Theoret. Chim. Acta (Berl.) 39, 241—246 (1975)

The Transformation of Aromatic Molecules into the Subspace of Their Double Bonds

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Received March 5, 1975

A model of new submolecules is presented. As an application some absorptions of aromatic radicals are interpreted in UV and visible spectra. Extension of the model to biological systems is prejudged.

Key words: Aromatic molecules

1. Introduction

It is sometimes possible to find a subspace, where the description of some property of molecules can be represented in a simple way. Here we report one, where the aromatic molecules have been transformed into the subspace of their double bonds, and as a test of this theory we shall interpret some main absorptions in the visible and near UV spectra of aromatic radical ions.

We define as holes the double bonds of a molecule. Then we transform these molecules, which have double bonds, into the subspace: hole space or double bond space. We describe the holes as black dots as in Fig. 1, and a connection line is drawn when the hole i is interacting with the hole j.

As an example we shall treat the naphthacene molecule. For naphthacene the three Kekule structures, shown in Fig. 1, can be drawn. The respective submolecules, which are spanned by holes, are also shown in Fig. 1.

For these submolecules we can solve the normal eigenvalue problem

$$C^{-1}HC=E, \tag{1}$$

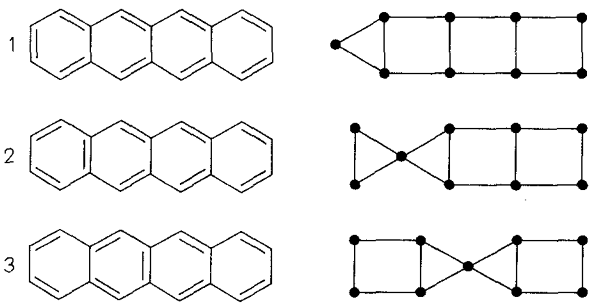


Fig. 1. The Kekule structures of naphthacene and the corresponding submolecules

where E is diagonal matrix. In the first approximation the skeleton or the incidence matrix of the submolecule is regarded as the linear transformer $[H_{ij}]$. The elements

$$H_{ij}=P_{ij}/R_{ij}^3, \tag{2}$$

where P_{ij} contains the square of the transition moment matrix of a double bond and R_{ij} is the distance between i and j. In the first approximation $H_{ij}=1$, in units of P_{ij}/R_{ij}^3, when $R_{ij}\leqq 2.67$ Å, otherwise $H_{ij}=0$.

2. Results and Discussion

The correlation of eigenvalues and the wavenumbers of the absorptions of radical anions in near UV and visible regions are shown in Fig. 2 for some aromatic radical anions (Table 1). As only some of the main absorptions in the near UV and visible regions can be interpreted by this model, the first trials include also wrongly determined absorptions. However, the correlation coefficient of the least-squares calculation is 0.956 in this case, where the most considerable absorptions are concerned. The intercept is $54000\,\mathrm{cm}^{-1}$. This is about the same size as the excitation energy of one double bond, which is $61300\,\mathrm{cm}^{-1}$ [1]. The slope is $-14000\,\mathrm{cm}^{-1}$, when the interaction energy between two double bonds is experimentally $-16600\,\mathrm{cm}^{-1}$ [1].

This gives a model with which some absorptions of the aromatic radical anions can be calculated. According to this model, using the equation

$$\bar{\nu}=A+B\cdot\text{eigenvalue}, \tag{3}$$

where $A=54000\,\mathrm{cm}^{-1}$ and $B=-14000\,\mathrm{cm}^{-1}$, the Table 1 is calculated.

If we try fitting only by tetracene and pentacene points, we obtain good correlation with coefficient 0.999, but now the intercept is $60000\,\mathrm{cm}^{-1}$ and the slope is $-16400\,\mathrm{cm}^{-1}$. If we are examining only the naphthalene points, we see that they form a straight line, but the slope is now only $-14000\,\mathrm{cm}^{-1}$. Because of this the interaction energy between the double bonds is somewhat greater in larger molecules than in smaller ones.

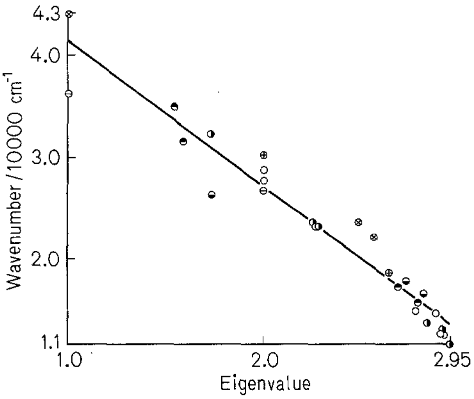
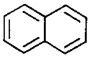
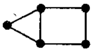
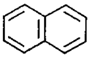
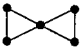
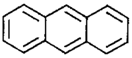
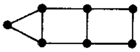
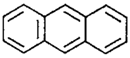
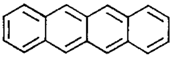
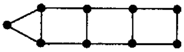
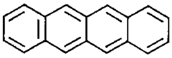
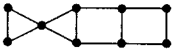
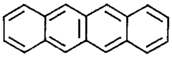
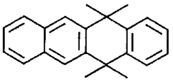
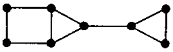
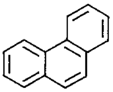
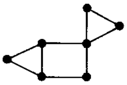
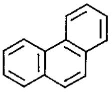
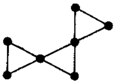
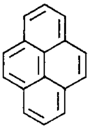
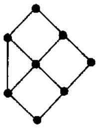
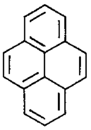
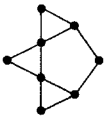
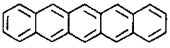
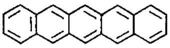
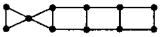
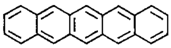


Fig. 2. Correlation of wavenumbers of aromatic radical anions (shown in Table 1) and eigenvalues of corresponding submolecules

Table 1. Calculated and experimental wave lengths for the electronic spectra of some aromatic mono-negative radical anions

Molecule	Kekule structure	Submolecule	Eigen-values	Wave length/nm	
				calculated	experimental
Benzene			2.00 1.00	380 250	385 [3] 280
Naphthalene			2.48	520	440 [3,5]
			2.56 1.00	550 245	470 230
Anthracene			2.68 1.54	600 310	600 [2,3,5] 330
			2.78 1.59	660 320	662 330
Naphthacene or Tetracene			2.77 2.00	650 380	700 [2,3,5,7] 370
			2.87 2.00	715 380	710 370
			2.90 2.00	745 380	826 408
5,12–Dihydro-naphthacene			2.64 2.00	580 380	550 [7] 360
Phenantherene			2.72	620	580 [3,6]
			2.81 1.73	670 330	650 310
Pyrene			2.91	745	830 [2,3]
			2.95 1.73	780 330	900 320
Pentacene			2.83 2.27	690 445	760 [3] 445
			2.91 2.28	745 445	770 445
			2.95 2.25	780 440	900 440

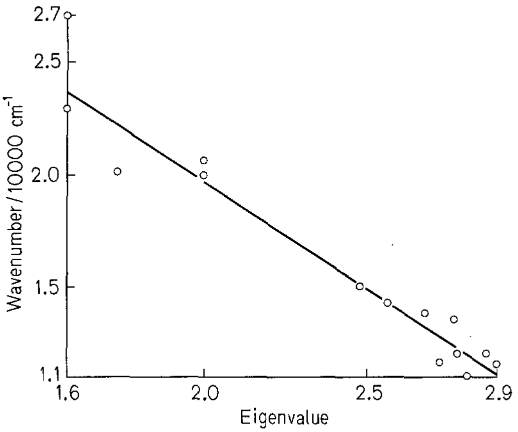


Fig. 3. Correlation of wavenumbers of aromatic radical cations and eigenvalues of corresponding submolecule

It is known that electronic spectra of ion radicals have been earlier interpreted by SCF-MO plus CI treatment [2, 3]. However, some main absorptions are uninterpreted just in those areas where this model gives absorptions. So this model gives an additional part to the absorptions in UV and visible regions.

If we calculate the limiting value of the lowest eigenvalue with this model, we get the value of 3.1 (for tetradecacene, 29 double bonds). This corresponds to the wave length of 1000 nm, when the parameters from the tetracene and pentacene case are used. This limit can be considered as a lower bound of the wave length of the absorption of solvated free electron. The solvated free electron pair has the absorption of 900 nm [4].

This model does not distinguish by which system the hole is filled. Naturally the parameters in the Eq. (3) must then also be varied. For instance, thus the transitions of the mononegative anions form one set and the dinegative anions another, as well neutral species and monopositive ions.

In Fig. 3 is shown the calculated correlation of the eigenvalues and the wavenumbers of the absorptions for some monopositive ions, shown in Table 2. The interaction energy is now $-10300\ \text{cm}^{-1}$ and the excitation energy is $40800\ \text{cm}^{-1}$.

In this model we see an enormous simplification when only one subspace is represented. But, however, this method in its largest sense, other subspaces than double bond space, might prove useful in biochemistry, especially with proteins, where great molar masses make exact quantum mechanical calculations impossible by modern size computers.

For instance, hole spaces can be drawn for the basic units, adenine-thymine and guanine-cytosine, of DNA molecule as shown in Fig. 4. The two lowest eigenvalues of this model are 2.236, 1.712 for adenine-thymine and 2.165, 1.811 for guanine-cytosine. If these units are interacted, which naturally can be calculated, for instance, also at CNDO level, and if the interaction parameters shown in Fig. 4 and 5 are used, we get the results for four lowest eigenvalues of the structures I

Table 2. Experimental and calculated wave numbers for the electronic spectra of some aromatic monopositive radical ions

Molecule	Eigenvalue	Wave number/10000 cm^{-1}	
		observed[a]	calculated
Naphthalene	2.48	1.50	1.53
	2.56	1.43	1.45
Anthracene	2.68	1.38	1.33
	2.78	1.20	1.23
	1.59	2.70	2.45
	1.54	2.28	2.50
Tetracene	2.77	1.35	1.24
	2.87	1.20	1.13
	2.90	1.15	1.10
	2.00	2.05	2.03
Phenanthrene	2.72	1.16	1.29
	2.81	1.10	1.20
	1.73	2.30	2.30
Cyclooctatetraene	2.00	2.00	2.03

[a] All values from Ref. [3].

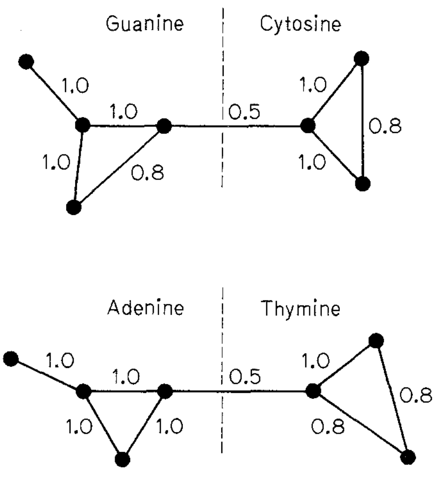


Fig. 4. Submolecules of the basic units of DNA molecule. Parameters are approximately determined according to the Eq. (2)

and II in Fig. 5 respectively 2.269, 2.186, 1.815, 1.723, and 2.252, 2.179, 1.842, 1.738. The four combinations of the two similar units can also be constructed:

$$\begin{pmatrix}\mathrm{G–C}\\\mathrm{G–C}\end{pmatrix}\quad\begin{pmatrix}\mathrm{G–C}\\\mathrm{C–G}\end{pmatrix}\quad\begin{pmatrix}\mathrm{A–T}\\\mathrm{A–T}\end{pmatrix}\quad\begin{pmatrix}\mathrm{A–T}\\\mathrm{T–A}\end{pmatrix}.$$

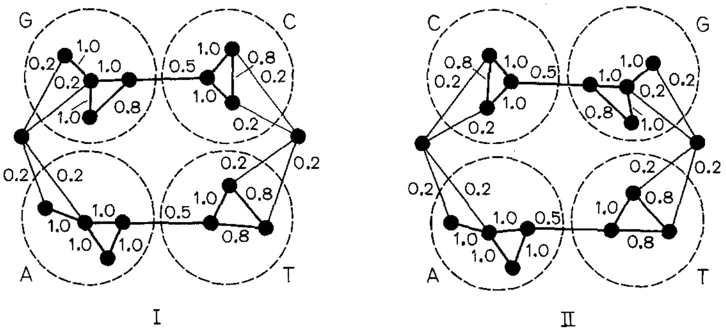


Fig. 5. Two combinations of the two basic units of DNA molecule

For these the eigenvalues of the subsystems are respectively:

$$2.197, 2.165, 1.866, 1.811; \quad 2.196, 2.166, 1.861, 1.815;$$
$$2.263, 2.236, 1.772, 1.712; \quad 2.259, 2.241, 1.760, 1.724.$$

Thus we can obtain one extendible measure for the genetic information content of DNA molecule.

3. Conclusion

A model of submolecules is presented here. It is probable that this simplifying method, transformation of molecules to some subspace, can be used for molecules which have repeatedly the same functional group.

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