Models for organic ferromagnetism

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Synthesis of a purely organic ferromagnet is an outstanding challenge in chemistry today. Theoretical formulation of models and their computational and experimental studies have engaged the attention of physicists, chemists and material scientists over the past several years. Various models have been suggested for ferromagnetism in organic systems. Experimental and computational studies have also dealt with this problem.

Quasi one-dimensional solid-state materials have attracted the attention of chemists, physicists and material scientists in the last few decades, owing to their unique physical properties and the theoretical insights gained from their study. These materials characterized by highly anisotropic electrical, magnetic and optical properties include a wide range of systems like (i) linear chain metal salts and complexes, (ii) stacked metal complexes, (iii) inorganic and organic polymers, and (iv) stacked organic charge transfer or ion-radical complexes[1-13]. The anisotropicity of the physical properties results either from the linear polymeric structure or the one-dimensional packing of atomic or molecular units in the solid state, with strong interactions along the column direction and much weaker interactions in the orthogonal directions. This review will be concerned with purely organic systems only.

The discovery of semiconduction in the perylene-bromine complex[14] and the development of tetracyanoquinodimethane salts[15] led to the fabrication of numerous organic conductors[4,6-8,10,12,16-18]. Suggestion of an excitonic model for organic superconductivity[19] sparked off intense research efforts, and,

overcoming the problem of Peierl's instability[20], several organic superconductors have now been developed[21-25], though not based on Little's model. Organic solids exhibiting interesting and useful nonlinear optical properties[26] is also currently an area of active research.

Quasi one-dimensional stacked organic charge transfer complexes show a wide variety of magnetic phenomena. The organic molecules that form the columnar stacked structures are usually good π-electron donors or acceptors. When they form donor-acceptor complexes with a high degree of ionicity or ion-radical salts, paramagnetic centres are obtained. Cooperative interactions are predominantly antiferromagnetic, due to kinetic exchange[27]. In one-dimensional systems, the susceptibilities are described by the numerical solution of Bonner and Fisher[28]. Low temperature deviations are usually attributed to spin-Peierls transition[29]. Triplet spin excitons[30], random exchange Heisenberg antiferromagnetic chains[31], activated paramagnetism in regular linear chains[32], etc. are some of the other kinds of magnetic phenomena encountered in the quasi one-dimensional organic solid state.

Cooperative magnetic interactions lead to a variety of magnetic orders[33]. Ferromagnetism is one of the most important among them, both from a theoretical and practical point of view. All ferromagnets known today involve metals. Thus the absence of an organic ferromagnet is very conspicuous with the development of organic conductors, superconductors, nonlinear optical materials, etc., mentioned above. Recently, several complexes involving metallocenes as donors and organic acceptors have been prepared and studied[34], some of which showed ferromagnetism. This has established the possibility of achieving molecular ferromagnetism. As far as purely organic systems are concerned, there have only been demonstrations of ferromagnetic couplings[35-41] and some very preliminary and apparently irreproducible reports on some ferromagnetic materials[42,43]. Recently, ferromagnetism has been reported in some triarylmethane resins[44] as well as a polymer incorporating indigo units[45]. Also, an organic molecule with nitrosyl radicals showing enhanced magnetism has been reported[46] and a polyradical with high spin concentration[47]. Very recently, Miller's group[48a] has claimed discovery of a room temperature ferromagnet obtained from the reaction of tetracyanoethylene and bis(benzene)vanadium and Wudl's group[48b] has found evidence for soft ferromagnetism in an equally reactive material, the complex between tetrakis (dimethylamino)ethylene and the fullerene C_{60}. In most of these cases structural details are not yet known and a convincing evidence for organic ferromagnetism is awaited.

The significance of experimental demonstration of organic ferromagnetism and fabrication of organic ferromagnets cannot be overemphasized. From a theoretical point of view, extended ferromagnetic exchange interactions through s and p orbitals will be novel and may provide valuable insights into the very phenomenon of magnetism. From a practical point of view, the immense synthetic flexibilities afforded by organic systems will enable the fine-tuning of the solid state magnetic characteristics. Fabrication of electronic devices at a molecular level[12] is an area of intense research activity, with tempting possibilities of application in modern computer technology. Similar development of molecular magnetic systems will be of immense technological value.

Several models have been suggested and experimentally tested to look for ferromagnetism in organic materials. The models are predominantly based on one-dimensional systems. It must be stressed at the outset that it is impossible to attain long range order in one dimension at finite temperatures[49]. This is because entropy gains on the formation of disorder in infinite systems, at finite temperatures always overwhelms energy destabilization. Hence ferromagnetism can be achieved only in quasi one-dimensional systems with appreciable two-dimensional and three-dimensional interactions.

Since the last brief reviews[50] the elusive nature of the problem of organic ferromagnetism has attracted novel theoretical and experimental approaches. The extensive literature available on organometallic systems is not included in this review, since excellent reviews are already available[34]. An exhaustive list of the various theoretical models proposed for ferromagnetic interactions in organic systems is given here.

Models for organic ferromagnetism

Negative spin density product model

The earliest proposal for achieving ferromagnetic interaction between free radicals was put forward by McConnell[51]. The overall exchange interaction between two aromatic radicals A and B with spins S_A and S_B can be approximated by the Hamiltonian

$$\mathscr{H} = -J S_A S_B = -\sum_{ij} J_{ij}^{AB} S_i^A S_j^B,$$

where S_i^A and S_j^B are the π-electron spins on atoms i and j of molecules A and B respectively. McConnell's argument is based on the fact that the interaction is ferromagnetic, if J_{ij}^{AB} and the product, $S_i^A S_j^B$ have the same sign. Since the largest exchange integrals J_{ij}^{AB} are usually negative, the product $S_i^A S_j^B$ should be negative by design, if the interaction is to be ferromagnetic. This

is possible if some atoms on A and B have negative spin densities and the orientations of A and B are such that spin densities of opposite signs couple most efficiently. Thus the trick is to exploit an inherently antiferromagnetic coupling to produce ferromagnetism. In particular, odd alternant radicals having large positive and negative atomic π-spin densities may be used.

Izuoka et al.[38] demonstrated McConnell's argument in a beautiful experiment using two diphenylcarbene units incorporated in a rigid [2.2] paracyclophane skeleton. In the pseudo-ortho and pseudo-para isomers shown in Figure 1, the overlapping modes of the spin distributions in the benzene rings are such that the $S_i^A \cdot S_j^B$ products are all negative, leading to ferromagnetic coupling of the two triplet carbenes and a quintet ground state as observed in electron spin resonance experiments. The overlapping mode in the pseudo-meta isomer, on the other hand, leads to antiferromagnetic coupling and hence a singlet ground state. Ab initio calculation using approximately projected UHF methods[52,53] as well as the semi-empirical AM1 studies of Lahti and Ichimura[54] are in agreement with these experimental observations.

The existence of ferromagnetic interactions in triphenylverdazyl radical solid[36] and mixed crystals of galvinoxyl radical and its precursory closed shell compound[37] have been attributed to similar mechanism as proposed by McConnell. In the latter case, the authors do not rule out the possibility of Anderson's potential exchange[27] being the cause of ferromagnetic couplings, rather than the negative product of spin densities. The galvinoxyl radical solid shows Curie–Weiss behaviour down to 85 K, at which temperature a phase transition destroys all paramagnetism. This transition is suppressed by mixing in hydroxygalvinoxyl. The ferromagnetic interaction has recently been explained[55] as being due to the combined effect of intramolecular spin polarization and intermolecular charge transfer. Overlaps of molecular orbitals (MO) calcu-

lated using the INDO method were estimated to demonstrate the favourable triplet stabilization. A similar mechanism is proposed for the ferromagnetic intermolecular interaction observed[39,40] in 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide. In this case, magnetic susceptibility follows a Curie–Weiss law behaviour with $\theta \approx +0.9$ K. The ferromagnetic interaction was estimated to extend over four radicals. Recently, Allemand et al.[41] reported detection of short-range ferromagnetic interaction in a similar system based on the 1,3,5-triphenylverdazyl radical. Molecular engineering of the specific crystal was dictated by the McConnel spin density argument.

Charge transfer models

Possibility of attaining ferromagnetic coupling of spins in a one-dimensional stack of an ionic molecular crystal was first suggested by McConnell[56]. If one assumes a mixed stack of the type ... $D^+A^-D^+A^-$..., where D^+ and A^- are ion radicals, a back charge transfer (from A^- to D^+) would lead to a singlet or triplet excited state respectively, depending on whether the neutral D and A have singlet ($S = 0$) ground state or one of them has a triplet ($S = 1$) ground state. Since $S = 0$ state is most common for neutral molecules, the excited state is often a singlet. Configurational mixing of this excited state with the ground state (Figure 2,a) of the ionic molecular crystal is the origin of the antiferromagnetic coupling commonly observed. If by design, D or A with triplet ground state is chosen, the excited triplet state obtained (Figure 3,a) would lead to ferromagnetic coupling through configuration interaction (Figure 2, b).

Breslow and coworkers[57–61] attempted to experimentally achieve this ferromagnetic coupling. They followed a slightly modified scheme (Figure 3,b) wherein D and A are chosen such that the redox potential matching leads to double ionization of D and A in the charge-transferred state. The requisite degeneracy of D or A is usually achieved using symmetric molecules. Even though novel donors (Figure 4) with required symmetry were synthesized and

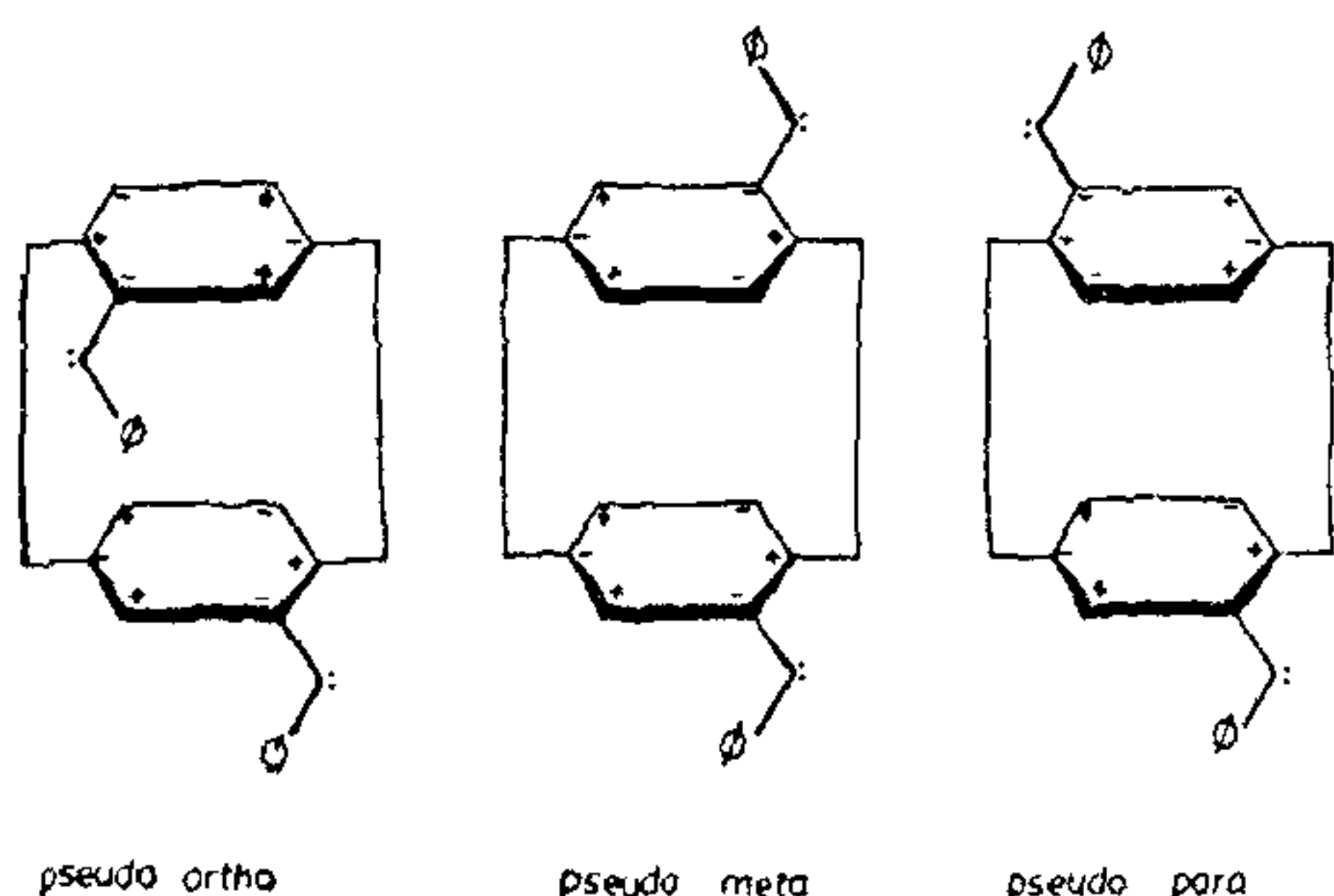pseudo ortho   pseudo meta   pseudo para

Figure 1. Spin density distributions of the diphenyl carbene units incorporated in [2.2] paracyclophane (ref. 38).
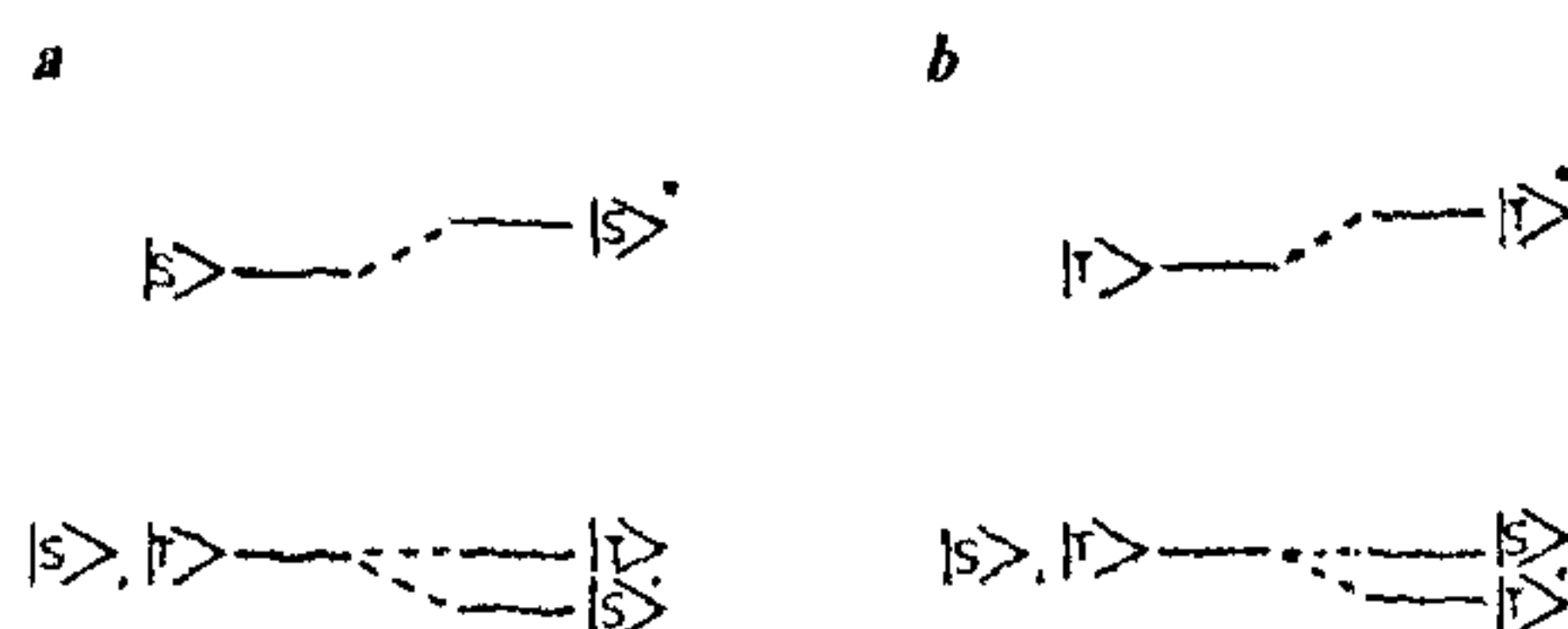

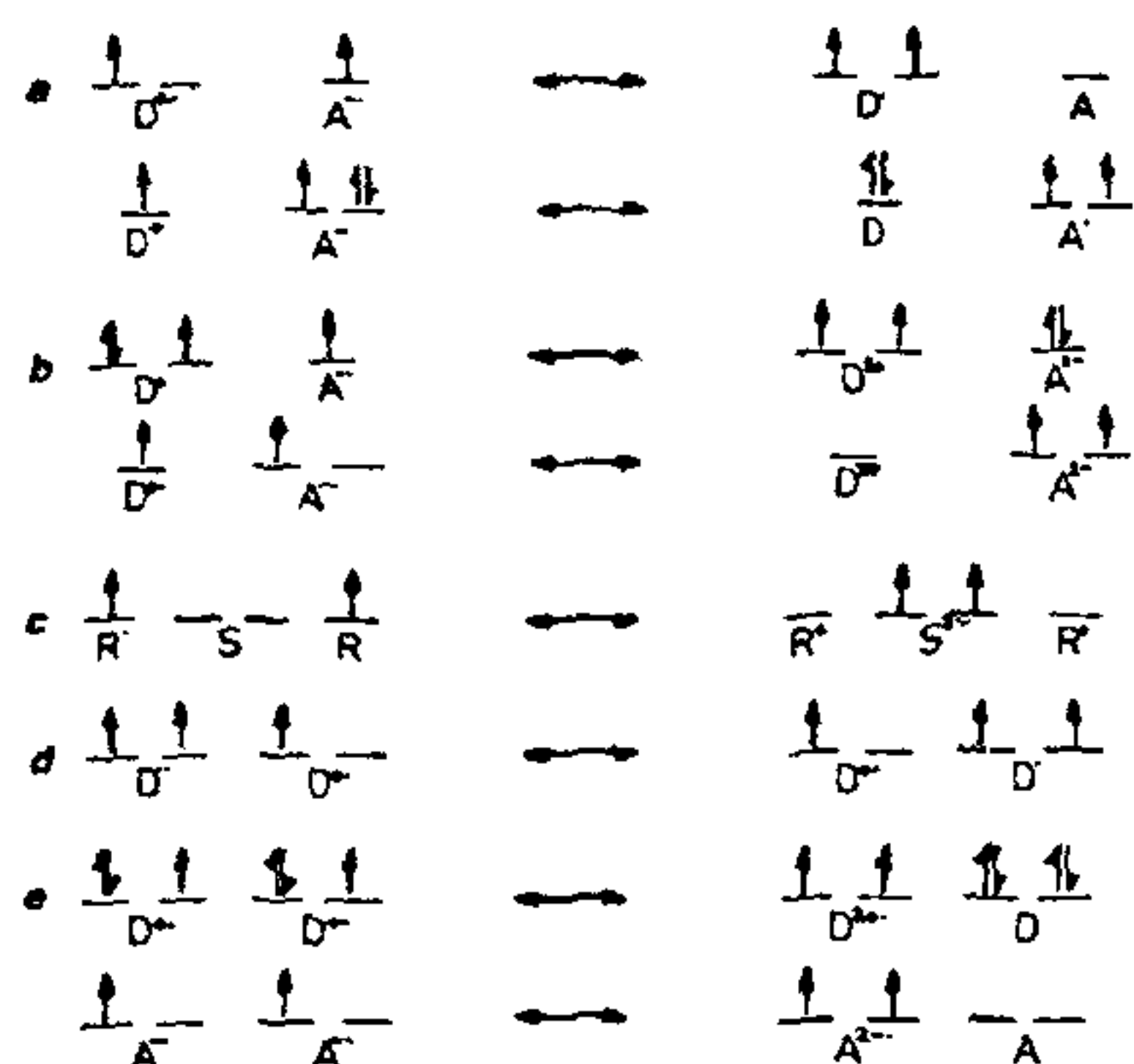Figure 2. Configuration interaction leading to (a) singlet and (b) triplet coupling of spins.

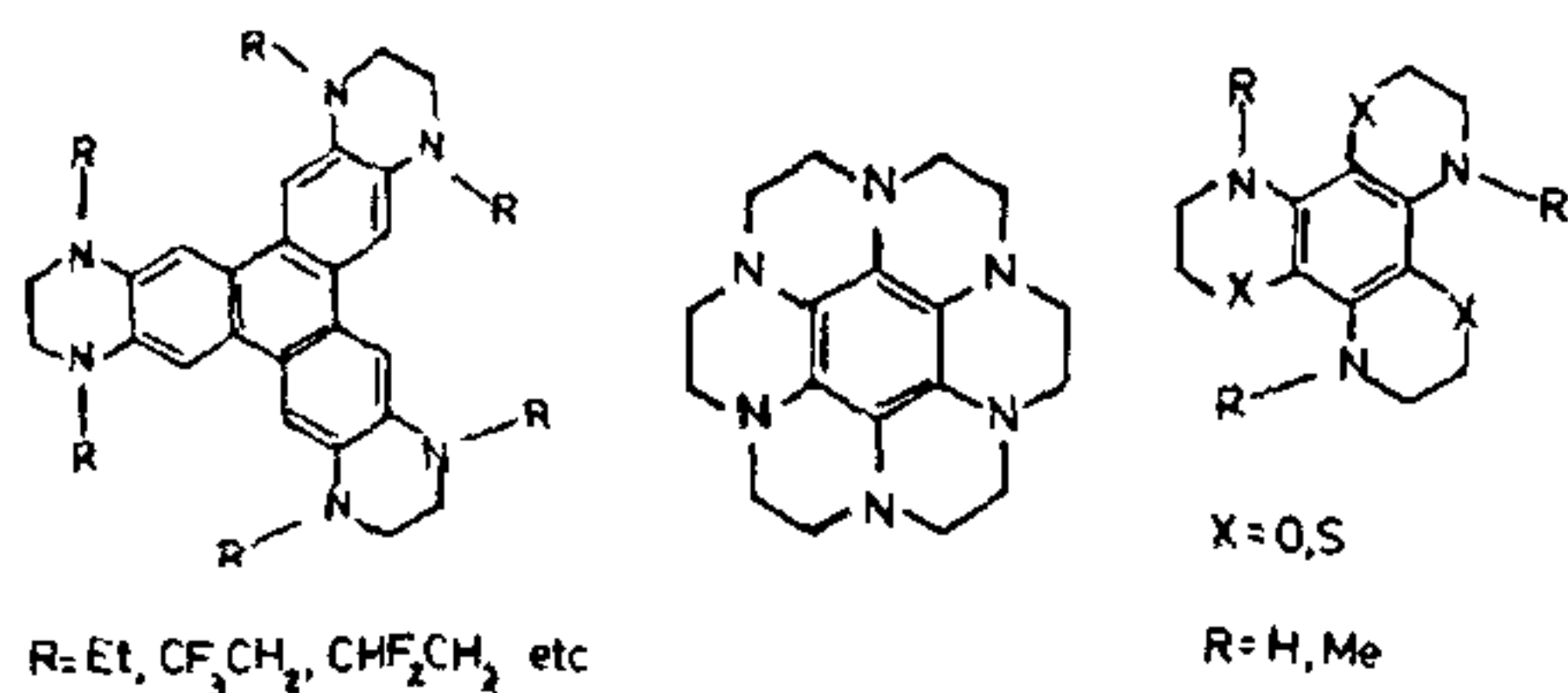Figure 3. Charge transfer schemes for different models (see text for details).

R=Et, CF_3CH_2, CHF_2CH_2 etc

X=O,S

R=H, Me

Figure 4. Symmetric donors synthesized by Breslow and coworkers. (refs. 59–61).

established to be ground state triplets in the D^{2+} state in most cases, the D^+A^- complexes have invariably been antiferromagnetic. A good overview of the efforts has been provided by Breslow[62]. I discuss in the final section, possible reasons for this observation. It should be noted that the approach of Miller and coworkers[34] to synthesize molecular ferromagnets based on organometallic systems is essentially based on the same McConnell model.

Several variations on the McConnell model have been proposed and tested. Soos and coworkers[63] have attempted to extend the superexchange mechanism known in inorganic systems to organic stacked complexes. In a mixed stack, ...R`SR`S... an excited triplet state may be obtained, if the spacer molecule S has degenerate orbitals to which the radical (R`) spins are transferred during the virtual excitation (Figure 3, c). It is important that the relevant molecular orbital degeneracy of S is maintained in the solid complex, which is possible only if the orientation of the R` which sandwich any S is such that the perturbations on the degenerate MO's of S are equal. Complexes based on

symmetric diamagnetic anion[63] and cation[64,65] spacers were synthesized and studied. Mixed stacking with inappropriate dihedral angle between radical cations was observed in the tetramethyl-p-phenylenediamine–pentacyanocyclopentadienide complex[63]. In the other complexes, segregated stacking[63b], dimerized mixed stacks[64] of the type ...$D^+D^+A^-A^-D^+D^+A^-A^-$..., with triplet excitons and mixed stacked structures showing interesting magnetic transitions[65] were observed. Ferromagnetic coupling was not obtained in any of the materials. Recently we have studied the magnetism of trisdimethylaminocyclopropenium hexacyanotrimethylenecyclopropanide, since the crucial orientation problem of radicals could not arise in this case for symmetry reasons. However, the magnetic susceptibility variation with temperature indicated a one-dimensional Heisenberg antiferromagnetic behaviour, implying the distinct possibility of segregated stacked structure[66]. Attempts to obtain the structural information are under way.

Wudl and coworkers[67] proposed another variation called the ferromagnetic organic metal. If a homomolecular stack is formed from stable neutral diradicals with triplet ground state and the radical ions derived from them, it would give rise to ferromagnetic interactions and a partially filled band. Charge transfer in these systems leads to degenerate configurations (Figure 3, d).

A scheme slightly different from that of Wudl would involve stacking of degenerate ion-radicals with no neutral species in between. Here the charge transfer excitations would lead to a triplet excited state (Figure 3, e) which is a consequence of the formation of the dication/dianion of the molecule which has the appropriate symmetry. The loss of degeneracy of the radical orbitals, due to Jahn–Teller distortions could be a crucial problem. But the orientation problem encountered in all the mixed stacked structures will not be present here. It may be noted that this model also envisages metallic band filling. Torrance et al.[43] suggested that this mechanism is operative in the sym-triaminobenzene–iodine complex, which showed ferromagnetic properties. These results have not been confirmed, though. Torrance and coworkers[68] reported SCF/CI calculations on benzene anion dimers to argue for the ferromagnetic couplings in these systems. However, Ramasesha and coworkers[69] find, on the basis of complete CI PPP calculations on benzene cation dimers, that if the erroneous assumption of ZDO of molecular orbitals is removed, the couplings are antiferromagnetic.

From an experimental point of view, the models described in Figure 3, a, b, d and e require, as a starting point, good donor/acceptor molecules with appropriate degenerate frontier orbitals. Further, their cation/anion has to be stable to distortions due to Jahn–Teller or solid-state effects, which destroy the crucial degeneracy.

Several groups are actively pursuing the synthesis and characterization of novel systems that would satisfy the above criteria[59-61,67,68,70-73]. The pitfalls that may be encountered in the delicate balance between singlet and triplet ground states are illustrated by the detailed study of the hexaazaoctadecahydrocoronene ions by Miller and coworkers[74].

Polycarbenes

Mataga[75] proposed that certain polymeric hydrocarbons with carbene or carbyne units would show ferromagnetic alignment of spins due to the topological nature of the molecular orbitals. A typical candidate is m-polydiphenylcarbene. On the basis of spin distribution and energy band diagram shown in Figure 5, Mataga suggested that the narrow band (N) formed from nonbonding π MO and σ type n-orbitals at bridge site, would be populated by ferromagnetically aligned spins. It was cautioned that, correlation effects might stabilize the nonmagnetic state and that at large molecular size, band gaps may become comparable to kT and thus upset the ferromagnetic state. However, Nasu[76] showed using mean-field calculations that, as the result of correlations and exchange interactions at the bridge site, the ferromagnetic state is the most stable. It was later shown[77] that the ground state becomes antiferromagnetic if the next-nearest-neighbour transfer terms exceed the intraatomic repulsion.

Tyutyulkov and coworkers[78] pointed out that for both one-dimensional and two-dimensional infinite polymers obtained from the benzyl unit, the Hückel π-band gaps flanking the N band are exactly the same as the corresponding molecular orbital separations in the monomer. Further, Hughbanks and Kertesz[79] argued that non-bonding bands are not necessary for making π-ferromagnets. Superdegenerate bands can arise in systems like polyfulvalene which, on extensive doping, may form π-ferromagnets.

Mataga's model resembles the interaction between conduction s-electrons and localized d-electrons in ferromagnetic metals, when one considers the delocalized π-electrons and localized non-bonding 'n' electrons at the bridge sites in the m-polydiphenylcarbenes. The largest oligomer reported so far is the pentacarbene[80].
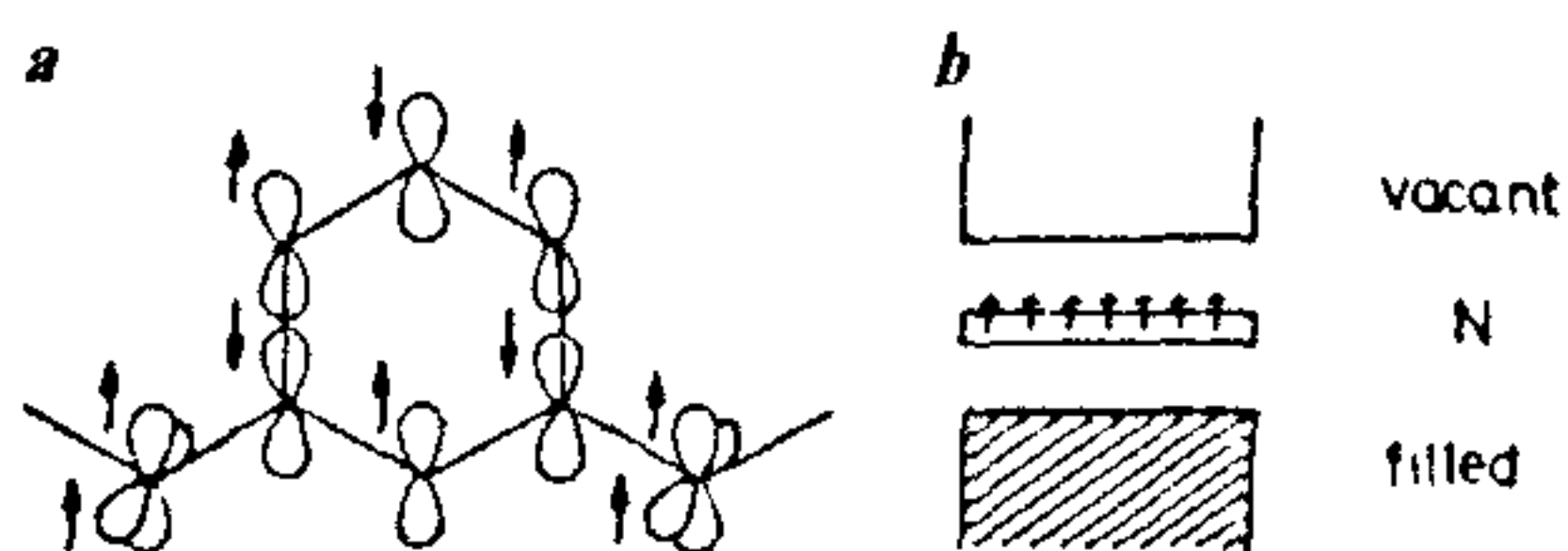
Figure 5. a, Spin distribution in m-polydiphenylcarbene (ref. 76) b, Energy band diagram (ref. 75)

The prototype m-phenylenebis(phenylmethylene) has a quintet ($S = 2$) ground state[81]. The tetracarbene reported[82] in 1983 has been studied in detail and shown to have a nonet ground state[83,84] The intramolecular interactions are clearly ferromagnetic, but the intermolecular exchanges when present, have been shown to be antiferromagnetic[85-87].

General synthetic methods for polycarbenes of different lengths are not yet available. Each oligomer has been prepared based on specific synthetic schemes. This has strongly limited the development of the polycarbene approach to organic ferromagnetism. Further, these materials are highly reactive and need to be handled at low temperature and in inert matrices.

Odd alternant polymers

Based on the theorem of Lieb[88], Ovchinnikov[89] showed that in an alternant molecule, if the number of starred and unstarred atoms are not equal, the ground state spin is nonzero and equal to half the difference in their numbers. On the basis of this result, Ovchinnikov suggested several hydrocarbons and heterocycles, which could at infinite size be considered ferromagnetic. A typical example is the macromolecule 1. It may be noted that Mataga's polycarbenes would also fit into the general scheme of high-spin polymer systems with the additional feature of σ-type n-orbitals. Klein et al.[90] supported the possibility of obtaining high-spin hydrocarbons on the basis of valence bond models in addition to calculations using classical structure or MO theory, cluster expansion methods and Hubbard and PPP Hamiltonians. But their conclusion is that cooperative magnetism in these systems is likely to be metamagnetic or superparamagnetic rather than ferromagnetic.

$$X = O, S$$
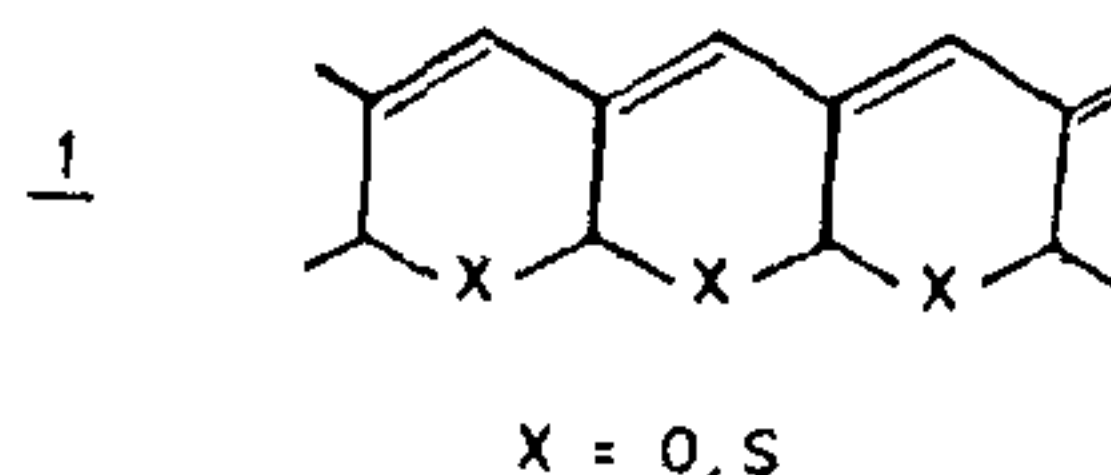
Calculations of Koutecky et al.[91] also verified the ground state spin prediction of Ovchinnikov. Sinha et al.[92] found high spin ground state for odd alternant π-conjugated organic molecules in the PPP and Hubbard models with weak correlation, even when the alternancy symmetry is destroyed. However, for strong correlations, the ground state switches to low spin. Their calculations also showed that the low-spin ground state is susceptible to lattice dimerization.

Tyutyulkov and coworkers[93] generalized the observation of Ovchinnikov to include non-alternant, non-Kekule systems as well as those containing hetero-

atoms. If N_t is the number of π-centres in a maximal non-bonded homoatomic set in a π-conjugated system with N atoms, $(2N_t - N)$ is the number of non-bonding MO's provided $2N_t > N$. This may open up a new series of polymers for investigation of ferromagnetic networks. We have developed a simple set of rules to predict the ground state spin of alternant and non-alternant hydrocarbons and heteroatom molecules not restricted by Tyutyulkov's conditions[94].

The simplest test system for the odd alternant hydrocarbon model is trimethylenemethane diradical (2a) which has been subjected to detailed experimental studies and established to be a ground-state triplet[95]. Another simple test system is benzene-1,3-bismethylene (2b), which is also a confirmed triplet[96-98]. 1,3-diazidobenzene stabilized by flourine substitution[99] and m-xylene derivatives involving chlorinated triphenylmethyl radical centres have also been studied recently[100] as model monomeric systems for organic ferromagnets.
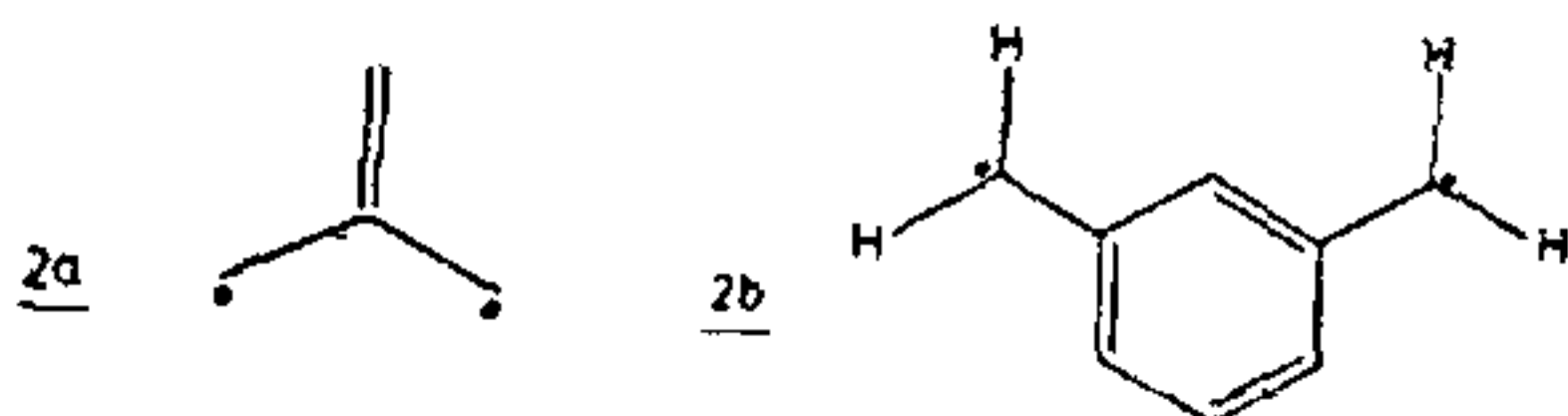
Ovchinnikov's group[42] reported an organic polymer based on polydiacetylene with nitrosyl radical centres (3) which was found to have 0.1% of the theoretical value of spontaneous magnetization. Magnetic separation gave particles with magnetization above 1 G. The Curie temperature was found to be 150–190°C for some samples. Miller and coworkers later reported a different phase of a similar polymorph[101] and recently showed[102] using very careful measurements, that both their as well as Ovchinnikov's heat-treated polymeric systems follow Curie-Weiss law behaviour with no detectable ferromagnetism except that contributed by metallic impurities.
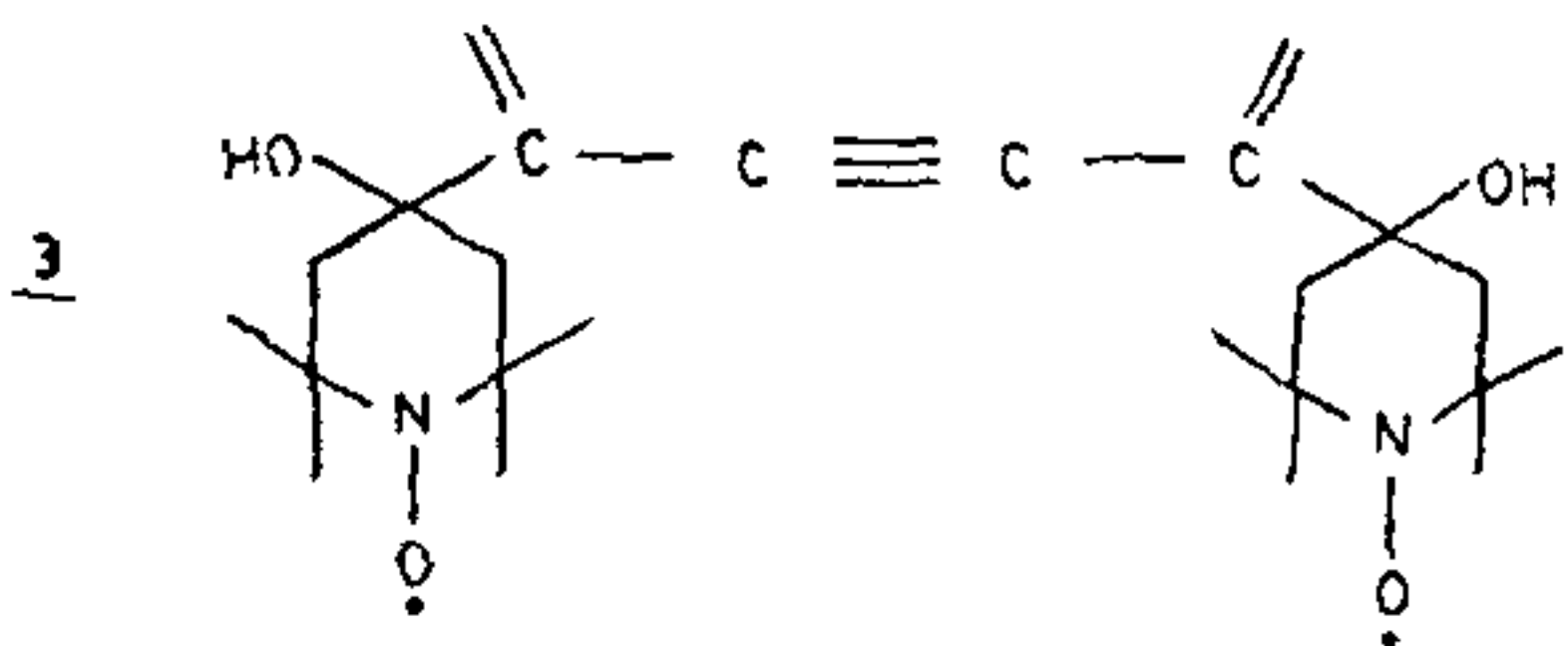
In order to investigate the magnetic interactions of radical centres in different regiochemical dispositions on a conjugated polymer backbone, Iwamura and Murata[103] studied systems containing two phenyl nitrene units connected through acetylenic and diacetylenic bridges. Their electron spin resonance experiments have demonstrated the validity of the theory of Ovchinnikov[89] and Klein[90]. It was observed

that two triplet nitrenes at m,p' and m,m' positions showed ferro- and antiferromagnetic interactions respectively. This is consistent with the simple rule proposed recently[94]. Extension to polymers is reported to be in progress. Thus, even though Ovchinnikov's model remains viable, the experimental results so far are far from satisfactory.

Buchachenko[104] has addressed early on, the problem of intermolecular exchange interactions in radical–polyradical systems. It was suggested that, ferromagnets may be obtained by cocrystallization of monoradicals with polyradicals. In effect one looks for a ferrimagnet in this case.

Recently Itoh et al.[105] reported model studies on an organic ferrimagnet. They demonstrated magnetic superexchange interactions through ether linkages in high-spin molecules. The topological requirements for ferro- and antiferromagnetic interactions were tested by electron spin resonance investigations on bis(phenylmethylene)diphenyl ether. A molecule containing ground state triplet diphenylmethylene moiety linked to quintet m-phenylenebis(phenylmethylene) through an ether bridge was also studied as a model ferrimagnet unit.

Polaronic ferromagnetism

Conducting conjugated polymers like polyacetylene, polyparaphenylene, polypyrrole, etc. are well known[12]. On doping such a polymer with an electron or hole, a polaron, an ion radical self-trapped in a local lattice distortion, is produced. Polyacetylene with a cationic polaron is represented in 4a. Fukutome et al.[106] proposed that, a polymer with alternating blocks A and B, where A gives a polaron on doping and B produces constructive interference of the spin polarization clouds of the polarons, will be a model for polaronic ferromagnetism. B should be a conjugated oligomer with odd chain length, and nondegenerate ground state (4b is an example). PPP model calculations suggest a possible ferromagnetic coupling in these polymers, but no conclusion is drawn about intermolecular exchanges.
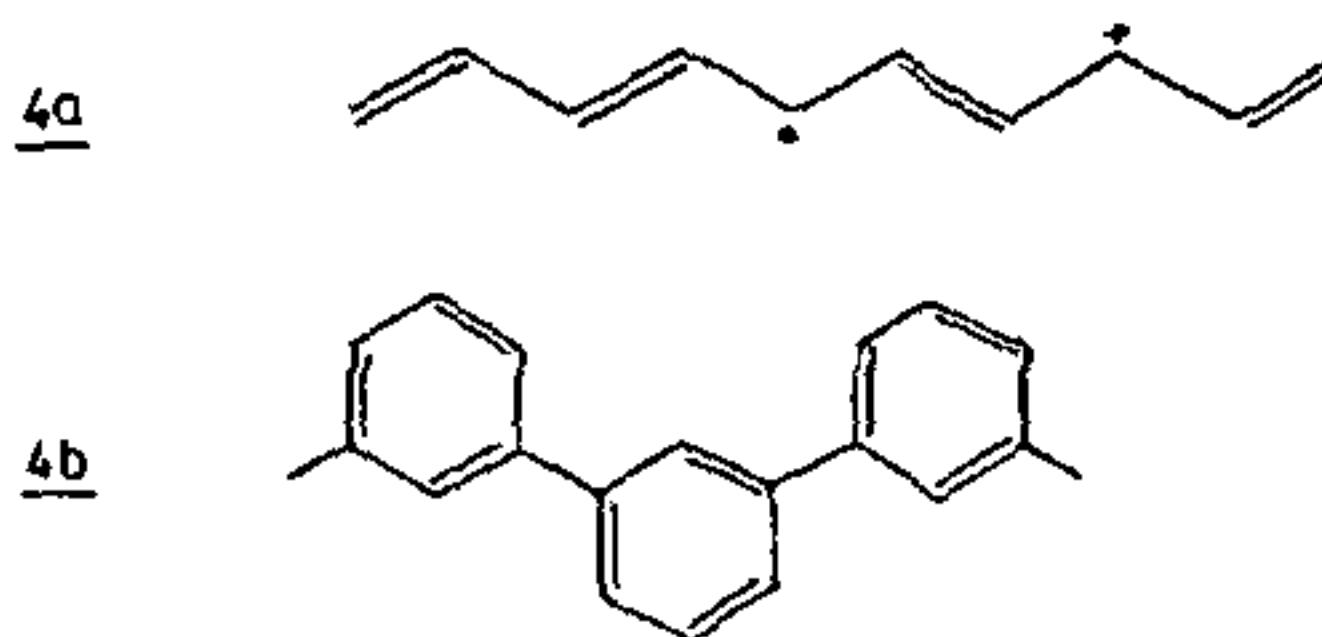
Dougherty and coworkers[107,108] proposed that localized 1,3-biradicals like cyclobutanediyls and cyclopentanediyls could also serve as ferromagnetic coupling units. Some initial results on m-substituted benzene coupling units have been reported[109]. In connection

with these studies on coupling units, it is worthwhile to pay attention to the papers of Borden and Davidson[110] and Platz[111] and recent studies of Berson[112] on Hund's rule violation in disjoint systems. Our rule[94] to predict *ground state spin of non-Kekulé systems is also* relevant.

Miscellaneous model systems

Kivelson and Chapman suggested[113] that, among the unusual properties expected in polyacenes, ferromagnetism is one. If one assumes a Hubbard model with small U, the mean field ground state of the polyacene can be ferro- or antiferromagnetic. Since in polyacenes, the Fermi surface lies at the edge of the Brillouin zone, even in undistorted molecule, the density of states diverges in the vicinity of the fermi surface, and could lead to a preference for ferromagnetic ground state. No experimental verification has been forthcoming so far.

Charge transfer complex of hexamethoxytriphenylene with tetrafluorotetracyanoquinodimethane, doped in the solid state with arsenic pentafluoride, has molecular formula $(HMT)_2$-$TCNQF_4$-$(AsF_{5.5})_y$, with $y = 2.0$-8.4. These doped systems showed[114] large spin densities of up to 1.6 spin 1/2 per $(HMT)_2TCNQF_4$. A charge-transfer model involving a ...ADDADDA... stack of $TCNQF_4$ (A) and HMT (D) and ferrimagnetic coupling of spins has been proposed[115] to explain the high bulk spin density. However, spin couplings were reported to be anomalously weak (Weiss constants < 0.6 K) and suggests the stabilization of HMT cation radicals by separating them using $TCNQF_4$. This could be important in charge-transfer complexes of the McConnell type, where stable dication triplets are needed.

An interesting system where spin dilution leads to enhanced magnetic susceptibility has been reported by Ashwell *et al.*[116]. In the system, [1,2-di(4-pyridino) *ethylene*$]_x^{2x+}$ [1,2-di(4-pyridyl) *ethylene*$]_{1-x}$ $(TCNQ)_3^{2x-}$, as x decreases below 0.5, the room temperature susceptibility increases above the Curie value up to about eight times in certain samples. The observation has been explained in terms of decrease of the antiferromagnetic coupling of $TCNQ^-$ spins. But the factors leading to ferromagnetic interaction are not clearly identified. The polyradical, poly(*para*-ethynylphenyl)galvinoxyl has been reported to show extraordinarily high spin concentration[47] but a Curie paramagnetic behaviour. Very recently, Dulog and Kim[46] described a triradical system 5, which shows an *experimental spin per molecule much higher than the* theoretical value. The mechanism operating is not established. Detailed study of all these preliminary findings may lead to interesting information on how to *tackle the organic ferromagnet problem.*

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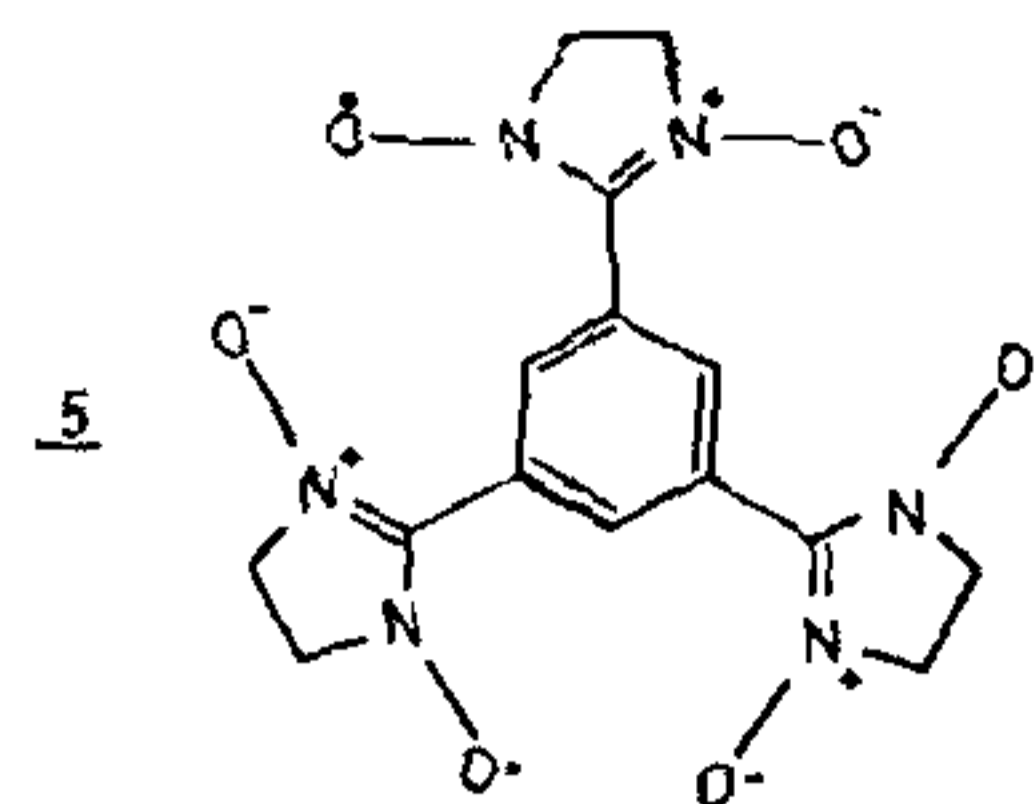
Theoretical studies

In the discussion above, we have noted various theoretical investigations that have been carried out in connection with some of the models presented. Groups of Ovchinnikov[89], Klein[90], Ramasesha[92] and Koutecky[91] have studied the odd alternant systems at various levels of theory. Torrance[68] and Ramasesha[69] *studied the benzene ion dimer systems computationally.* Nasu and coworkers[76,77] carried out calculations on the polycarbene systems. Some of the other theoretical studies mentioned above were due to Yamaguchi[52,53], Lahti and Ichimura[54], Kinoshita[55] and Tyutyulkov and coworkers[93]. I mention below some general mathematical models suggested for organic ferromagnetism and computational approaches developed to analyse ferromagnetic couplings.

Pohl[117] discussed the conditions required to produce a persistent magnetization in a ring-shaped organic molecule. Based on a one-particle operator model, he concluded that such a molecule should have large size, *of the order of 100 Å diameter, and the synthesis should* take place in a pre-existing strong magnetic field. It is *also argued that, maximum magnetizability is present if* the number of π-orbitals is a multiple of 4. This will *obviously be a problem because of the instability of $4n\pi$ systems.*

Yamaguchi and coworkers calculated effective exchange integrals, J_{ab} in a number of cases. *Ab initio generalized MO method was used to calculate J_{ab} for* molecules and their ions in which radical centres are connected through π-networks (e.g. benzene-1,4-bismethylene and benzene-1,3-bismethylene) to elucidate spin polarization and spin delocalization effects[118]. These results can be used to *design organic magnetic polymers. Intermolecular exchange integrals between* organic radicals were also calculated[119,120] and the *results are consistent with the spin density product* argument of McConnell[51]. Approximately projected UHF and UHF Moller-Plesset procedures were employed[52] to calculate the effective exchange integrals *for dimers and pentamers of triplet carbenes. Basis set* and correlation dependences were also studied. As pointed out earlier, this study also quantified the experimental results of Izuoka *et al.*[38] in terms of the *values of the effective exchange integrals between*

diphenylcarbene units locked in different relative orientations in a p-cyclophane framework. The importance of stacking modes for the magnetic interactions of aromatic free radicals has been investigated by Yamaguchi *et al.*[121] using spin-projected UHF and UMP methods. A variety of magnetic orders like superparamagnetism, mictomagnetism, etc., were invoked to explain the implications of the *ab initio* results.

Li and Tang[122] carried out UHF crystal orbital (CO) calculations on several organic polymers of interest in connection with organic ferromagnetism. They find that the ferromagnetic state is the lowest in energy compared to spin density wave or charge-density wave states. UHF and MP2 configuration interaction calculations carried out on some clusters supported the CO calculation results.

Recently, Chu *et al.*[123] reported some analytical and numerical results for the free energy and magnetization of organic polymers with side chains. It is shown that the ferromagnetic case corresponds to those polymers in which the numbers of sites within a unit cell with and without side chains are both odd. It is interesting to note that this result can be restated in terms of the odd alternant model of Ovchinnikov.

Overview

I have listed the different schemes put forth over the past 25 years or so to tackle the fascinating problem of achieving an organic ferromagnet. Success so far has been limited to demonstration of ferromagnetic coupling in a few cases[35-41], which are not extended systems. Extended interactions have been claimed in some preliminary reports[42-46] and needs validation. Confirmed studies are available only for the organometallic complex donor/organic acceptor systems studied by Miller and coworkers[34]. Extended ferromagnetic couplings and ferromagnetic ordering in organic systems remain to be convincingly demonstrated.

Models involving polymers appear to pose synthetic problems. Instability of radicals at ambient conditions makes the prospect of obtaining a practically useful polymer ferromagnet difficult. The polymeric systems reported so far, have had only very low concentration of magnetic domains. However, ferromagnetic interaction, if attained, will be stronger in polymeric systems than in stacked complexes, because of the more effective exchange pathways through chemical bonds.

In my opinion, the charge transfer complexes in stacked structures offer more scope for the realization of an organic ferromagnet, from the synthetic point of view. Preparation of symmetric organic molecules with good electron donor/acceptor properties is being actively pursued in many research groups. Even if the non-trivial problem of obtaining organic donors or

acceptors with stable triplet ionic states is solved by ingenious synthetic strategies, there remains the crucial effects of solid state packing. Packing of the donor/acceptor molecules into appropriate stacks and orientations is a problem that has so far defied any systematic approaches. In any mixed stack arrangement the species with the appropriate degenerate orbitals has the counterions for neighbours and vice versa. If the neighbours have lower symmetry than the degenerate system, it is very likely that the requisite degeneracy will be lifted due to the resulting uneven perturbations. This problem exists in the McConnell–Breslow and Soos approaches. It has been discussed in detail in connection with the latter model[63]. The segregated stacked models of Torrance and Wudl avoid this complication. In this regard, models envisaging minimum packing constraints are the most appealing.

Most models have focused on intrastack or intrachain exchange interactions. Interstack and interchain interactions will be crucially important to attain ferromagnetic ordering. At this stage, even extended intrastack ferromagnetic interactions have not been convincingly established in purely organic systems. It may be hoped that once appropriate one-dimensional exchange interactions are achieved, attainment of magnetic order will be solved along the lines of strategy successfully tried in the suppression of Peierl's instability in organic superconductors. It is significant to note that the likes of the two-dimensional interactions observed in organic superconductors should be built in as far as exchange pathways in organic magnets are concerned.

Note added in proof: Since the submission of this article several papers have appeared in the literature which are relevant to the problem of organic ferromagnetism. I would like to draw attention in particular to the following papers which present a critical analysis of the McConnell's charge transfer complex model and its application to the metallocene complexes: (i) Kollmar, C. and Kahn, O., *J. Am. Chem. Soc.*, *1991*, **113**, 7987; (ii) Kollmar, C., Couty, M. and Kahn, O., *J. Am. Chem. Soc.*, *1991*, **113**, 7994; and (iii) Kollmar, C. and Kahn, O., *J. Chem. Phys.*, *1992*, **96**, 2980.

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