ELECTRONIC STRUCTURES OF ELECTRICALLY CONDUCTIVE FRAGMENT MODELS IN PYROLYZED POLYMERS

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The electronic structures of polynuclear aromatic compounds are studied as the electrically conductive fragment models in pyrolyzed polymers. It is found that the manner of the distribution of the frontier electrons, which is important in determining the path of the conduction carriers, can be broadly classified into two groups depending on the shape of each fragment.

In recent years investigations of electrically conductive organic materials stable in air have been of keen interest in the field of synthetic metals from both fundamental and applied points of view. One such group has polymer structures commonly constructed from condensed aromatic rings and is called one-dimensional (1D) graphite as a whole[1]. The electronic properties of several 1D-graphite members such as polyacene[2], polyacenacene[3a,b] or polyperylene (polyperynaphthalene)[4] have been theoretically examined. Attempts of syntheses of these polymers are in progress, where electrical conductivity of synthesized polyperylene has been reported to be 570 S cm^{-1} (ref.[5]).

Meanwhile there has been considerable progress in studies of polyacenic semiconductive material prepared by pyrolytic treatment of phenol-formaldehyde resin as proto-type of 1D-graphite materials[6a,b]. This polyacenic material shows a wide range of electrical conductivity $(10^{-11}-10^0$ S cm^{-1} or more) according to the degree of the carbonization or "graphitization" that is controlled by the pyrolytic temperature applied. It has also been demonstrated that the doping of this material

with appropriate electron acceptor or donor is effective for the increase in the conductivity[6a,b]. Electrical transport study of this material prepared under rather higher temperatures (~900°C) strongly supposed the existence of polycrystalline structure consisting of mixed polyacenic skeletons[7], some of which make metallic fragments as illustrated in Fig. 1. It is supposed that each fragment is made of condensed aromatic rings with the size of the order of 1 ~ 10 nm mainly based on the result of the X-ray diffraction measurement[8].

The fragments consisting of polynuclear aromatic components are of interest not only per se from the viewpoints of cancer initiators (see for instance ref.[9]), their topological properties[10] and so on, but also as electrically conductive fragment models of the minimum units existing in pyrolyzed polymers. Hence, in this article, we would like to discuss the electronic structures of various models of these from the latter aspect.

The electronic structures of all the fragment models employed here are calculated in the framework of the Hückel molecular orbital (MO) method, since what we deal with are rather approximation-invariant properties. In the calculation, the values of the Coulomb integral (α) and the resonance integral (β) are fixed to be those proposed for the sp^2 carbon in aromatic compounds, that is, -7.06 eV and -2.49 eV, respectively (see for instance ref.[11]). Emphasis is to be put on the distribution of the frontier electrons in view of checking the path of the conduction carriers. In order to discuss the distribution of the frontier electrons, we employ the HOMO (highest occupied MO) electron densities, not the HOMO patterns, because the HOMO of most of the models are typically degenerated. In the following sections, these will be discussed rather pictorially.

Distribution of the Frontier Electrons

The HOMO electron densities of four basic cluster models, 1−4, having triangle, square and two kinds of hexagonal shapes are illustrated in Fig. 2. Data of the dimension of these models are listed in Table I. There are two manners of the distribution of the frontier electrons. That is, in 1, 2, and 3, the frontier electron exists only on the carbons at the outer-edge of their skeletons or on the "surface" carbons. Note that 3 and 4 belong to the same symmetrical group, D_{6h}. This result is compared with that of the ^{13}C NMR observation on the polyacenic materials prepared by pyrolysis of phenol–formaldehyde resin claiming that the conduction carriers mainly flow on the "surface" carbons of the polynuclear aromatic components[12].

In Fig. 3 the HOMO electron densities of 5 and 6, being larger version of 3 and 4, respectively, are illustrated. From the comparison between 3 and 5 or 4 and 6, it is clear that the distribution of the frontier electron of these are related not to their size but to their shapes.

We have previously analyzed the electronic properties of 1D-graphite models consisting of laddered-polyacetylene (PA) chains[1]. For instance, in the model con-

sisting of laddered chains of *trans*-PA, the frontier electron localizes on the "surface" carbons of the polymer. On the other hand, in the model of laddered chains of *cis*-PA, it delocalizes over all carbons of that. Hence the distribution of the frontier electrons strongly depends on the structures of the original PA chains.

TABLE I

Dimension and the calculated orbital levels of the fragment models (n_C number of carbon atoms contained, r approximate diameter)

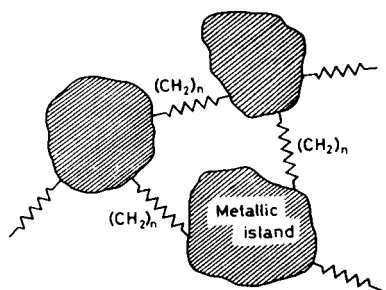| Model	n_C	r nm	Energy levels, eV		
			LU	HO	NHO
1	46	1·12	−7·06	−7·06	−8·92
2	36	0·97	−6·82	−7·30	−8·29
3	54	1·21	−6·21	−7·91	−8·50
4	42	1·12	−5·90	−8·22	−8·60
5	96	1·70	−6·49	−7·63	−7·96
6	114	1·96	−6·34	−7·78	−8·09

FIG. 1

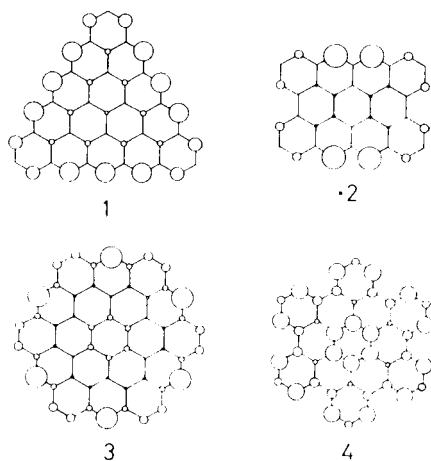Schematic models of fragments as metallic islands in pyrolyzed polymer

FIG. 2

The HOMO electron densities of the four typical models. The size of circles approximately represents the magnitude of the HOMO electron density on each carbon atom throughout this article

It is of interest to note that all or nearly all the "surface" of 1, 2, 3, and 5 consist of *trans*-PA-like shape, the frontier electrons localizing thereon but that *cis*-PA-like shape is prevailing on the "surface" of 4 and 6. In this sense, the present results of the fragment models are consistent with the case of 1D-graphite polymers. These are also compared with the discussion of the positions being chemically reactive in highly condensed benzenoid compounds[13].

The calculated energy values of several MO levels of 1 − 6 are listed in Table I. The HOMO and the LUMO (lowest unoccupied MO) levels are degenerate in 1 due to the symmetry (D_{3h}) as a matter of course, which manifests pure metallic nature independent of the cluster size. Model 4 with delocalized frontier electron has more stable HO energy and less stable LU energy in comparison with 3, suggesting stronger aromaticity of 4. In 5 and 6, the HO and the NHO (next HO) levels appreciably approach, but the patterns of these HNO's localize on the "surface" carbons in both 5 and 6. This tendency may also be interpreted in terms of the transverse trans-formation of MO's as extensively discussed in the stacking model of ethylene molecules[14]. Growth of the cluster size should obviously lead to the electronic structure of graphite itself.

Negative values of the LUMO levels of these cluster models represent their large electron affinity, which agrees well with the tendency of 1D-graphite polymers such as polyacene[2], polyacenacene[3a,b] etc., and also with the experimental observation that the polyacenic material mentioned above can be readily doped with n-type dopant[6a,b].

It is expected that the difference in the electronic structures, especially the distribution of the frontier electron, of the above cluster models can be distinguished by
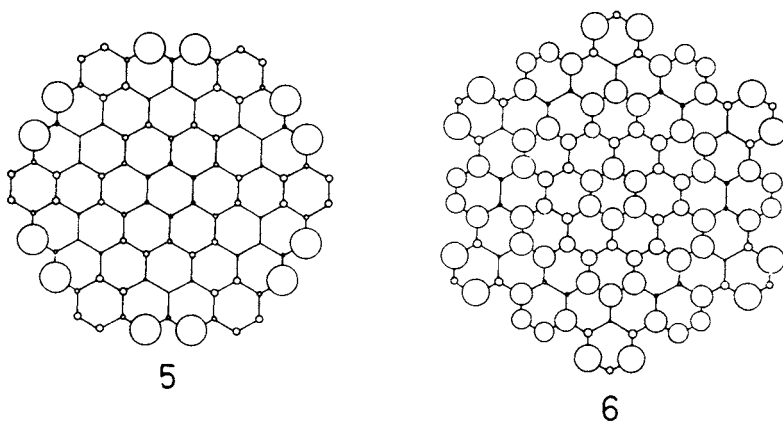

FIG. 3
The HOMO electron densities of the larger-sized models of 3 and 4

appropriate topological index. Randić indices[15] calculated for **1**, **3** and **4**, with the same length of the surface, are shown:

Model	1	3	4
Values	12·798	12·798	12·899

It is seen that **1** and **3**, the frontier electrons of which both localizes on the surface area, have equal value of the index (12·798). Hence the graph-theoretical approach such as the count of Randić indices seems to be of some help in understanding the electronic behaviour of simple cluster models.

Ludo of Cluster Models

Carbonization process through pyrolysis of organic material is generally considered to consist of aromatic growth and polymerization to aromatic macromolecules.
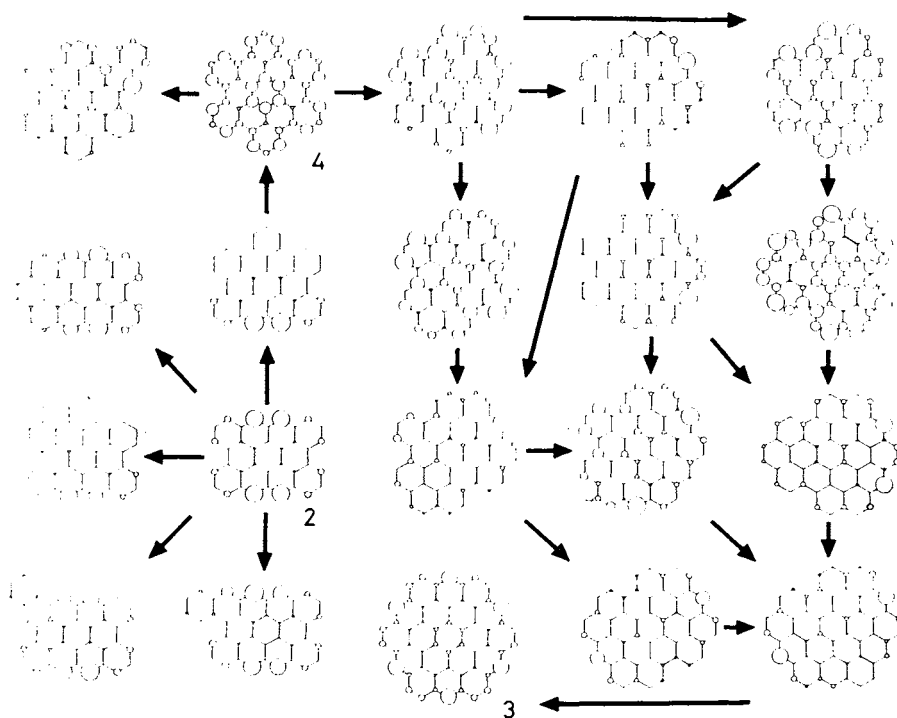
FIG. 4
The HOMO electron densities of various cluster models in a ludo style

Overall process of these reactions seems to be extremely complicated. Some intermediate structures of pyrolyzed naphthalene and anthracene have been investigated in order to pursue the carbonization process[16].

The distributions of the frontier electrons are examined here about various cluster models formed by gradual addition of benzenoid unit, that could appear in carbonization process. The HOMO electron densities of these are illustrated in Fig. 4. Arrows show the direction of the addition of a benzenoid unit. Starting from 2, like a ludo, it is possible to make five new compounds depending on the manner of condensation reaction of a benzenoid unit.

It is clearly seen that according to the position of the additive condensation, the distribution of the frontier electron largely differs. Thus the manner of the distribution is sensitive to the geometrical structure or, more specifically, the "surface" structure of the fragment models. This complexity will also probably influence the growth of condensed aromatic rings in the carbonization process.

Skeleton Structures and Holey Models

Since only the nearest-neighbour interactions between πAO's are employed to describe the shape of molecules in the framework of the Hückel method, the configura-
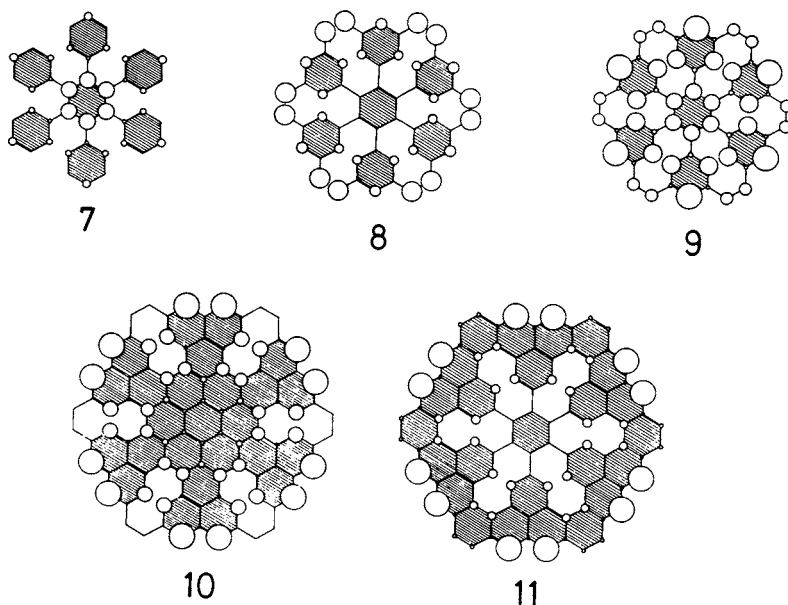

7

8

9

10

11

FIG. 5

The HOMO electron densities of the skeleton structures of 3, 4, and 5. Shadowed area represents complete aromatic ring

tion of the molecules therein is represented in a topological manner. In such configurations it is possible to consider rather fictitious skeleton structures of the above fragment models.

TABLE II

Shape of the "surface" of holey models. *Trans* and *cis* signify the *trans*-PA and the *cis*-PA shapes, respectively

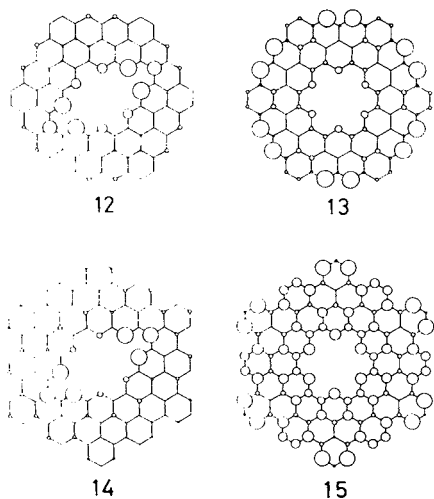| Model	12	13	14	15
Outside surface	*trans*	*trans*	*cis*	*cis*
Inside surface	*trans*	*cis*	*trans*	*cis*

FIG. 6

The HOMO electron densities of holey models based on **5** and **6**
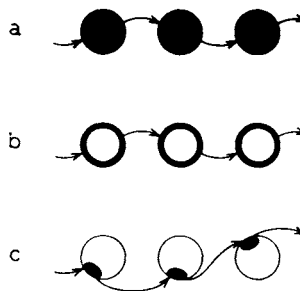

FIG. 7

Schematic representation of flows of the conduction carrier indicated in bold black and arrows: a metallic islands with delocalized frontier electrons, b those with localized frontier electrons on the "surface" area, and c hopping of carriers occurring at specific sites (see text)

In Fig. 5 the calculated HOMO electron densities are shown for the skeleton structures of **3** and **4** (that is, **7** – **9**) and of **5** (that is, **10** and **11**). It is seen that the manner of the distribution of the frontier electrons is influenced by both the connection of the outside of the fragment models ("surface") and the place of voids where normal chemical bonds are missing.

Moreover, there can be fractions of graphite possessing holes inside in carbonized materials developed inhomogeneously. The HOMO electron densities of such holey models of **5** and **6** are shown in Fig. 6. It is clearly seen that the shape of the hole significantly influence the distribution of the frontier electron in these models. In Table II the modes of the "outside" and the "inside" surfaces are listed. It is understood from Fig. 6 and Table II that the frontier electrons again tend to localize on the "surface" having the shape of *trans*-PA and that the inside surface with this shape attracts the frontier electrons more strongly as seen in **12**.

The models employed in this section are of interest in that they could represent the microscopic structures of porous graphitic materials. Particularly, it will be important to consider the electrode reactions accompanied by doping-undoping process when such materials are used as semiconductive electrodes in rechargeable batteries[17].

Concluding Remarks

The electronic structures of fragment models consisting of polynuclear aromatic components have been studied from the viewpoint of the models of metallic islands in pyrolyzed polymers. Although the distributions of the frontier electrons are different according to each model, we can classify these into two groups by the distribution. One is such group as the frontier electrons localize on the "surface" carbons and the other as they delocalize over all carbons.

This result is of interest since the electrical conduction inside these models behaving as metallic islands takes place on the different path depending on the structure of the island as illustrated in Fig. 7a, b. The conduction between these fragments is another interesting problem. It is broadly considered to occur by some active process like hopping (see for instance ref.[18]). However, considering the distribution of the frontier electrons, there can be some sites for carriers to hop favourably as shown in Fig. 7c. These will actually rule the microscopic transport properties in pyrolyzed polymer which will raise the new problem in understanding the electrical transport in such amorphous organic materials.

REFERENCES

1. Tanaka K., Yamashita S., Yamabe H., Yamabe T.: Synth. Met. *17*, 143 (1987).
2. Tanaka K., Ohzeki K., Nankai S., Yamabe T., Shirakawa H.: J. Phys. Chem. Solids *44*, 1069 (1983).
3a. Yamabe T., Tanaka K., Ohzeki K., Yata S.: Solid State Commun. *44*, 823 (1982).
3b. Tanaka K., Koike T., Ueda K., Ohzeki K., Yamabe T., Yata S.: Synth. Met. *11*, 61 (1985).
4. Tanaka K., Ueda K., Koike T., Yamabe T.: Solid State Commun. *51*, 943 (1984).
5. Murakami M., Yoshimura S.: Mol. Cryst. Liq. Cryst. *95*, 118 (1985).
6a. Yamabe T., Tanaka K., Ohzeki K., Yata S.: J. Phys., Colloq. C3, Suppl. No. 6, *44*, 645 (1983).
6b. Tanaka K., Ohzeki K., Yata S.: Synth. Met. *9*, 41 (1984).
7. Tanaka K., Yamanaka S., Koike T., Yamabe T., Yoshino K., Ishii G., Yata S.: Phys. Rev., B *32*, 6675 (1985).
8. Tanaka K., Ueda M., Yamabe T., Yata S.: Polym. Prepr. (Jpn.) *33*, 2475 (1984).
9. Harrey R. G.: Sci. Am. *70*, 386 (1982).
10. Dias J. R.: Acc. Chem. Res. *18*, 241 (1985).
11. Oiwa M.: *Shoto-Ryoshi-Kagaku* (*Elementary Quantum Chemistry*), p. 186. Kagaku-Dojin, Kyoto 1965.
12. Terao T., Maeda S., Yamabe T., Ohzeki K., Yata S.: *Proc. Symp. Molec. Struct., Tokyo, 21—24 Oct. 1982*; pp. 10—11 (2A03).
13. Stein S. E., Brown R. L.: Carbon (Oxford) *23*, 105 (1985).
14. Yamabe H.: *Thesis*. Kyoto University, Kyoto 1973.
15. Randić M.: J. Am. Chem. Soc. *97*, 6609 (1975).
16. Lewis I. C.: Carbon (Oxford) *20*, 519 (1982).
17. Yata S., Hato Y., Sakurai K., Osaki T., Tanaka K., Yamabe T.: Synth. Met. *18*, 645 (1987).
18. Mott N. F., Davis E. A.: *Electronic Processes in Non-Crystalline Materials,* 2nd ed., Chap. 2. Clarendon, Oxford 1979.