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Atom-Atom Correlation Order and its Relation to the Molecular Properties

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The atom-atom correlation order is defined and shown to have the special characteristics of the periodic change of its sign along the successive atom pairs and to be useful for the interpretation of some properties of aromatic molecules, that is, stabilities and reactivities. Moreover, the special appearances of the spectra of the alternant and non-alternant hydrocarbon isomers, e. g. naphthalene and azulene, are well understood by using this correlation order.

Die „zwischenatomare Korrelation“, deren Vorzeichen sich charakteristisch mit dem Abstand zweier Atome in Kette oder Ring ändert, wird definiert. Sie erweist sich als nützlich bei der Diskussion von Stabilität und Reaktivität von Aromaten sowie bei einem Vergleich der Spektren und Naphthalin und Azulen.

On définit la »corrélation interatomique« dont le signe change périodiquement avec la distance des deux atomes (en chaîne ou cycle). Elle est utile à l'interprétation des stabilités et réactivités de molécules aromatiques, et reflète les caractéristiques des isomères alternant et non-alternant d'hydrocarbures, par exemple naphtalène et azulène.

Introduction

The π-electron theory based on the simple m. o. scheme has been successfully used in the discussions of the stability, the reactivity and the spectra of various organic molecules. For example, the so-called Hückel's $4n + 2$ compounds are shown to be stable because only such compounds give the singlet ground states. **Brown** [2] discussed the reactivities of organic molecules for the Diels-Alder reaction in terms of localization energies and the difference in the spectral appearances between two hydrocarbon isomers, naphthalene and azulene, has been discussed by many authors.

It is shown in this paper that the newly defined quantity, "atom-atom correlation order" can explain as well various π-electron phenomena such as stated above in a simpler way.

Definition of Atom-Atom Correlation Order

The "atom-atom correlation order" is defined as the non-diagonal matrix elements of the following density matrix:

$$\varrho = (\varrho_{rs} = P_{rs}) = \sum_i n_i \, C_{ir} \, C_{is} \qquad (1)$$

where C_{ir} and C_{is} are the coefficients of the atomic orbitals of carbon atoms r and s of i-th molecular orbital, and n_i is the number of the electrons which occupy the i-th m. o. The diagonal element of the above matrix element is the well-known π-electron density, and if r and s atoms are neighbors, the element P_{rs} is the usual

π-bond order [4]. As well known, the P_{rs} has a special periodic characters both in the linear and ring compounds. These characters are shown [1, 8] by

$$P_{rs} = \frac{1}{n+1} \sin\left[(r-s)\frac{\pi}{2}\right] \cdot \left[\frac{1}{\sin\left(\frac{r-s}{n+1} \cdot \frac{\pi}{2}\right)} + \frac{(-1)^{s+1}}{\sin\left(\frac{r+s}{n+1} \cdot \frac{\pi}{2}\right)}\right] \cdot \tag{2}$$

$$P_{rs} = \frac{2}{n} \cdot \frac{\sin\left[(r-s)\frac{\pi}{2}\right]}{\sin\frac{r-s}{n}} \tag{3}$$

for linear and $(4n+2)$-membered ring polyenes, respectively, where the bracket of Eq. (2) and the denominator of Eq. (3) are positive quantities. Tab. 1 shows the signs of P_{rs} for linear ($n = 14$) and ring ($n = 8$, 10, 12 and 14) polyenes.

Table 1. *The signs of P_{1s} for linear and ring polyenes*

s	2	3	4	5	6	7	8	9	10	11	12	13	14
linear polyene													
$n = 14$	+	0	−	0	+	0	−	0	+	0	−	0	+
ring polyene													
$n = 8$	+	0	−	0	−	0	+						
$n = 10$	+	0	−	0	+	0	−	0	+				
$n = 12$	+	0	−	0	+	0	+	0	−	0	+		
$n = 14$	+	0	−	0	+	0	−	0	+	0	−	0	+

Stability of Unsaturated Ring Molecules

By Hückel method of m. o. theory, the total energy of π-electron system is expressed by the equation [4],

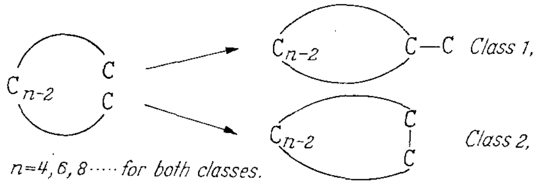
$$E = 2 \sum_{r<s}^{\text{bonds}} P_{rs}\,\beta + \sum_{r} Q_r\,\alpha_r \tag{4}$$

where the first summation is only over directly bonded atom pairs.

Now, let us consider the formation of the ring polyene by introducing one bond between both end atoms or special atom pairs t and u of the linear polyene. The change of the total π electron energy thus introduced is approximately calculated by the first order perturbation method as follows [1, 8],

$$\Delta E = 2\,P_{tu}\,\beta\,, \tag{5}$$

where one bond between t and u atoms is then considered to be introduced and the values of Q_r and α_r are assumed to be invariant for the perturbation. As shown in Tab. 1, the sign of the P_{rs} shows the periodic changes. Then, if one bond is formed between atoms t and u, where P_{tu} is positive, the total energy will increase and the ring compound thus obtained will become more stable than the parent linear polyene. On the contrary, if P_{tu} is negative, the corresponding ring compound will be less stable than the parent linear polyene. In the case of $P_{tu} = 0$, the stabilities of the ring compounds obtained are considered to be comparable with those of the parent linear polyenes. These ring compounds are divided into two classes:



Class 1 contains the odd-membered ring compounds, which are all derived by the ring formation between the atom pairs having $P_{tu} = 0$.

Class 2 contains the even-membered ring compounds, and is divided in two sub-groups: one is the $4n + 2$ membered compounds, the other $4n$ membered's. In the former subgroup, the ring formation is between two atoms whose P_{tu} has the positive sign, while the sign is negative in the latter. This shows the special stability of $4n + 2$ compounds.

Similarly we can discuss the stability of the ramified ring compounds formed by inserting one cross-link bond to the simple ring polyene. As seen in Tab. 1, the sign of P_{tu} of the ring polyene shows also characteristic periodic changes. In the cases of the $4n + 2$ ring polyenes, the positive P_{1s} suggests the formation of the stable ramified compounds by the introduction of one cross-link bond between atoms r and s, and the zero value of P_{1s} the compounds containing the odd-membered ring with the comparable stability to the parent ring compounds. However, the $4n$ ring compounds are suggested to be unstable from the above discussions and then any ramified ring compounds derived from these $4n$ ring compounds should not be stable. If such compounds can be formed, they would be supposed to have non-planar structures, as in an example of cyclo-octatetraene. However, as seen in the case of the ring polyene ($n = 12$), the signs of P_{1s} of atom pairs 1,6 and 1,8 become positive. This suggests the possibility of the formation of a kind of condensed ring compound composed of six- and eight-membered rings only if the stabilization energy meant by the positive $P_{1,6}$ overcomes the unstability energy of the parent 12-membered ring polyene whose formation from the linear polyene is denied by the negative sign of $P_{1,12}$ of the linear polyene.

Application to the Diels-Alder Reaction

BROWN [2] has discussed the reactivity of aromatic molecules for the Diels-Alder reaction in terms of the localization energies on the basis of the Hückel m.o. theory. The atom-atom correlation orders of the paired atoms in para position of eleven molecules are listed in Tab. 2. From these values one can see that the larger the size of the molecules, the more negative the atom-atom correlation orders become, and these tendencies are in good parallelism with the decrease of para-localization energies. Here, let us consider the meaning of the negative sign of the P_{rs} in para position of these molecules. For that purpose it is illustrative to consider the case of ethylene molecule. In the ground state of this molecule, both two π electrons occupy the bonding m. o. and give the value of $P_{rs} = 1$. On the contrary, if both two π electrons are transfered to the antibonding m. o., the P_{rs} will have the value of -1. This virtual state corresponds to the complete repulsive

Table 2. *Atom-Atom correlation order in para position and para localization energy*

	r, s	P_{rs}*	L (β)**
Linear polyene			
butadiene C = C − C = C 1 2 3 4	1 − 4	− 0.447	2.47
hexatriene	1 − 4	− 0.388	2.99
	2 − 5	− 0.087	4.99
octatetraene	1 − 4	− 0.367	3.05
	2 − 5	− 0.104	4.69
	3 − 6	− 0.333	3.52
Polyacene			
benzene	1 − 4	− 0.333	4.00
naphthalene	1 − 4	− 0.362	3.68
anthracene	1 − 4	− 0.368	3.63
	9 − 10	− 0.404	3.31
naphthacene	1 − 4	− 0.371	3.62
	5 − 12	− 0.414	3.25
pentacene	1 − 4	− 0.371	3.61
	5 − 14	− 0.418	3.23
	6 − 13	− 0.428	3.18
Angular polyacene			
phenanthrene	1 − 4	− 0.345	3.77
	9 − 12	− 0.241	4.46
	2 − 12	− 0.267	4.51
	4 − 5	− 0.137	4.37
3:4-benzphenanthrene	1′ − 4′	− 0.349	3.74
	2 − 12	− 0.274	4.25
	1 − 4	− 0.237	4.52
	4′ − 13	− 0.099	5.00
1:2-3:4-dibenzanthracene	1′ − 4′	− 0.327	3.83
	9 − 10	− 0.382	3.49
	5 − 8	− 0.346	3.70

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* Values calculated by the present authors.

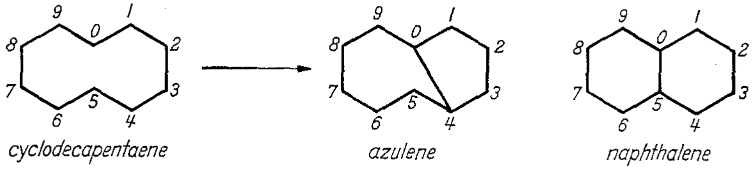
** Para-localization energies calculated by Brown.

state or a kind of biradical state of this molecule. This example illustrates the limits of P_{rs}, that is, $-1 \leq P_{rs} \leq +1$, and the meaning of the positive and negative signs of P_{rs}. Usually the bond order has been used as a good measure for the reactivity of the bond attack reagent [*3*]. Quite similarly one can propose the correlation order in para position as the measure of the Diels-Alder reaction. Furthermore, this fact suggests the determining step of the reaction is the repulsive or biradical state of the two electrons in para position of these molecules.

Characteristic Appearances of the Absorption Spectra for the Isomers of Alternant- and Non-Alternant-Hydrocarbons

As one example of these isomeric molecules, let us consider the case of naphthalene and azulene molecules. It is well known that there is a great difference in the appearance of the spectra of these isomeric molecules [*6*]. Moffitt [*7*] has explained the difference of the spectra of these molecules in an elegant manner. The same problem is shown to be explained by the atom-atom correlation order in a simpler way. The atom-atom correlation orders of cyclodecapentaene ($n = 10$)

as the common parent molecule of both azulene and naphthalene are shown already in Tab. 1. The introduction of a bond between the zeroth and fourth atom corresponds to the formation of azulene, and between the zeroth and fifth atom to the formation of naphthalene:



The atom-atom correlation orders are so far all considered only in the electronic ground state. The same quantity for the excited state could give information about the spectral behavior of the ramified ring compounds. The energy changes by introducing one cross-link bond at both excited and ground state are given as follows, respectively,

$$\Delta E_{\text{excited}} = 2\, P^{e}_{tu}\, \beta\,, \qquad \Delta E_{\text{ground}} = 2\, P^{g}_{tu}\, \beta\,,$$

and then,

$$\Delta h\nu = \Delta\,(\Delta E) = \Delta E_{\text{excited}} - \Delta E_{\text{ground}} = 2\,\beta\,(P^{e}_{tu} - P^{g}_{tu}) = 2\,\Delta P_{tu}\,\beta\,, \tag{6}$$

where the t-u atom pair is taken to be $0 - 4$ for azulene and $0 - 5$ for naphthalene molecule, respectively with cyclodecapentaene as parent compound. Therefore, to get the information of the characterictic spectral behaviors of these isomers, it is necessary to calculate the difference $\Delta\, P_{tu}$ between the related excited and ground states. As well known, the wave functions of each m. o. of cyclodecapentaene are written as,

$$\begin{aligned} \psi_j &= A_j \sum_t \cos\left(\frac{2\pi j}{n}\, t\right) \varphi_t\,, \quad (j = 0, 1, 2, 3, 4 \text{ and } 5)\,, \\ \psi_j &= A_j \sum_t \sin\left(\frac{2\pi j}{n}\, t\right) \varphi_t\,, \quad (j = 1, 2, 3 \text{ and } 4) \end{aligned} \tag{7}$$

where,

$$A_0 = A_5 = \sqrt{\frac{1}{n}}\,, \; A_j = \sqrt{\frac{2}{n}}\,, \quad (j = 1, 2, 3 \text{ and } 4)\,.$$

Each m. o. except $j = 0$ and 5 is doubly degenerate. The excited states produced by the transition of one electron from the level $j = 2$ to the level $j = 3$ can be then classified into the four states with the following electronic configurations as,

$$\begin{aligned} &(\text{I})\ (\text{inner configuration})\ [\sin\,(j = 2)]^2\ [\cos\,(j = 2)]\ [\cos\,(j = 3)], \\ &(\text{II})\ (\text{inner configuration})\ [\cos\,(j = 2)]^2\ [\sin\,(j = 2)]\ [\sin\,(j = 3)], \\ &(\text{III})\ (\text{inner configuration})\ [\sin\,(j = 2)]^2\ (\cos\,[j = 2)]\ [\sin\,(j = 3)], \\ &(\text{IV})\ (\text{inner configuration})\ [\cos\,(j = 2)]^2\ [\sin\,(j = 2)]\ [\cos\,(j = 3)]\,. \end{aligned} \tag{8}$$

These four excited states are degenerate unless the interelectronic interactions are taken accounts. Here, we assume these degeneracies have been eliminated by this electronic interaction and the above four electronic configurations correspond to the four splitted lower excited states of cyclodecapentaene. Then, we consider how the energies of these excited states of cyclodecapentaene will change under the perturbation of "one cross-link bond" corresponding to azulene or naphthalene molecules. This is done by the calculation of the four $\varDelta\, P_{tu}$:

$$\varDelta P_{tu} = \mp \frac{4}{n} \sin\left[\frac{\pi}{2}(t+u)\right]\left\{\sin\left[\frac{\pi}{n}(t+u)\right] \pm (-1)^u \sin\left[\frac{\pi}{n}(t-u)\right]\right\}, \tag{9}$$

Config. (I) and (II),

$$\varDelta P_{tu} = \mp \frac{4}{n}\left\{\cos\left[\frac{\pi}{2}(t+u)\right]\cos\left[\frac{\pi}{n}(t+u)\right] \pm \sin\left[\frac{\pi}{2}(t-u)\right]\sin\left[\frac{\pi}{n}(t-u)\right]\right\}, \tag{10}$$

Config. (III) and (IV) .

With the numbering of each carbon atom in cyclodecapentaene molecule as 0, 1, 2, ..., 9, the relation $0 < t-u \leq t+u < n$ is always satisfied. Then, the sign of the bracket in Eq. (9) is positive. $t+u=4$ corresponds to the production of azulene and $t+u=5$ to the production of naphthalene molecule. The signs of $\varDelta h\nu$ calculated by Eq. (6) for the four excited electronic configurations (I), ... (IV) are as follows;

	azulene	naphthalene
(I)	zero	positive
(II)	zero	negative
(III)	positive	negative
(IV)	negative	positive

The first band in the spectrum of azulene molecule is situated at the extreme long wave length compared with that of naphthalene molecule. From the results stated above it is only the transition to the excited state (IV) to give a band of azulene spectrum such a large red shift. On the other hand, the spectra of naphthalene has the following two characters: One is the small separation between the first and the second bands, and the other is the location of the first band in the u. v. region compared with that of azulene. Considering these facts and the above results of the characteristic changes of $\varDelta\, h\,\nu$, one can draw the following schematic diagram for the excited states of naphthalene and azulene molecules. In Fig. 1 the numbers (I), ... (IV) written aside each level indicate the corresponding excited electronic configurations stated above. The symmetries of these excited states are given on the basis of the molecular symmetries, D_{2h} for naphthalene, D_{10h} for cyclodecapentaene and C_{2v} for azulene. MOFFITT has developed the more elaborate theory on the same problem by taking account of the symmetries of the degenerate excited

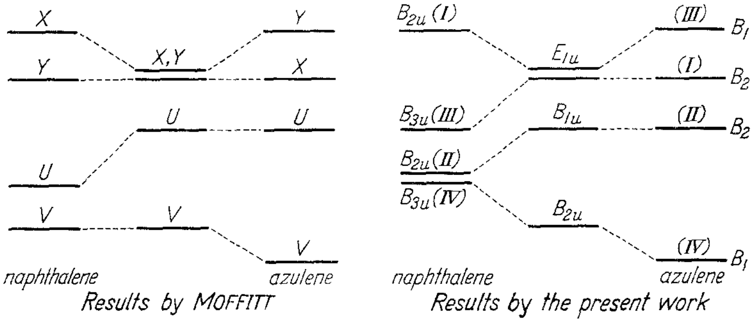


Fig. 1. Excited states of azulene and naphthalene molecules

states which are neglected in the present treatment. Therefore, in the case of azulene molecule where such accounts for the degeneracy of the excited states are not necessary, both results give a good agreement. However, both results show a little different appearance in the case of naphthalene, which may be attributed to the neglection of the consideration of the symmetries of the degenerate excited states.

Throughout these applications, it is necessary to stress that the atom-atom correlation order has given not only the useful informations, but also the meanings included in these problems.

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