentioned Pauling originally assumed that the importance of the ionic structures depended on the difference in electronegativity between bonded atoms. This assumption would imply that homonuclear bonds would have little RE contribution.[33] However, Figure 2 shows that for N=N, O=O, P=P and S=S, RE accounts for a significant part of the total bond energy! Clearly the RE is dependent on more than simply the electronegativity difference.

Table 6 shows that the RE increases along a descending diagonal as the electronegativity increases and orbitals become more compact. The increase in RE with orbital compactness has been noted previously by Shaik and Hiberty[34] as being due to a reduction of kinetic energy in the bonding region. Upon bonding, the atomic orbitals contract[35a] and lower thereby the potential energy of the atoms. This orbital contraction is attended, however, by an increase of the kinetic energy of the electrons in the atomic regions. To compensate for this kinetic energy increase and lower thereby the total energy, the kinetic energy of the electrons must decrease in the bonding region (interatomic region[35]). This decrease in the kinetic energy is manifested in the covalent–ionic RE. The larger the RE, the more significant is the kinetic energy decrease in the bonding region.[34] Thus, the RE contribution is the factor that enables the atoms to contract and lower the molecular energy when they enter into bonding. As the electronegativity of an atom goes up, its atomic orbitals are, to begin with, compact, and their further contraction upon bonding leads to a significant increase of the kinetic energy of the atoms. As a means to compensate and lower the molecular energy, electronegative atoms would require a large RE; much more so than when less electronegative atoms enter into bonding.

That the RE is dependent on orbital compactness can be seen by inspecting the RE values for the homonuclear cases (Table 6). The RE is small for the atom with the most diffuse orbitals, Si (15.6 kcal mol$^{-1}$) and increases as the orbitals become more compact through P (21.4 kcal mol$^{-1}$), S (27.5 kcal mol$^{-1}$), C (29.7 kcal mol$^{-1}$), N (46.7 kcal mol$^{-1}$) and O (55.7 kcal mol$^{-1}$). Figure 3 displays a plot of RE versus the sum of electronegativity for the entire A=B set. The only points which deviate considerably from linearity are C=O, O=Si and Si=S, all of which have a large atomic electronegativity difference. This shows that while RE is strongly dependent on the *sum* of electronegativities, the electronegativity *difference* plays also an important role in the determination of the covalent–ionic RE as is apparent from the VB mixing diagram in Scheme 5. In order to incorporate the two factors, we have devised an equation for the RE [Eq. (7)] based on *both* the sum and the difference of the electronegativities of the bound atoms.

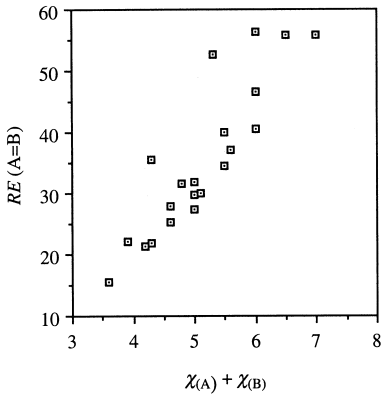


Figure 3. The relation between $RE_{A=B}$ and the sum of electronegativities of atoms A and B. RE is in kcal mol$^{-1}$. Electronegativity values $\chi$ are from Pauling (Ref. [2]). Other electronegativity values (e.g. in Ref. [31d] and [37]) were plotted with similar results.

$$RE_{A=B}\ (\text{kcal mol}^{-1}) = 11.35\ (\chi_A+\chi_B)+4.00(\chi_A-\chi_B)^2-25.22 \quad (7)$$

Equation (7) is valid within ±3.5 kcal mol$^{-1}$ for *all* molecules in the present study. This Equation incorporates the Pauling term that depends on the electronegativity difference [ref. [2]; Eqs. (3)–(10) and (3)–(11)], and the orbital compactness term which depends on the electronegativity sum.[36]

**Charge-shift bonding in π bonds**: When the RE due to covalent–ionic mixing becomes a prominent feature of the bond energy, the bond is neither covalent nor ionic, a situation which has been termed by Shaik and Hiberty as "charge shift" (CS) bonding.[31a–c, 34] Figure 2 demonstrates that quite a few of the π bonds qualify as CS bonds. It is interesting therefore, to elucidate the factors which enhance this bonding quality.

Previously, CS bonding was noted for σ bonds[31a–c, 34] and was shown to manifest under two conditions: i) when the

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atomic orbitals are compact, and ii) when covalent bonding due to $\Phi_{HL}$ is weakened by the LPBWE.[31d] These effects are manifest also in the present π bonds. Thus, in all the π bonds $D_{HL}$ is deprived due to the σ-constraints as well as to the inherently small $p_\pi - p_\pi$ overlap. Furthermore, most π bonds exhibit a CS character which gets more prominent when the bond involves more electronegative constituents, as predicted by Equation (7).

The interplay of orbital compactness and strength of $D_{HL}$ can also explain why the RE in most π bonds involving C (the best HL atom) and Si=Si (the most diffuse orbitals) contributes a smaller portion to the total bond energy. CS bonding and its dependence on orbital compactness thus increase the "blanket" beyond Pauling's original suggestion.

## Conclusion

Pauling's statement that "the energy of an actual bond between unlike atoms is greater than (or equal to) the energy of a normal covalent bond between these atoms,"[3] has formed a basis for the generation of his widely used electronegativity scale. The applicability of this statement to π bonds was tested by employing a novel technique that leads to in situ π bond energies in the presence of an intact σ frame. Our test reveals that Pauling's statement extends to π bonds made from constituents belonging to the same row of the Periodic Table, but breaks down for comparisons involving inter-row π bonds. This break down originates in the constraints applied by the σ frame which result in overstretched heteronuclear π bonds relative to homonuclear π bonds, thus disabling a comparison in the light of Pauling's statement.

Pauling's statement was based on the consideration of the covalent–ionic resonance energy (RE), due to mixing of the ionic into the covalent structure and on the assumption that this RE is negligible in homonuclear cases and significant in heteronuclear cases. While we agree with Pauling that his rule must be traced to the RE patterns rather than to the pure covalent energy, we are at variance with his assumption about the RE of homonuclear bonds. Our study reveals that REs are *always* significant and are determined by two fundamental quantities; the electronegativity difference $(\chi_A - \chi_B)$ which scales the covalent–ionic energy gap and the electronegativity sum $(\chi_A + \chi_B)$ which scales as the mixing matrix element and is determined by the combined compactness of the atoms and their orbitals. Indeed the computed REs exhibit a nice fit to these two quantities as shown in Equation (7). Since the rationale for this Equation is not restrictive, a general expression for the covalent–ionic RE of a bond should be stated as follows:

$$RE_{A=B}\ (\mathrm{kcal\,mol^{-1}}) = a(\chi_A+\chi_B)+b(\chi_A-\chi_B)^2 - c \qquad (8)$$

Thus, for a given compactness, the covalent–ionic RE of a bond increases as the electronegativity difference of the constituents increase while for a given electronegativity difference, the RE increases as the atomic constituents become more compact.

The partitioning of the total binding energy into covalent, $D_{HL}$, and covalent–ionic REs ($D_\pi = D_{HL}$+RE) allows to classify the π bonds. Since in most cases, the RE constitutes a major portion of the bond energy, many of the π bonds are neither covalent nor ionic; they are charge-shift (CS) bonds.[31a–c, 34] The CS character of the π bond is more prevalent the higher the electronegativity sum of the bond constituents.

Thus, the in situ π-bond energies enable to draw some fundamental conclusions, hitherto impossible, regarding the applicability of Pauling's statement to π bonding and to determine that CS bonding, which is induced by orbital compactness and weakened covalent bonding, exists in π bonds. The present study is yet another indication that CS bonding may be a ubiquitous bonding form. Just how common CS bonding really is in both single and multiple bonds across the entire Periodic Table remains to be determined.

## Acknowledgement

The work at the HU is funded by the ISF established by the Israel Academy of Sciences and Humanities, and partially by the Lady Davis Fellowship Trust at the Hebrew University.

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Received: August 30, 1999 [F2008]

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