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Possible "Ferromagnetic States" of Some Hypothetical Hydrocarbons

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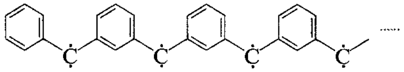
It has been suggested that several hypothetical hydrocarbons with conjugate π-electron systems will show ferromagnetic spin alinement due to the topological nature of the MO's. Some qualitative discussions have been given for the mechanism of the realization of this "ferromagnetic state".

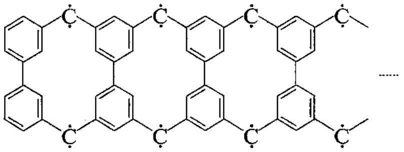
The origin of the ferromagnetism of metals is not yet well understood. As it is well-known, there are two extreme theories, one of which is Heisenberg's theory [1] of the electron exchange between localized electronic systems and the other of which is the so-called collective electron theory originally due to Bloch [2]. These two theories correspond, respectively, to the valence bond method and the MO method in the theory of molecular electronic structure. Therefore, the various difficulties in the theory of the magnetism are essentially the same as in the theory of molecular electronic structure. It is well-known that, at present, the ferromagnetic substances are limited only to metals with *d*-electrons, the electronic structures of which are quite complex and are not so well understood as those of the organic substances with *s* and *p* electrons only.

We would like to suggest here quite different model substances from the ordinary ones which will be interesting from the viewpoint of the origin of the ferromagnetic state and also of the nature of the molecular electronic structure. Let us consider the electronic structures of the following hydrocarbons:

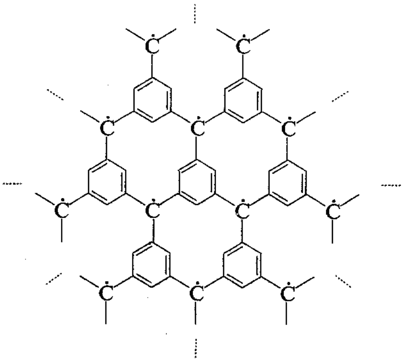
(I)



(II)



(III)



These compounds are all alternant hydrocarbons (even or odd according to the number of the groups and atoms). (I) and (II) are polymers of the so-called carbenes and (III) is the extension of the triphenylmethyl radical, and they are all meta-substituted compounds. In the case of carbenes, it is assumed that one of the AO's of the divalent carbon participates in conjugation with the ring π-electrons while the other of them remains as a "n-orbital."

It may be possible for (I) to take various conformations because of the rotations around the bonds connecting the divalent carbons to the benzene rings while such a circumstance may not be possible for (II) and (III) being approximately co-planar. For the sake of simplicity, we assume here that these compounds are all co-planar. Then, it is well-known that these meta-substituted hydrocarbons have non-bonding π-MO's (π-NBMO's) according to the Hückel MO or PPP theory. The number of such π-NBMO's is equal to the number of carbon atoms with unpaired electrons as indicated in the structural formulae. In the case of (I) and (II), there are many σ-type n-orbitals in addition to the π-NBMO's. The orbital energies of the π-NBMO's are not necessarily equal to those of the n-orbitals, although they are probably close to each other. Then, the orbitals of these hydrocarbons will be as indicated in Fig. 1a, where f, v and N indicate respectively the π-MO's doubly occupied by electrons with antiparallel spin, the vacant π-MO's in the ground electronic state and the non-bonding orbitals including the π-NBMO's and the σ-type n-orbitals. If the orbital energy differences between the non-bonding orbitals are sufficiently small, all unpaired electrons will have parallel spin according to Hund's rule as indicated in Fig. 1a. In other words, whether the spins are in the parallel alignment or all paired depends on the magnitude of the exchange integral $\langle \pi n | 1/r_{12} | n\pi \rangle$ between the π-NBMO and the n-orbital on the one hand, and on the orbital energy difference between these orbitals, on the other hand.

It should be noted here that the LCAO coefficients of the π-NBMO's are on the whole larger then those in the f- or v-π MO's because the former ones are non-vanishing only on the starred atoms. Therefore, although the π-NBMO's are extended over the whole molecule, the electron charge density in a π-NBMO is relatively concentrated on each starred atom. In this situation, the electronic structure on each carbon with the n-orbital in the case of (I) and (II) may be rather atom-like, the "intra-atomic" interactions there probably being of such a nature as to aline the electron spins in all the n-orbitals. This circumstance seems to be rather akin to the Heisenberg (or atomic) model of ferromagnetism. Nevertheless, the electrons in the π-NBMO's can move over the whole molecule, and this aspect is characteristic of the Bloch model. These results arise from the topological nature of the π-MO's.

In the case of (III) which does not have n-orbitals, the atomic nature of the spin alinement is sparse and is more akin to the Bloch model.

It has been experimentally proved already that the type (I) compounds with two unpaired electrons (diphenylmethylene and it derivatives) are triplet in the ground state [3] and that the same type compound with four unpaired electrons (m-phenylene-bis-phenylmethylene) is quintet in the ground electronic state [4]. Furthermore, the optical spectra [5, 6] of these compounds in the visible and near ultraviolet regions can be well interpreted by the ASMO CI method based on the orbital configurations indicated in Fig. 1a.

When these molecules become very large, the orbital energies will become almost continuous as indicated in Fig. 1b. However, because of their non-bonding nature, the N-band will remain sufficiently narrow for the electron spins in that band to be all parallel. On the other hand, when the molecules become very large, the energy gap between the N-band and the f-band as well as that between the v-band and the N-band will become very small. If the energy gap becomes comparable to the thermal energy, a ferromagnetic spin arrangement in the N-band may no longer be possible except at extremely low temperatures. However, there might be some bond alternation effect which causes a sufficiently large finite value of the energy gaps.

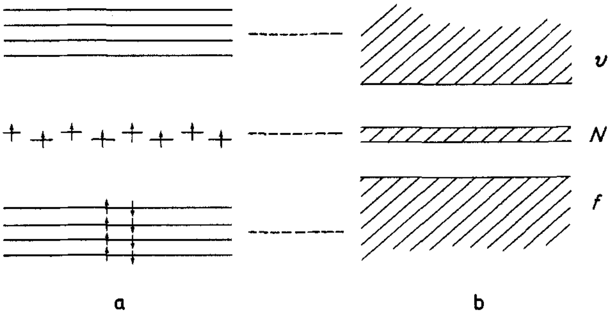


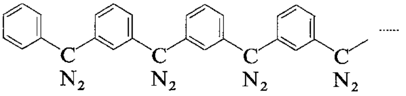
Fig. 1. Arangements of the orbitals and bands in the hypothetical hydrocarbons

Although we have discussed the magnetic behavior of compounds (I), (II) and (III) on the basis of a very simplified orbital picture, we must take into account the effect of electron correlation in a more detailed discussion. In general it is mainly the correlations between electrons with anti-parallel spin which are of significance because electrons with parallel spin are already kept apart by the Fermi-Dirac statistics even in the orbital approximation (i. e. the Hartree-Fock approximation). Therefore, the introduction of correlation effects will lower the energy of the non-magnetic states more than that of the ferromagnetic states, thus making the condition for the realization of the ferromagnetic state more hard. In the case of compounds (I) and (II), the exchange integral $\langle \pi n | 1/r_{12} | n\pi \rangle$, which may be fairly large because the n-orbital is codensed on one carbon atom, seems to play very important role for the realization of the ferromagnetic spin alignment and, moreover, the correlation effects may not affect the spin states so severely as to make the non-magnetic state the lowest electronic state, in view of the fact that we have already the actual example of a quintet ground state for the type (I) compound with four unpaired electrons. However, in the case of the type (III) compounds – since the exchange integral between the π-NBMO's, $\langle \pi_1 \pi_2 | 1/r_{12} | \pi_2 \pi_1 \rangle$, may not be so large as the $n-\pi$ exchange integral for the type (I) and (II) compounds – it might be possible that the correlation effects make the non-magnetic state the lowest one. Our detailed theoretical studies on these compounds using the Hartree-Fock method and also the field theoretical method, taking into consideration the effects of electron correlation, will be published in the near future.

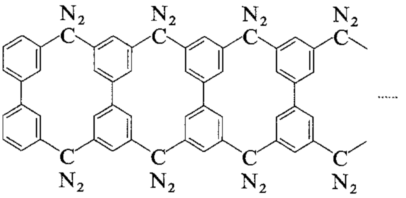
The compounds (I), (II) and (III) may be produced by photolysing or by chemically treating the parent compounds (I′), (II′) and (III′), respectively, where

X represents some halogen atom. Although the synthesis of these parent compounds will be quite difficult and, moreover, the compounds (I), (II) and (III) may be moderately stable only at low temperatures or at extremely low temperatures because of their relatively large chemical reactivity, the studies on their magnetic and optical properties may be very interesting and important for the elucidation of the nature of the magnetism and the molecular electronic structure in general.

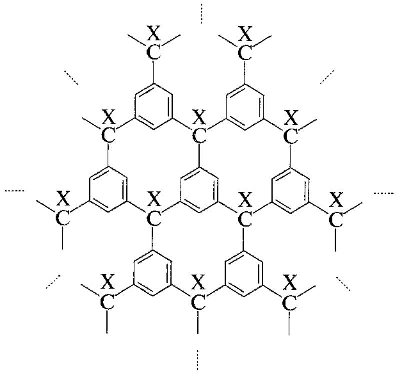
(I')



(II')



(III')



We are now making experimental and detailed theoretical studies on the relatively small compounds of these types which will supply basic informations for the present problem. However, the synthesis and studies on larger compounds of these types will be of crucial importance for this problem, even if the synthesis of the very large polymers is not possible.

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