Multicenter bonds, bond valence and bond charge apportion

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ABSTRACT

In the same way that the valence of an atom issues from the definition of bond index, we show here that the three-center bond index lends itself to the definition of a bond valence. Within the charge of a bond, we show that its self-charge (i.e., the amount of electrons kept by the atoms involved in the bond) is parted in such a way that the more electronegative atom tends to allot more eletronic charge than the other atom. We give examples of these quantities and discuss the results for different kinds of chemical systems. We also show some results for four-center indices and report six-center indices for hexagonal rings.

Key-words: Multicenter bond index; Bond charge partition; Bond valence.

1. Introduction

Along a series of works, we have been concerned with invariants arising from molecular orbital (MO) calculations, linked to chemically significant molecular quantities. Thus, we have defined a bond index I_{AB} between atoms A and B [1, 2] (generalization of Wiberg's [3] to non-orthogonal bases), the valence of an atomic group [4], a group-group bond index leading to a definition of molecular valence [5] and a multicenter bond index [6]. The word invariant is meant strictly in the tensorial sense, i.e. a scalar.

It should be reminded that the concept of three-center (3c) bond is almost contemporary of the Lewis two-center electron pair bond [7]. Chemists have been familiar with multicenter bonds for many years (see for example [8–10]).

In this work we deal mainly with 3c bond indices I_{ABC}, as well as some four-center (4c) and six-center (6c) ones. We show that the definition of a bond valence V_{AB} arises naturally from the extension of the definition of the valence of an atom within a molecule V_A [2, 11, 12]. We also show that the indices I_{AAB} and I_{ABB} account properly for the partition of the bond charge between A and B.

Although we have used *ab-initio* methods in Ref. [6], we utilize here semiempirical approximations whicch are the most appropriate to our purposes [13]; we have shown elsewhere [14] that both approaches are equally competitive for these kinds of concepts.

2. Bond indices

For non-orthogonal bases and closed shells, the first-order density matrix is a mixed tensor [2]

$$2\Pi_a{}^b = 2 \sum_i x_{ia} x^{ib} \tag{1}$$

where $x_{ia}(x^{ib})$ are covariant (contravariant) coefficients of the i-th MO and a(b) denote atomic orbitals. The properties of Π have led us to introduce a multicenter bond index $I_{ABCD\cdots L}$ [6]

$$I_{ABC\cdots L} = 2^{L-1} \sum_{\substack{a \in A \\ b \in B \\ c \in C \\ \vdots \\ \ell \in L}} \Pi_a^b \Pi_b^c \cdots \Pi_\ell^a \tag{2}$$

In that work [6], we centered our attention on 3c bonds. The Mulliken atomic charge q_A may be parted (in a different way than Mulliken's) into self-charge I_{AA} and active

charge $\left(\sum_{B \neq A} I_{AB} \right)$ [1, 2, 15]

$$q_A = \frac{1}{2} \left(I_{AA} + \sum_{B \neq A} I_{AB} \right) = \frac{1}{2} \left(I_{AA} + V_A \right) \tag{3}$$

where V_A is the valence of atom A [11, 12] and the bond index I between atoms A and B is [1–3][1]

$$I_{AB} = 4 \sum_{\substack{a \in A \\ b \in B}} \Pi_a^b \Pi_b^a \tag{4}$$

Before returning to the multicenter bond index, let us explain briefly what is our model when I_{AB} is defined and how it differs from Mulliken's. If is well known [1, 2, 14] that Wiberg devised his index for orthogonal bases [3], as overlap population vanishes in this case. Now, in the hydrogen molecule our model assigns half an electron, both for self-charge and active charge, to each of the hydrogen atoms: I_{AB} is thus equal to one. We have seen in Ref. [1] that in hydrocarbons the hydrogen active charge is still very close to 0.5, its net charge varying thus at the expense of self-charge. The overlap population for H_2 is of course different from 1, just as for most homonuclear and other typical molecules it is appreciably different from the integer values expected for single, double or triple bonds. The integer values are self-consistent *a priori*, in the terms of Ref. [17].

On the other hand our model up to here, as Mulliken's, suffers from the disadvantage of charge equipartition of the bond population between the two atoms involved [18, 19]; therefore it is appropriate for covalent bonds and not for ionic bonds. Our model, unlike Mulliken's, does not make a distinction between bonding and antibonding situations.

Different definitions have been proposed in order to overcome the equipartition question. The best known at present is undoubtly Bader's topological theory [20]. Refs. [19,21-24] are worthwhile mentioning. In Extended Hückel approach [25] a weight is introduced in the off-diagonal terms of the Hamiltonian [26], in order to improve Mulliken population analysis. We ourselves have considered the problem twice [27, 28]. In the appendix of Ref. [2] we have returned to the definition proposed in Ref. [27], containing a weight factor involving the difference between the electronegativities of A and B. Anyway, we left it aside, for our results in other kinds of molecules were not satisfactory enough.

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[1]I_{AB} has also been named V_{AB} and has been called valence of the AB bond when studying reactions [16].

Needless to say, our model, as Mulliken's, is quite different from the Lewis pair bond model [14].

3. Multicenter bond index, bond charge partition and bond valence

Let us now use definition (2) in the 3c case, leading to a bond valence definition. We may write I_{AB} in the form [29]

$$I_{AB} = \frac{1}{2} \sum_C I_{ABC} \tag{5}$$

In Refs. [29–31], the authors suppose that the sum over C runs over $C \neq A, B$. Nevertheless, it may be seen that actually

$$I_{AB} = \frac{1}{2} \left(I_{AAB} + I_{ABB} \right) + \frac{1}{2} \left(\sum_{C \neq A,B} I_{ABC} \right) \tag{6}$$

Similarly to (3) the first terms may be thought of as the amount of electrons kept by the bond AB, while the *bond AB valence* V_{AB} is the active charge of the bond

$$V_{AB} = \sum_{C \neq A,B} I_{ABC} \tag{7}$$

We could even generalize

$$V_{ABC} = \sum_{D \neq A,B,C} I_{ABCD} \tag{8}$$

and so on, but we shall restrain ourselves to using V_{AB} in this work.

The bond valence V_{AB} may be positive or negative. Sannigrahi and Kar [29] assert that negative 3c bond indices have no chemical significance. Now, a distinction is usually made between two-electron (2e) and four-electron (4e) 3c bonds [7]. It is used in Ref. [32], associating negative values to (3c-2e) bonds and positive values to (3c-4e) bonds. Using Grassmann algebra, we have shown [33] that, within the Hartree-Fock approximation, multicenter bond indices represent the correlation between the fluctuations of the charges in each atom from their average values; explicit formulae are given for 3c and 4c bond indices. From these results, no *a priori* distinction appears between positive and negative values.

We have also defined χ, the number of electrons involved in a 3c bond [14]:

$$\chi = I_{AB} + I_{BC} + I_{AC} \tag{9}$$

and we have seen that χ is fractionary; its values ranging from about 1 to somewhat more than 4 in the systems studied. The sign does not depend on χ. For example, both in CO and C_3 we obtained $\chi \gtrsim 4$, while their I_{ABC} values differ in sign, being negative for CO_2 and positive for C_3.

Returning to Eq. (7), in a triatomic molecule, $V_{AB} = I_{ABC}$. Therefore, $V_{AB} = V_{BC} = V_{AC}$; although this does not sound as entirely satisfactory, it is equivalent to charge equipartition in the most familiar 2c-case.

What is the meaning of I_{ABC} if A or B are equal to C? Looking at eq. (6), let us postulate that I_{AAB} and I_{ABB} are, respectively, the contributions of atoms A and B to I_{AB} (I_{ABC} is invariant for any permutation of indices [6]). Thus, we offer a way out to the 2c-equipartition problem, for the self-charge *of a bond* is hence made of the *different* contributions of the two atoms involved.

We could, similarly, split I_{ABC} in 4c-indices and thus avoid the equipartition involved in V_{AB}; nevertheless, we shall stop here.

4. Results and discussion

Despite the overwhelming success of *ab initio* calculations, semiempirical MO methods still make sense [13, 34]. We shall apply here CNDO/2 [35], the Iterative Extended Hückel (IEH) [13, 25, 36] method and MOPAC-PM3 [37]. Besides, we have seen that the I_{ABC}'s order of magnitude are qualitatively independent of the bases used in the calculations and that, for the kind of concepts that we deal with in this work, semiempirical methods are as competitive as *ab initio* ones [14].

Tables 1 and 2 contain some of the different indices studied in this paper, for neutral and charged systems involving the same 3c-group. We may thus compare the behaviour of each group with the indices obtained.

Table 1 reports the main results for a few systems containing the CO_2 3c-bond. It has already been mentioned [6, 8, 14] that "long bonds" or "secondary bonds" are most important in 3c-bonds. A significant I_{ABC} value is always parallel to an expressive I_{AC} index. For example, the IEH approximation gives a range of $0.52 - 0.57$ for I_{23} between the corresponding oxygen atoms for the three systems in the Table. The values of χ_{123} for the three systems also show the influence of the "secondary bonds".

In CO_2, the long-bond structures have been found to make a considerable contribution in advanced valence bond (VB) calculations [40]. It is well known that MO and VB calculations are equivalent at the same sophistication level [13]. It is therefore satisfactory

that both pictures predict an equally important role for "long bonds".

Within each calculation method for the charged species there is a close agreement between the values of I_{123}, the bond self-charge and the valence of the CO bond. The difference between the results of charged and neutral systems may be partly due to the difference in geometry. Nevertheless, it could be expected that the charges -1 and -2 would lead to a larger range of values than the one shown in the table.

The systems in Table 2, containing the NO_2 3c-bond, exhibit some different features. The first three species have, within the same calculation method, an I_{ONO} index and χ_{ONO} similar respectively to I_{OCO} and χ_{OCO} of the charged systems in Table 1. The valences of CO and NO in the corresponding 3c-bonds cover a broader range. The nitrite ion is isoelectronic with ozone, and ascribes similar importance to the long-bond structure [2, 8].

In (b), the bond charges where N_1 is involved correspond to two roughly one-and-a-half bonds and one single bond. In (c), the third bond of N_1 is an NN one and the N_4O_5 bond is a double one. The $ONNO_2$ molecule involves a very long NN bond, where repulsion between nitrogen lone-pair electrons play an appreciable role [41]; the NN bond index is almost half than that of a typical single bond as hydrazine's. As we have remarked for N_2O_4 [2], the longer O_2O_5 bond is too weak to lock the system in a planar conformation [8, 42]. Besides, the 1-2 and 1-3 bonds have practically equal valence, for the *cis* or *trans* position of the other oxygen is almost immaterial.

The nitrate ion has different characteristics from the other systems in the table, having also higher symmetry than the others. It is the anion of (b) and its I_{123} values are around half I_{123} for (b). As to the apportion of the bond self-charge, CNDO would predict equipartion; IEH and MOPAC predict opposite polarity.

From both Tables 1 and 2, it is seen that the more electronegative atom generally allots more electrons to the bond self-charge. In these tables, IEH has enhanced values for I_{ABC} and MOPAC seems to exaggerate the differences between I_{AAB} and I_{ABB}.

The geometry for the isoelectronic NO and SN dimers is drawn in Fig. 3. Two different structures have been proposed for the NO dimer: the *cis*-(C_{2v}) structures (a) and the rectangular C_{2h} one (b) [39]. The literature reports arguments favouring one or the other.

The small I_{NN} value in (a) (~ 0.24) is due to the long NN bond that, as in O_2NNO_2 and $ONNO_2$, has been underlined and partly ascribed to the repulsion between the nitrogen lone-pair electrons [41].

In Table 3, the I_{123} index corresponds to an NNO 3c-bond for structure (a) and to

an NON 3c-bond for structure (b). Furthermore, the geometry of both molecules is appreciably different. Despite these two circumstances, there is a remarkable agreement between the I_{123} values predicted by the three calculation methods for both structures. The 4c indices are also quite close to each other and significant, of the same order of magnitude than several 3c indices.

The valence of nitrogen coincides in this case with χ_{123}. Although somewhat lower than usual values it remains, as expected, higher than V_O; V_O keeps within the range $2.37 - 2.54$.

Table 4 shows results for the SN dimer, isoelectronic with the NO dimer. For this system only, we have included two other calculation options, both of them Extended Hückel without iteration: the first, with the same parameters than IEH, the second one with different parameters including d orbitals for sulfur [44]. It is seen that the inclusion or not of these orbitals makes most of the difference, for CNDO includes them automatically for second-row atoms. Thus, CNDO results are qualitatively very similar to those labelled EH2, except for the sign of I_{1234}. Instead, I_{NSN} and the 4c index issuing from the other methods are much closer, respectively, to I_{123} and I_{1234} of Table 3. In this molecule, V_S coincides with χ_{SNS} and V_N with χ_{NSN}. It is seen that the inclusion of d orbitals increases, of course, the sulfur's valence.

Although not shown in the Table, there is also a high value for the secondary NN bond, predicted in IEH (0.66) and MOPAC (0.42) results. For the EH1 calculation, the secondary SS bond is more important than the secondary NN one; the same thing happens when $3d$ orbitals are included in the sulfur basis. A STO-6G VB study [45] concludes that structures including $3d$ sulfur orbitals do not contribute substantially, while the structure involving the NN long bond is dominant in the ground state.

Hydrazoic acid HN_3 is the subject of several works dealing with hypervalence or not of the central nitrogen (see for example Refs. [47] and [48]). Ref. [47] makes an appealing distinction between geometric and electronic hypervalence, concluding that HN_3 can be considered geometrically but not electronically hypervalent, while Ref. [48] mentions $N_1N_2N_3$ as a (4e-3c) bond, meaning the four π electrons from the three nitrogens. We show our results in Table 5. We obtain a somewhat-more-than-four-electrons-3c bond, our electrons being $(\sigma + \pi)$, for in our model part of them are kept by the nitrogen atoms as self-charge. As [47], we predict for the central nitrogen a valence near to 4, while N_1 and N_3 have a valence around 3. The "long bond" N_1N_3 is of course responsible for these results. The values for bond valences are noteworthy, for the three calculation methods bonds N_1N_2 and N_2N_3 have practically the same valence, while the bond self-charges are

very different.

In Ref. [48], VB hybridization values are assigned to the atomic orbitals h of each nitrogen, through the formula $h = s + \lambda p$:

for N_1, in the $N_1 - N_2$ bond $h = s + 2.8p$

for N_2, in the same bond $h = s + p$

for N_3, in the $N_2 - N_3$ bond $h = s + 1.41p$

As the electronegativity increases with increasing s character, this should yield $I_{122} > I_{112}$ and $I_{223} > I_{233}$, in agreement with the CNDO and IEH results in Table 5. The MOPAC values invert in the first case and predict equipartition in the second one. The 4c index is higher than other 3c-ones not shown in the Table and the methods show a qualitative agreement.

Cianopolyynes (HC_nN) form an appealing family of compounds, from which a recent study has picked HC_6N [49]; we have in turn chosen from this study the three most probable structures, shown in Fig. 4, and reported our most significant results for indices and bond valences in Table 6.

The most striking of them is I_{ABC} for the C_3 ring in (a) and (b). For the sake of comparison, we have calculated the analogous index for three-membered rings $(CH_2)_2X(X = CH_2, NH, O, S, SO$ and $SO_2)$ and for cyclopropene. According to the same three approximations that we have used in the present work, they are generally lower than 0.06. Despite the difference in the groups at each side of the double bond, its bond self-charge roughly obeys equipartition; for the single bond, instead, the carbon with an electron lone pair contributes clearly less than the other one to the bond self-charge.

For structure (c), the $C_5 - C_6$ and $C_6 - C_7$ bonds are both double bonds at first sight; actually, however, $C_5 - C_6$ is a somewhat-less-than-double bond $(1.357)\mathring{A}$) and $C_6 - C_7$ a somewhat-more-than-double one $(1.301\mathring{A})$, the former having a bond valence lower than the last one. The partition of charge is different for both bonds, more emphasized by MOPAC.

The absolute values of I_{1234} for (a) and (c) are very high and correspond to a bond sequence triple-single-triple. The values of I_{123} and I_{234} for (a) and (c) are low; this is due to the lack of the corresponding "secondary bonds" (1-3) and (2-4). Accordingly, the χ values are lower than, for example, χ_{123} in Table 5. Also for (a) and (c), χ_{1234} is near to 7, the number expected from classical Lewis structures. In (b) it is appreciably lower. $|I_{1234}|$ for (b) and other $|I_{ABCD}|'s$ for the three molecules that do not appear in the Table, have

values within the range $0.05 - 0.10$, including different kinds of multiplicity in the bond sequences. Let us emphasize that I_{1234} values for (a) and (c) are similar to significant three-center indices, such as those of strong hydrogen bonds and peptide bonds [6].

Table 7 shows results for the most typical monosubstituted benzenes. The apportion of bond self-charge in the CX bond shows an agreement between CNDO and IEH, while MOPAC predicts inverted behaviour in benzene and toluene and bond self-charge equipartition for aniline. In toluene the bond concerned may be considered to be $C(sp^2) - C'(sp^3)$; as such, due to the difference in electronegativity, an electronic displacement towards the ring is produced. For phenol and fluorebenzene the more electronegative atom again contributes more to I_{CX}. The bond valence V_{CX} is quite small for benzene and toluene; this means that the CX bond is practically not involved in multicenter bonding, while the other compounds evidence some degree of participation.

For the ring index, the agreement between the three calculation methods is very close. The index value is significant and quite similar for the five molecules. It is tempting to associate this behaviour to the similar corresponding values of the conjugation energy (within 8% [51]).

Table 8 reports the ring 6c-index for a few standard pattern rings. Benzene and pyridine, which are known to have similar aromaticity, have equal values of I^2. Borazine has physical properties very close to benzene's, its chemical properties are instead different and they suggest little aromatic character [39, p. 238]. Even if MOPAC-PM3 does not provide parameters for boron, the CNDO and IEH values are clearly lower than those of benzene and pyridine.

The last decades have seen an ever growing interest in unsaturated sulfur nitrogen compounds, of which the $(S_3N_3)^-$ ring system is a prototype [52]. This is a 10 π-electron six-membered ring [53]. It has been recently concluded that this kind of electron-rich systems have weak aromaticity, their bonding strength decreasing with respect to the 6π-electrons counterparts [54]. It is therefore satisfactory that the $(S_3N_3)^-$ ring indices in the table are two orders of magnitude lower than benzene's or pyridine's and also much lower than borazine's.

5. Conclusions

– The three-center indices lead to a straightforward definition of a bond valence.

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[2]The 6c-I value of pyridine in Ref. [6] is wrong

– In the bond self-charge apportion, the more electronegative atom tends to allot a greater amount of electrons in the bond than the other atom.

– Four-center bond indices are usually lower than three-center ones. However, we show here structures of a cianopolyyne where an index I_{ABCD} involving two triple bonds is of the same order of magnitude than other significant I_{ABC} values, for example those of strong hydrogen bonds and peptide bonds.

– The six-center ring index in benzene, monosubstituted benzenes and other six-center rings may be related to aromaticity.

Acknowledgement

Figure Captions

Figure 1. Systems containing the CO_2 3c-bond. Geometries from: (a) [38], p. 267; (b) optimized through MOPAC-PM3; (c) [39], p. 523. All distances in $\mathring{A}$.

Figure 2. Systems containing the NO_2 3c-bond. Geometries from [39]; (a), (b), (c), (d) respectively in pp. 522, 536, 521 and 526. All distances in $\mathring{A}$.

Figure 3. Conformations for the NO and SN dimers. (a) and (b) from [39], p. 513; (c) [43]. All distances in $\mathring{A}$.

Figure 4. The most probable structures for HC_6N [49].

$$O_2 \overset{1.159}{=\!=\!=} C_1 =\!=\!= O_3$$

(a)

$$\left(H_4 \overset{1.114}{-\!\!-\!\!-} C_1 \overset{1.254}{\underset{O_3}{\overset{O_2}{<}}} 123^o \right)^{-}$$

(b)

$$\left(\underset{O_3}{\overset{O_2}{>}} 126^o \; C_1 \overset{1.57}{-\!\!-\!\!-} C_4 \overset{1.25}{\underset{O_6}{\overset{O_5}{<}}} \right)^{2-}$$

(c)

Fig. 1

(a)

(b)

(c)

(d)
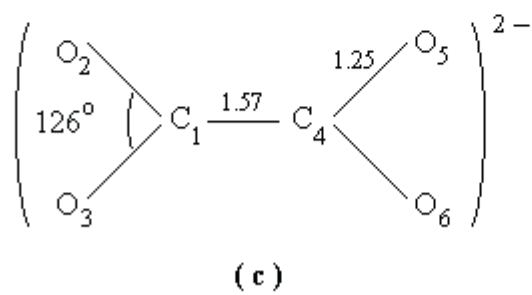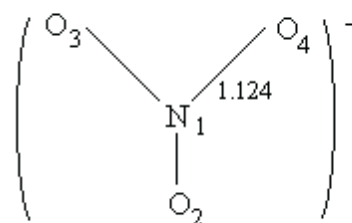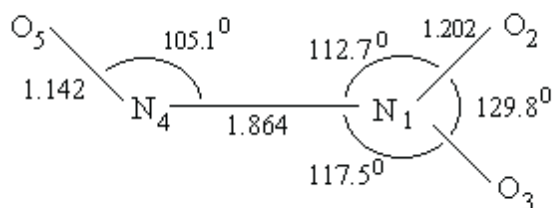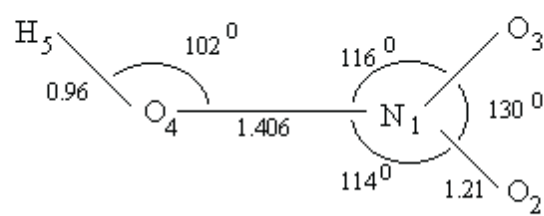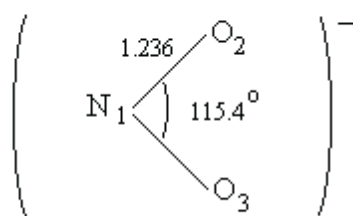
Fig. 2
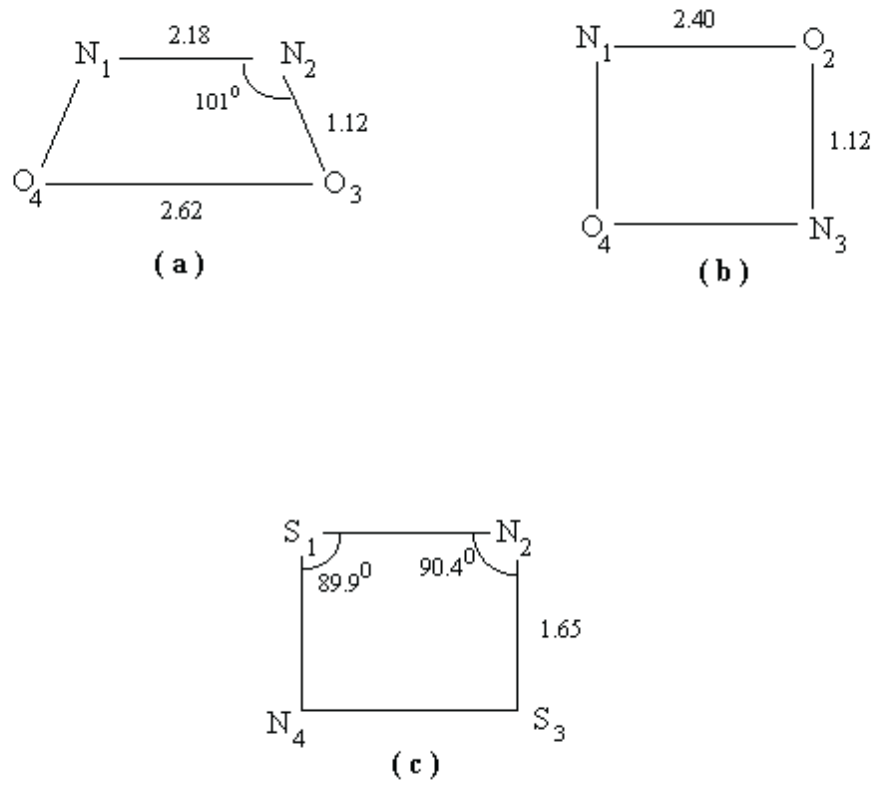
Fig. 3
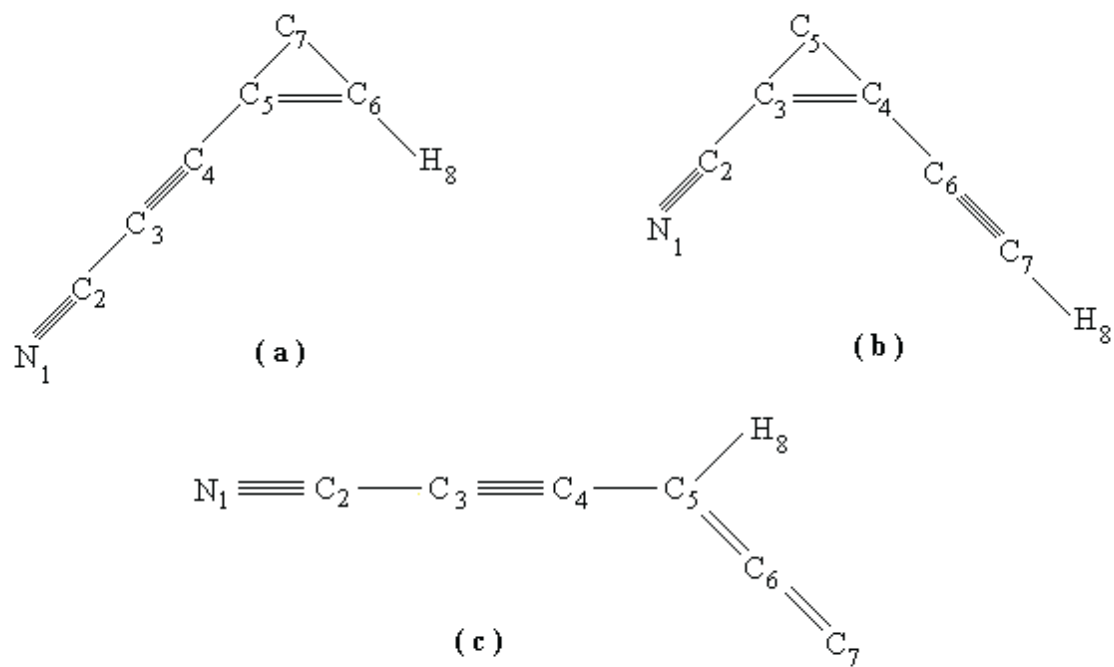
Fig. 4

Table 1. Systems containing the CO_2 3c-bond. See Fig. 1 for geometries and labelling.

		CNDO	IEH	MOPAC
(a)	I_{123}	-0.3522	-0.5440	-0.3485
	χ_{123}	4.1338	4.4738	4.1058
	I_{112}	1.6719	1.8544	1.6626
	I_{122}	2.5246	2.5900	2.4895
	V_{12}	-0.3522	-0.5440	-0.3485
(b)	I_{123}	-0.2115	-0.3570	-0.2234
	χ_{123}	3.2361	3.3307	3.1481
	I_{112}	1.3941	1.4083	1.2811
	I_{122}	1.9306	1.7539	1.9434
	V_{12}	-0.2631	-0.3862	-0.2609
(c)	I_{123}	-0.2115	-0.3233	-0.2146
	χ_{123}	3.1106	3.2174	3.0951
	I_{112}	1.3217	1.3442	1.2509
	I_{122}	1.8417	1.7009	1.9152
	V_{12}	-0.2356	-0.3521	-0.2503
	V_{14}	-0.0690	-0.1714	-0.1146

Table 2. Systems containing the NO_2 3c-bond. See geometries and labelling in Fig. 2

		CNDO	IEH	MOPAC
(a)	I_{123}	-0.2240	-0.3443	-0.2385
	χ_{123}	3.1379	3.3218	3.1439
	I_{112}	1.4356	1.4962	1.3209
	I_{122}	1.7328	1.6461	1.8580
	V_{12}	-0.2240	-0.3443	-0.2385
(b)	I_{123}	-0.2324	-0.2925	-0.2055
	χ_{123}	3.1583	3.3169	3.1898
	I_{124}	-0.0639	-0.1272	-0.0855
	I_{112}	1.6400	1.6234	1.9565
	I_{122}	1.6065	1.5788	1.4172
	I_{114}	0.9838	0.9467	0.8233
	I_{144}	1.0529	0.9500	1.1522
	I_{445}	1.1429	1.0989	1.1512
	I_{455}	0.7624	0.8348	0.6886
	V_{12}	-0.2957	-0.4182	-0.2901
	V_{14}	-0.1285	-0.2529	-0.1707
	V_{45}	-0.0018	0.0069	-0.0124

Table 2. (cont.)

		CNDO	IEH	MOPAC
(c)	I_{123}	-0.2522	-0.3454	-0.2489
	χ_{123}	3.2514	3.5223	3.3072
	I_{124}	-0.1107	-0.1001	-0.1241
	χ_{124}	2.8877	2.6792	2.8414
	I_{112}	1.6413	1.6763	1.4586
	I_{122}	1.7443	1.7605	1.6999
	I_{113}	1.6077	1.6656	1.4692
	I_{133}	1.6550	1.7286	1.9463
	I_{114}	0.6360	0.5013	0.6490
	I_{144}	0.8151	0.6020	0.7308
	I_{445}	1.9780	1.9153	1.8856
	I_{455}	2.4831	2.5114	2.5533
	V_{12}	-0.3174	-0.4480	-0.3375
	V_{13}	-0.3091	-0.4407	-0.3251
	V_{14}	-0.2125	-0.2517	-0.2536
	V_{45}	-0.1513	-0.1717	-0.1759
(d)	I_{123}	-0.1165	-0.1703	-0.1181
	χ_{123}	2.7029	2.6846	2.7028
	I_{112}	1.4109	1.3777	1.1521
	I_{122}	1.4123	1.2739	1.6846
	V_{12}	-0.2330	-0.3406	-0.2363

Table 3. NO dimers (see Fig. 3). For (b), $V_{23} = V_{12}$.

	(a)			(b)		
	CNDO	IEH	MOPAC	CNDO	IEH	MOPAC
I_{123}	-0.1385	-0.1465	-0.1450	-0.1417	-0.1451	-0.1468
χ_{123}	2.8904	2.8286	2.8348	2.7057	2.7556	2.7629
I_{234}	-0.0440	-0.0696	-0.0567	-0.1013	-0.0928	-0.0865
χ_{234}	2.3711	2.4693	2.3970	2.5390	2.5360	2.5041
I_{112}	0.7164	0.6081	0.6618	0.3443	0.3308	0.3197
I_{122}	0.7164	0.6081	0.6618	0.3848	0.3831	0.3801
I_{223}	1.8894	1.8740	1.8340	2.6652	2.6863	2.6393
I_{233}	2.5528	2.6374	2.5991	1.8218	1.8426	1.8604
I_{1234}	0.0325	0.0461	0.0405	0.0590	0.0566	0.0544
V_{12}	-0.2770	-0.2930	-0.2900	-0.2430	-0.2379	-0.2333
V_{23}	-0.1825	-0.2161	-0.2017			

Table 4. SN dimer (see Fig. 3). ($*$) Non-iterated option in Ref. [35]. ($**$) Non-iterated option. Parameters inclusing $3d$ orbitals for sulfur [44]

	CNDO	IEH	MOPAC	EH1$^{(*)}$	EH2$^{(**)}$
I_{SNS}	-0.1843	-0.0416	-0.1097	-0.1367	-0.2282
$V_S = \chi_{SNS}$	3.8571	2.4060	2.6530	2.6636	4.3412
I_{NSN}	-0.0278	-0.1519	-0.1706	-0.1115	-0.0523
$V_N = \chi_{NSN}$	3.0825	2.9587	2.8525	2.4862	3.1349
I_{SSN}	1.1438	1.3226	1.3411	0.9845	1.0333
I_{NNS}	1.6352	1.1712	1.3722	1.5671	1.7854
I_{1234}	-0.0164	0.0329	0.0597	0.0600	0.0198
V_{SN}	0.1560	-0.1935	-0.2803	-0.2482	0.1758

Table 5. Hydrazoid acid $(N_1{=}N_2{-}N_3{-}H_4)$. Geometry from [46].

	CNDO	IEH	MOPAC
I_{123}	-0.2999	-0.4667	-0.3266
χ_{123}	4.1530	4.3860	4.2614
I_{1234}	-0.0447	-0.0265	-0.0388
χ_{1234}	5.1452	5.3821	5.2448
V_{12}	-0.3119	-0.4828	-0.3451
V_{23}	-0.2882	-0.4524	-0.3069
V_1	2.8128	2.9733	2.8547
V_2	3.8481	3.6783	3.9249
V_3	2.6373	3.1165	2.7266
I_{112}	2.4656	2.2169	2.7129
I_{122}	2.7522	2.6798	2.5635
I_{223}	1.6562	1.7693	1.6004
I_{233}	1.4156	1.5910	1.6049

Table 6. Some multicenter indices for the structure of HC_6N shown in Fig. 4. Geometry from Ref. [49]

		CNDO	IEH	MOPAC
(a)	I_{123}	-0.0123	-0.0429	-0.0031
	χ_{123}	3.9868	3.9480	3.9523
	I_{234}	0.0145	0.0141	0.0089
	χ_{234}	3.8205	3.6994	3.8279
	I_{567}	0.2794	0.2172	0.2414
	χ_{567}	3.9875	3.8290	4.0147
	I_{556}	1.3364	1.3945	1.5082
	I_{566}	1.3374	1.3865	1.4290
	I_{557}	1.1891	1.1007	1.3388
	I_{577}	0.8891	0.8009	0.7846
	I_{1234}	-0.1545	-0.2147	-0.1131
	χ_{1234}	6.7826	6.6013	6.8024
	V_{56}	0.2568	0.1834	0.2140
	V_{57}	0.2976	0.2498	0.2468
(b)	I_{123}	-0.0168	-0.0328	0.0055
	χ_{123}	3.9785	3.9269	3.9308
	I_{345}	0.2651	0.2026	0.2309
	χ_{345}	3.8676	3.6463	3.9189
	I_{334}	1.2751	1.3068	1.4671
	I_{344}	1.2514	1.2911	1.3932
	I_{445}	1.2388	1.1703	1.3193
	I_{455}	0.9372	0.8728	0.7924
	I_{1234}	-0.0656	-0.0953	-0.0505
	χ_{1234}	5.4444	5.4193	5.5215
	V_{34}	0.2501	0.1567	0.1807
	V_{45}	0.3208	0.2313	0.2436

Table 6 (cont.)

		CNDO	IEH	MOPAC
(c)	I_{123}	-0.0026	-0.0218	0.0014
	χ_{123}	3.9870	3.9463	3.9530
	I_{234}	0.0131	0.0195	0.0076
	χ_{234}	3.8054	3.7273	3.8283
	I_{567}	0.1662	0.1309	0.1765
	χ_{567}	4.0350	3.9236	3.9144
	I_{556}	1.5449	1.5848	1.3801
	I_{566}	1.5609	1.5238	1.7700
	I_{667}	2.4221	2.2708	2.5641
	I_{677}	1.8604	1.8435	1.4175
	I_{1234}	-0.1541	-0.2191	-0.1138
	χ_{1234}	6.7639	6.6392	6.8039
	V_{56}	0.1506	0.1106	0.1459
	V_{67}	0.2023	0.1893	0.2082

Table 7. Monosubstituted benzenes. Geometries of 1, 2 and 5 from [50]. Geometries of 3, 4 optimized by MOPAC-PM3. X means respectively H, C', N, O and F. I(ring) is the 6c-index.

	I_{CXX}, I_{CCX}			V_{CX}			I(ring)		
	CNDO	IEH	MOPAC	CNDO	IEH	MOPAC	CNDO	IEH	MOPAC
benzene	0.9572	0.9635	1.0637	-0.0081	-0.0017	0.0015	0.0888	0.0894	0.0883
	0.9641	0.9862	0.8683						
toluene	1.0391	1.0096	0.9325	0.0054	0.0027	-0.0005	0.0850	0.0872	0.0864
	1.0205	0.9885	1.0528						
aniline	1.1943	1.3137	1.1153	-0.0585	-0.1199	-0.0799	0.0825	0.0782	0.0797
	0.9514	0.9504	1.1128						
phenol	1.2447	1.3588	1.2577	-0.0819	-0.1395	-0.0935	0.0829	0.0786	0.0807
	0.8614	0.8119	0.9538						
fluoro-benzene	1.2618	1.3578	1.2201	-0.0874	-0.1446	-0.0768	0.0840	0.0798	0.0841
	0.7454	0.6634	0.8926						

Table 8. Six-center ring index for typical systems

	I(ring)		
	CNDO	IEH	MOPAC
benzene	0.0888	0.0894	0.0883
pyridine	0.0880	0.0879	0.0875
borazine	0.0384	0.0547	–
$(S_3N_3)^-$	0.0054	0.0017	0.0078

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