Calculation of CNDO Characters Orders with Account of Virtual Pars Orbital Contributions

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The contribution of virtual pars orbitals to the occupied molecular orbitals is taken into account in the CNDO approximation. On this basis a new index $\bar{\varrho}_L$ is introduced, which is similar to the character order ϱ_L in the π-electron approximation. The calculated values of $\bar{\varrho}_L$ for the 19 compounds under investigation correlate well with the experimental bond lengths, as well as with a number of other physical and chemical properties.

1. Introduction

In the original form of the pars orbital (PO) theory [1] in the π-electron approximation, the character order ϱ_L is defined as the difference of the contributions of the occupied and virtual PO's to the occupied molecular orbitals φ_k of a molecule M in question. Recently, an attempt was made to extend the PO method beyond the limits of the π-electron approximation [2], so that it can be used with all valence electron methods, particularly CNDO. On this basis a new definition for bond order was also proposed. In Ref. [2], however, the character order is a quantity which takes into account only the contributions of the occupied PO's ($\chi_1, \chi_2, \ldots, \chi_l$) of the reference molecule L to the occupied molecular orbitals (MO's) ($\varphi_1, \varphi_2, \ldots, \varphi_m$) of the molecule M; it is a function of A_L, where

$$A_L = \sum_{\mu=1}^{l} \sum_{k=1}^{m} |\langle \tilde{\varphi}_k | \tilde{\chi}_\mu \rangle|^2 . \tag{1}$$

$\tilde{\varphi}_k$ and $\tilde{\chi}_\mu$ are expanded in the basis functions (AO's) ψ_s as follows

$$\chi_\mu = \sum_{s \in \tilde{L}}^{\tilde{l}} f_{s\mu} \psi_s , \quad \tilde{\varphi}_k = \sum_{s \in \tilde{M}}^{\tilde{l}} C_{sk} \psi_s . \tag{2}$$

In Eq. (2) only those atomic orbitals ψ_s which belong to the considered fragment $\tilde{M}$ of the molecule M and the corresponding fragment $\tilde{L}$ of the reference molecule L are taken into account. It is obvious that the number $\tilde{l}$ of basis functions ψ_s in $\tilde{M}$ and $\tilde{L}$ is equal, and that in the case of HMO $\tilde{L} \equiv L$. The meaning of $\tilde{\varphi}_k$ and $\tilde{\chi}_\mu$ is more fully discussed in [2].

The purpose of the present paper is to take into account the contribution of the virtual PO's to the occupied MO's in the CNDO approximation. While the index A_L in [2] corresponds to the quantity r_L in [1], here a new index will be introduced which in CNDO should correspond to ϱ_L in [1]. An attempt will be made for a suitable normalization (to unity) of this new index.

2. Calculation of the Contribution of the Occupied and Virtual PO's to the Occupied MO's

The contribution of the μ-th PO of L to the k-th MO of M is given by

$$\begin{aligned} \langle \tilde{\varphi}_k | \tilde{\chi}_\mu \rangle &= \sum_{s,\, r=1}^{\tilde{l}} \sum^{\tilde{l}} C_{sk} f_{r\mu} \langle \psi_s | \psi_r \rangle \\ &= \sum_{s=1}^{\tilde{l}} C_{sk} f_{s\mu} = A_{k\mu} \end{aligned} \tag{3}$$

since $\langle \psi_s | \psi_r \rangle = \delta_{sr}$ in the CNDO approximation. If in the basis $\chi(\chi_1, \ldots, \chi_l, \chi_{l+1}, \ldots, \chi_n)$ the first l pars orbitals χ_μ are occupied ($\mu \in [1, l]$), and the remaining $(n-l)$ ones are virtual ($\mu \in [l+1, n]$), from Eq. (1) and (3) we obtain for A_L

$$\begin{aligned} A_L &= \sum_{k,\, \mu=1}^{m} \sum^{l} A_{k\mu}^2 = \sum_{k,\, \mu=1}^{m} \sum^{l} \Big(\sum_{s=1}^{\tilde{l}} f_{s\mu} C_{sk} \Big)^2 \\ &= \sum_{k,}^{m} \sum_{\mu,}^{l} \sum_{r,\, s=1}^{\tilde{l}} \sum^{\tilde{l}} f_{s\mu} f_{r\mu} C_{sk} C_{rk} \\ &= \sum_{r,\, s=1}^{\tilde{l}} \sum^{\tilde{l}} \Big(\sum_{k=1}^{m} C_{rk} C_{sk} \Big) \Big(\sum_{\mu=1}^{l} f_{r\mu} f_{s\mu} \Big) \\ &= \tfrac{1}{4} \sum_{r,\, s=1}^{\tilde{l}} \sum^{\tilde{l}} P_{rs}^{\tilde{M}} P_{rs}^{\tilde{L}} , \end{aligned} \tag{4}$$

where the quantities

$$P_{rs}^{\tilde{M}} = 2 \sum_{k=1}^{m} C_{rk} C_{sk} , \quad P_{rs}^{\tilde{L}} = 2 \sum_{\mu=1}^{l} f_{r\mu} f_{s\mu}$$

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are the elements of the density matrices of the fragments $\tilde{M}$ and $\tilde{L}$, respectively.

The elements $P_{rs}^{\tilde{M}}$ constitute a submatrix $P_{\tilde{M}}$ of the charge density bond order matrix P_M of the molecule M; the AO's r and s which belong to the considered fragment $\tilde{M}$ take part in it. Similarly, by $P_{\tilde{L}}$ we shall denote the corresponding submatrix of the reference molecule. The fragments $\tilde{M}$ and $\tilde{L}$ are constructed using the same set of AO's common to both; therefore, the square symmetric $\tilde{l} \times \tilde{l}$ matrices $P_{\tilde{M}}$ and $P_{\tilde{L}}$ are of the same dimensions. Thus the quantity A_L defined by equation (4) can be expressed by means of the trace of the product of the matrices $P_{\tilde{L}}$ and $P_{\tilde{M}}$:

$$\begin{aligned} A_L &= \tfrac{1}{4}\sum_{r=1}^{\tilde{l}}\left(\sum_{s=1}^{\tilde{l}} P_{rs}^{\tilde{M}}\, P_{sr}^{\tilde{L}}\right) \\ &= \tfrac{1}{4}\sum_{r=1}^{\tilde{l}} (P_{\tilde{M}}\, P_{\tilde{L}})_{rr} = \tfrac{1}{4}\operatorname{Tr}(P_{\tilde{M}}\, P_{\tilde{L}})\,. \end{aligned} \tag{5}$$

Similarly to A_L, we can define the quantity $A_L{}'$ to take into account the contribution of the virtual pars orbitals of L to the occupied molecular orbitals of M:

$$\begin{aligned} A_L{}' &= \sum_{k=1}^{m}\ \sum_{\mu=l+1}^{n} A_{k\mu}^2 = \sum_{k=1}^{m}\ \sum_{\mu=l+1}^{n}\left(\sum_{s=1}^{\tilde{l}} f_{s\mu}\, C_{sk}\right)^2 \\ &= \sum_{r,\,s=1}^{\tilde{l}}\sum^{\tilde{l}}\left(\sum_{k=1}^{m} C_{rk}\, C_{sk}\right)\left(\sum_{\mu=l+1}^{n} f_{r\mu}\, f_{s\mu}\right) \\ &= \tfrac{1}{2}\sum_{r}^{\tilde{l}}\sum_{s=1}^{\tilde{l}} P_{rs}^{\tilde{M}} \sum_{\mu=l+1}^{n} f_{r\mu}\, f_{s\mu}\,. \end{aligned} \tag{6}$$

where n is the total number of basis AO's in L. The sum over μ in (6) can be calculated from the fact that the MO's of the molecule L form a square unitary matrix:

$$\begin{aligned} &\sum_{\mu=1}^{n} f_{r\mu}\, f_{s\mu} = \sum_{\mu=1}^{l} f_{r\mu}\, f_{s\mu} + \sum_{\mu=l+1}^{n} f_{r\mu}\, f_{s\mu} = \delta_{rs}\,, \\ &\sum_{\mu=l+1}^{n} f_{r\mu}\, f_{s\mu} = \delta_{rs} - \tfrac{1}{2}\, P_{rs}^{\tilde{L}}\,. \end{aligned} \tag{7}$$

Replacing in (6), we obtain:

$$\begin{aligned} A_L{}' &= \tfrac{1}{2}\sum_{r,\,s=1}^{\tilde{l}}\sum^{\tilde{l}} P_{rs}^{\tilde{M}}(\delta_{rs} - \tfrac{1}{2}\, P_{rs}^{\tilde{L}}) \\ &= \tfrac{1}{2}\sum_{r=1}^{\tilde{l}} P_{rr}^{\tilde{M}} - \tfrac{1}{4}\sum_{r=1}^{\tilde{l}}\left(\sum_{s=1}^{\tilde{l}} P_{rs}^{\tilde{M}}\, P_{rs}^{\tilde{L}}\right) \\ &= \tfrac{1}{2}\operatorname{Tr}(P_{\tilde{M}}) - \tfrac{1}{4}\operatorname{Tr}(P_{\tilde{M}}\, P_{\tilde{L}}) \end{aligned} \tag{8}$$

or

$$A_L{}' = \tfrac{1}{2}\operatorname{Tr}(P_{\tilde{M}}) - A_L\,. \tag{9}$$

$\operatorname{Tr}(P_{\tilde{M}})$, however, is exactly the electron charge of the fragment $\tilde{M}$, and therefore $A_L{}'$ is a quantity similar to $r_L{}'$ defined in [1].

The basic difference between the quantities A_L and r_L is in their physical content: in the π-electron approximation $\tfrac{1}{2}P_{\tilde{L}} \equiv \tfrac{1}{2}P_L = R_L$ is an idempotent matrix and the quantity r_L can be interpreted as a projection of the electron density of the fragment $P_{\tilde{M}}$ on the subspace of the occupied ground state MO's of the reference molecule L. In our case $\tfrac{1}{2}P_{\tilde{L}}$ is not an idempotent matrix, and the quantity A_L is not a projection. Nevertheless, the sum of A_L and $A_L{}'$ corresponds to the electron density in the fragment $\tilde{M}$, in analogy to the π-electron approach. This enables us to interpret A_L and $A_L{}'$ as defined in (5), (6) and (9) at least qualitatively as a measure of the similarity between the electronic structure of M and L.

3. Definition and Normalization of Character Order in the CNDO Approximation

The quantities A_L and $A_L{}'$ introduced in the CNDO approach depend strongly upon the number of basis AO's in $\tilde{L}$. On the other hand, a reference molecule L can be truncated in different ways $\{\tilde{L}_i\}$ the $\tilde{L}_i$'s correspond with fragments $\tilde{M}_j$ which are different in structure and dimension. It is meaningless, therefore, to compare results based only upon A_L and $A_L{}'$, even for one and the same reference molecule L, in methods taking into account all valence electrons.

That is why the need arises for the introduction of U_L and $U_L{}'$, as this was partly described in [2].

$$\begin{aligned} U_L &= \tfrac{1}{4}\operatorname{Tr}(P_{\tilde{L}}\, P_{\tilde{L}})\,, \\ U_L{}' &= \tfrac{1}{2}\operatorname{Tr}(P_{\tilde{L}}) - U_L\,. \end{aligned} \tag{10}$$

In the CNDO approach the difference $(U_L - A_L)$ as shown in [2] does not depend upon the dimension of the matrices $P_{\tilde{M}}$ and $P_{\tilde{L}}$ although both quantities — U_L and A_L — strongly depend on it. Therefore this difference should be used for the normalization of A_L. From Eqs. (5), (9) and (10) we obtain

$$\begin{aligned} &(U_L - A_L) + (U_L{}' - A_L{}') \\ &\qquad = \tfrac{1}{2}\operatorname{Tr}(P_{\tilde{L}} - P_{\tilde{M}})\,. \end{aligned} \tag{11}$$

Multiplying (11) by (-1) and adding $(+1)$ to both sides of the equation we get:

$$\begin{aligned} &1 - (U_L - A_L) - (U_L{}' - A_L{}') \\ &= 1 - \tfrac{1}{2}\operatorname{Tr}(P_{\tilde{L}} - P_{\tilde{M}})\,. \end{aligned} \tag{12}$$

The term $1-(U_L-A_L)$ defined as character order in [2] was derived taking into account only the contribution of the occupied PO's to the occupied MO's, while the terms $(U_L'-A_L')$ and $\mathrm{Tr}(P_{\tilde{L}}-P_{\tilde{M}})$ arise only when taking into account the contribution of the virtual PO's of L to the occupied MO's of M. Therefore the left hand side of (12) represents the unnormalized character order corrected by the terms U_L and U_L' respectively.

Transforming (12), we obtain

$$\frac{1-(U_L-A_L)}{1-\frac{1}{2}\mathrm{Tr}(P_{\tilde{L}}-P_{\tilde{M}})}+\frac{-(U_L'-A_L')}{1-\frac{1}{2}\mathrm{Tr}(P_{\tilde{L}}-P_{\tilde{M}})}=1\,. \tag{13}$$

Denoting the first term by B_L, and the second by B_L', (13) is reduced to:

$$B_L+B_L'=1\,. \tag{14}$$

Just as in [1], now in the all valence methods a corrected and normalized character order can be defined as the difference between these two quantities, B_L and B_L' where the first one mainly represents the contributions of the occupied and the second one those of the virtual pars orbitals.

$$\bar{\varrho}_L=B_L-B_L'=2B_L-1\,. \tag{15}$$

The transition from Eq. (12) to Eq. (13) is somewhat arbitrary in the sense that the unity can be distributed to any one of the two terms in Equation (12). We have chosen to add it to first term, since this has the advantage of leading directly to the correlation parameters introduced by Coulson-Golebiewski [5].

From (13), (14) and (15) it follows that when $P_{\tilde{M}}=P_{\tilde{L}}$, $\bar{\varrho}_L=B_L=1$; $B_L'=0$.

Despite the complete formal analogy to the character orders in the π-electron approximation, the quantities B_L, B_L' and $\bar{\varrho}_L$ do not have the same concrete physical meaning as r_L, r_L' and ϱ_L in [1]. As mentioned before, most complications in CNDO are due to the fact that there PO's cannot be defined as a unitary transformation of MO's (cf. [1] and [2]), which also makes it impossible to use the number of electrons in the reference molecule as a normalization factor.

Another significant difference between the methods taking into account all valence electrons and π-electrons only is in the specific meaning of the concept "two-center character order", which, together with the Coulson [3] and Wiberg [4] indices, can be used as an important characteristic of the chemical bond (cf. [2]). In the π-electron approach the two-center character order is unambiguously defined as the ϱ_L value in relation to a particular reference molecule e.g. ethylene, formaldehyde, ethyleneimine, etc. In the CNDO approach the quantity $\bar{\varrho}_L$ pertains to a particular fragment L_i of a given reference molecule L, from which one or more hydrogen atoms have been removed (cf. [2]). Obviously in this case the two-center character order $\bar{\varrho}_{\mathrm{I,II}}$ will be determined in reference to the two-center fragment of the molecule L. When calculating the quantities $A_{\mathrm{I,II}}$ and $U_{\mathrm{I,II}}$ only those AO's which belong to the atoms participating in the chemical bond are taken into account (e.g. C—C, C=C, C≡C, C=N, C=O, etc.).

4. Numerical Results and Discussion

The molecules shown in Fig. 1 were calculated using the standard CNDO/2 method. A good way to evaluate the applicability of the quantities derived above is to compare the two-center character order $\bar{\varrho}_{\mathrm{I,II}}$ with a basic property of the bond (I, II), for instance with the experimental bond length — $d_{\mathrm{I,II}}$. This comparison is shown in

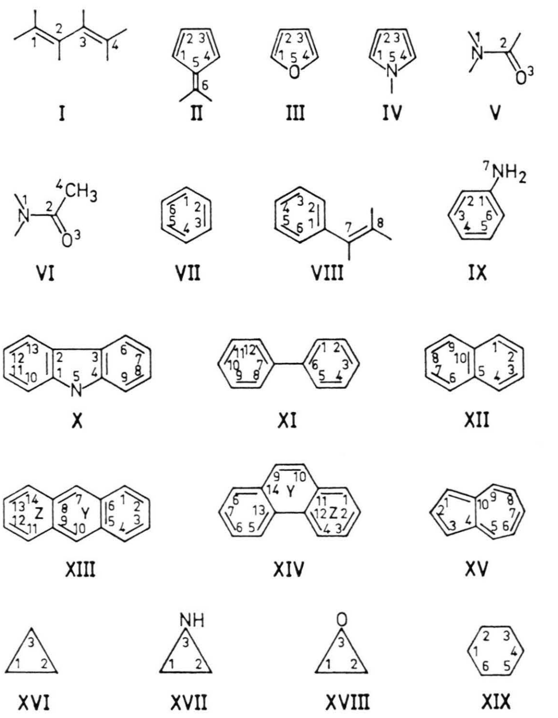

Fig. 1. Calculated compounds. In structure XIV the sequence of labels"... 5, 6, 7, 6..." should read as follows: "...5, 6, 7, 8..."

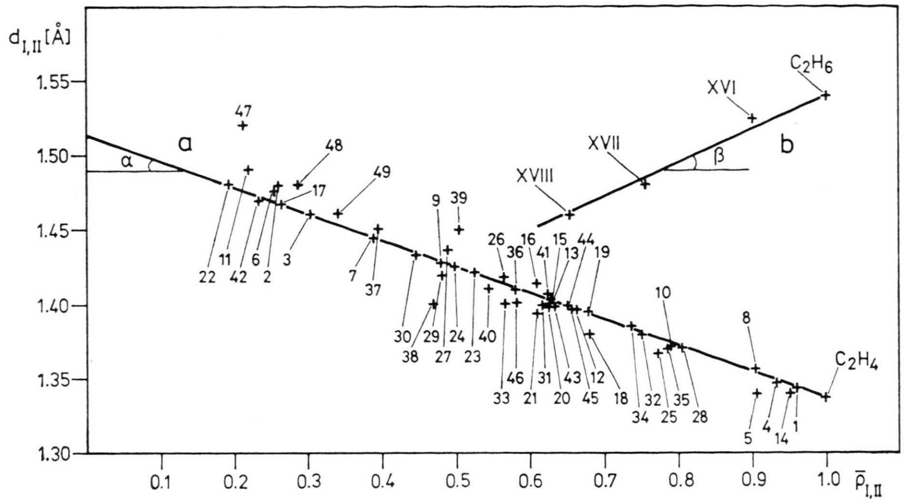

Fig. 2. Relationship between the two center ethylenoid (a) and ethanoid (b) character orders and bond lengths. The points in Fig. 2 correspond to a given bond (μ, ν) of the compounds, represented in Fig. 1 in Roman numerals.

1—(1, 2) I
2—(2, 3) I
3—(2, 3) II
4—(5, 6) II
5—(3, 4) II
6—(4, 5) II
7—(2, 3) III
8—(3, 4) III
9—(2, 3) IV
10—(3, 4) IV
11—(2, 4) VI
12—(1, 2) VII
13—(1, 2) VIII
14—(7, 8) VIII
15—(4, 9) X
16—(3, 4) X
17—(2, 3) X
18—(8, 9) X
19—(6, 7) X
20—(7, 8) X
21—(3, 6) X
22—(6, 7) XI
23—(2, 3) XII
24—(1, 10) XII
25—(1, 2) XII
26—(10, 5) XII
27—(5, 6) XIII
28—(1, 2) XIII
29—(2, 3) XIII
30—(1, 6) XIII
31—(6, 7) XIII
32—(1, 2) XIV
33—(2, 3) XIV
34—(3, 4) XIV
35—(9, 10) XIV
36—(11, 12) XIV
37—(12, 13) XIV
38—(10, 11) XIV
39—(1, 11) XIV
40—(4, 12) XIV
41—(9, 10) XV
42—(4, 10) XV
43—(1, 2) XV
44—(7, 8) XV
45—(8, 9) XV
46—(1, 10) XV
47—(1, 2) XVI
48—(1, 2) XVII
49—(1, 2) XVIII

Fig. 2a for the ethyleneoid and in Fig. 2b for the ethaneoid two-center character order. It can be observed from Fig. 2a that $d_{\mathrm{I,II}}$ depends linearly on $\bar{\varrho}_{\mathrm{I,II}}$ (ethyleneoid), and that this linear dependence is rather strictly observed in the whole range of 1.33—1.52 Å.

Extrapolation of this line until it intersects the ordinate $\bar{\varrho}_{\mathrm{I,II}} = 0$ leads to a direct determination of the "true" length of the single bond — 1.517 or 1.513 Å [5, 6]. Statistical processing of the correlation 2a gives:

$$d_{\mathrm{I,II}} = 1.514 - 0.177\, \bar{\varrho}_{\mathrm{I,II}}\,. \qquad (16)$$

It is of special interest to note that the coefficients obtained by us practically coincide with those of Coulson-Golebiewski (1.517 and 0.18) [5] and of Simmons (1.513 and 0.175) [6], although the latter pertain to the relationship between $d_{\mathrm{I,II}}$ and the π-electron bond order P. This gives us a confirmation to consider the quantity $\bar{\varrho}_{\mathrm{I,II}}$ as a characteristic index of the chemical bond in CNDO, which qualitatively corresponds to Coulson's bond order in π-electron methods. This conclusion is supported by the fact that in π-electron methods the two-center ethyleneoid character order is identical to Coulson's bond order [1].

The dependence of the bond length of some single C—C bonds upon the ethaneoid character order is linear too (Fig. 2b), with an angular coefficient tg $\beta = 0.225$. It should be noted that this coefficient coincides with the angular coefficient at the steepest part of Coulson's curve (bond length-bond order), which corresponds to the longest bonds (cf. [7]).

The two-center ethyleneoid and ethaneoid character orders can also be used for elucidation of the properties of organic compounds which formally contain single bonds, but show a partly unsaturated

Table 1. Ethanoid $\bar{\varrho}_{\mathrm{C=C}}$ and ethyleneoid $\bar{\varrho}_{\mathrm{C-C}}$ two center character orders.

	XIX	XVI	XVII	XVIII
$\bar{\varrho}^{(1)}_{\mathrm{C=C}}$	—	0.024	0.065	0.085
$\bar{\varrho}^{(2)}_{\mathrm{C=C}}$	0.088	0.211	0.285	0.339
$\bar{\varrho}_{\mathrm{C-C}}$	0.902	0.849	0.752	0.615

Table 2. CNDO character orders.

A) Cyclopentadienyl anion									
II	III	IV	XV						
0.495	0.336	0.612	0.700						
B) Benzene									
VII	VIII	IX	XI	XII	XIII-Z	XIII-Y	XIV-Z	XIV-Y	X
1.000	0.941	0.932	0.908	0.740	0.611	0.570	0.780	0.439	0.869
C) Cyclopropan									
XVI	XVII	XVIII							
1.000	0.634	0.456							
D) Cis-Butadiene									
II	III	IV	VII	VIII	XI	XII	XIII	XIII	
				3–4	5–6	1–2	1–2	7–8	
				5–6	7–8	3–4	3–4	9–10	
0.785	0.902	0.702	0.573	0.565	0.256	0.721	0.764	0.408	

character. Such compounds are cyclopropane (XVI), ethyleneimine (XVII) and ethylene oxide (XVIII). Table 1 illustrates their respective character orders calculated in relation to two-center fragments of the reference molecules ethylene and ethane. It can be seen that in cyclohexane (XIX) the ethaneoid character is highest, while the ethyleneoid character is negligible. The ethaneoid character decreases in the order XVI, XVII, XVIII, while the ethyleneoid character increases, which qualitatively corresponds to the change in the length of the C—C bond in these compounds — 1.52, 1.48, 1.46 Å, respectively. The relatively high ethyleneoid character in this set of compounds finds experimental confirmation in the fact that they possess a number of properties characteristic of unsaturated conjugated systems — cf. [8].

The calculated ethyleneoid character $\bar{\varrho}_{C=C}$ of the above mentioned compounds depend rather strongly upon the orientation in space of the ethylene reference molecule: $\bar{\varrho}_{C=C}$ takes on large values when the plane of the ethylene molecule is perpendicular to the triatomic cycle — $\bar{\varrho}^{(2)}_{C=C}$ (see Table 1), while the $\bar{\varrho}^{(1)}_{C=C}$ values obtained when M and L lie in one plane are negligible. This shows that the C—C bond in the studied compounds bears a definite similarity only to such an ethylene reference molecule whose π-electron axes lie in the plane described by the triatomic cycle, i.e. the pseudo π-bond between the carbon atoms lies in the plane of the molecule, and not outside it, as is usual in unsaturated compounds. Thus the CNDO pars orbital study of the triatomic cycles in an independent way confirms the model of Coulson and Moffitt (cf. [8]) — the so-called "banana" bond in these compounds.

The results discussed above show that the two-center character order $\bar{\varrho}_{I,II}$ as defined in this work is a quantity which correlates well with some physical and chemical properties of the chemical bond. It is therefore to be expected that multi-center character orders will also give good results. Table 2 gives the benzeneoid, cis-butadieneoid, cyclopentadienylanionoid and cyclopropaneoid characters of some molecules shown in Figure 1. It can be seen that in the order furane, fulvene, pyrrole the cyclopentadienylanionoid character increases, while the cis-butadieneoid character decreases. This fact is in agreement with the clearly demonstrated ability of furane to take part in diene syntheses as a diene, and also correlates with the increased aromaticity of pyrrole and thiophene. The high value calculated for the cyclopentadienylanionoid character of azulene is confirmed by the high value of the dipole moment — 1.00 D [9] of this hydrocarbon. The strongly expressed cis-butadieneoid character of fragments (1, 2, 3, 4) and (11, 12, 13, 14) of anthracene, as well as the high p-localization at atoms 9 and 10 reflect the capability of this molecule to react like a "biradical", in a Diels-Alder reaction, for instance.

The benzeneoid character orders of the studied aromatic compounds once again confirm the conclusions reached in [1] in relation to Clar's full and empty sextets.

The cyclopropaneoid multi-center character orders of ethyleneimine and ethylene oxide have been calculated (Table 2). The relatively high values obtained indicate a certain similarity to cyclopropane in their properties which depend on the triatomic cycle as a whole. Indeed, the analysis of their Raman spectra [10] shows that ethylene oxide, just like cyclopropane, has the ability to conjugate with aromatic and unsaturated fragments.

In conclusion, it can be said that taking into account the contribution of the virtual pars orbitals in CNDO allows a definition of character order which corresponds more closely to that given in [2]. This quantity ($\bar{\varrho}_L$) is similar to the ϱ_L value in [1], and should be useful in studying the electron structure and properties of organic molecules.

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