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Organic and molecular ferromagnetics: advances and problems

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ABSTRACT. The possible ways of creating organic and molecular ferromagnetics are analysed and the principles of the molecular design of these magnetic substances are examined. Comparison of the theoretical predictions with the experimental results permits certain conclusions and predictions as to whether different ways of creating molecular ferromagnetics are realistic.

The bibliography includes 68 references.

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I. Introduction

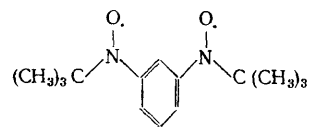
All the known ferromagnetics are made up of metal atoms with unfilled *d* or *f* electron shells, i.e. on the basis of the spin magnetism of the inner *d* and *f* electrons. The question arises whether it is possible to create ferromagnetics on the basis of *s* and *p* electrons. Experiment shows that alkali and alkaline earth metals, in the atoms of which the spin is due to the outer *s* or *p* electrons, are non-magnetic. Organic radicals with outer *p* electrons also lose their paramagnetism at low temperatures and become non-magnetic. Solid oxygen is diamagnetic, although the oxygen molecule is paramagnetic. These phenomena have a common cause: for all the atoms with *d* and *f* electrons, the exchange interaction (i.e. that part of the Coulombic, electrostatic interaction of electrons which depends on their spin) is positive and arranges the electron spins on the neighbouring atoms in parallel (in a ferromagnetic manner); for atoms with *s* and *p* electrons, the interatomic (or intermolecular) exchange interaction is negative and gives rise to an antiparallel arrangement of the electron spins on the neighbouring atoms or molecules (in an antiferromagnetic manner).

The problem of "organic" ferromagnetism is how to obviate this difficulty and how to find ways and procedures whereby a ferromagnetic arrangement of electrons in organic paramagnetic molecules, i.e. in molecules with *s* or *p* unpaired electrons, can be achieved. An organic ferromagnetic is understood to be a magnetic material made up of purely organic paramagnetic molecules; this is a special albeit important case of a molecular ferromagnetic in which paramagnetic molecules may contain metal atoms (for example, organometallic molecules).

In order to create an organic or molecular ferromagnetic, two main conditions are essential. Firstly, a building material is needed, namely organic multispin paramagnetic molecules (high-spin molecules are best) with a high density of oriented spins in order to ensure an appreciable magnetisation. Secondly, a procedure is needed (and this is the main problem) for organising these molecules in the crystal or in an amorphous body in such a way that a ferromagnetic arrangement of the spins is achieved.

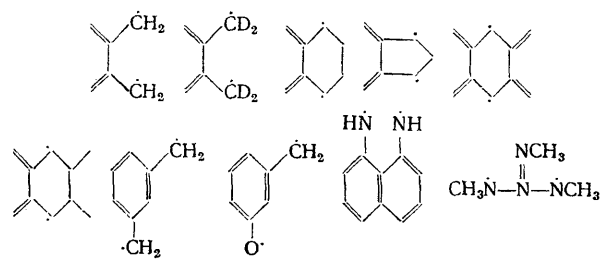
II. Multispin and high-spin molecules

The construction of high-spin molecules is the first part of the problem and here most progress has been achieved. Independently of organic ferromagnetics and long before their appearance, major advances were made in the chemistry and physics of stable organic radicals and an enormous number of such radicals with a wide variety of structures belonging to various chemical classes were synthesised.[1] Many stable biradicals were created on their basis, most of them being of the low-spin type ($S = 0$, singlet ground state). However, among them there are many high-spin species ($S = 1$, triplet ground state), for example:



as well as certain bisphenoxyls, bisverdazyls, etc. (for further details, see Buchachenko and Vasserman[1]).

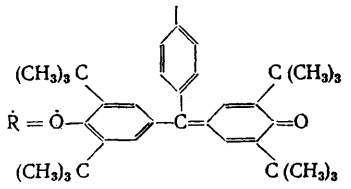
In connection with organoferromagnetics, interest in these biradicals was revived from new standpoints: the question arose how the unpaired electrons within the molecule interact, under what conditions is their exchange interaction positive and arranges the spin in a ferromagnetic manner (triplet ground state), and when is it negative (zero overall spin, singlet ground state). Many simplest biradicals of the type



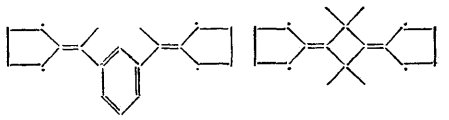
were synthesised (they were obtained at low temperatures mainly by the photolysis of the corresponding azo-compounds and other precursors). It has been demonstrated convincingly (by EPR) that

they all have the spin $S = 1$ and a triplet ground state and that the dipole interaction of their electrons amounts to $D \simeq 0.01-0.03$ cm^{-1}.[2,3] We may note that it has been frequently predicted quantum-chemically that these biradicals have singlet ground states and the idea actually arose that Hund's rule breaks down for such π-conjugated non-Kekulé structures. However, experiment confirmed the presence of the triplet state—in agreement with the simplest valence bond scheme.

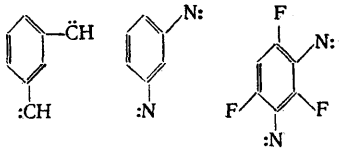
High-spin molecules based on polyradicals, carbenes, and polycarbenes are also known. For example, the stable tetraphenoxyl $C\dot{R}_4$, i.e.



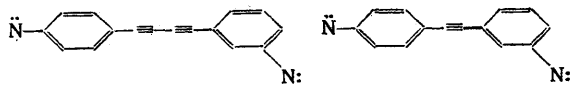
has a quintet ground state ($S = 2$, exchange interaction with $J \simeq 600$ MHz);[4] the tetraradicals



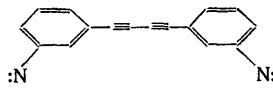
also have a quintet ground state ($S = 2$).[5] In the bicarbenes and binitrenes



the exchange interaction of the electrons is positive and stabilises the high-spin (quintet) state.[3] In binitrenes, compounds with acetylenic and diacetylenic bridges of the *para—meta* type (one nitrogen atom is in the *para*-position and the other is in the *meta*-position relative to the substituent), i.e.

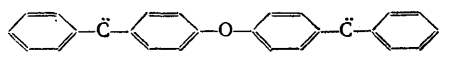


the high-spin state with $S = 2$ is also stabilised, but if the combination of the nitrenes is of the *meta—meta* type, i.e.

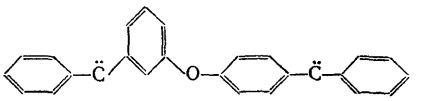


the low-spin singlet state (with $S = 0$) is stabilised.[6] (One can predict that a compound of the *para—para* type will also stabilise the singlet state.)

By combining carbene systems, it is likewise possible to obtain both high-spin and low-spin molecules. Thus the combination of two diphenylcarbenes (each of these fragments is in a high-spin triplet state) of the *para—para* type, i.e.



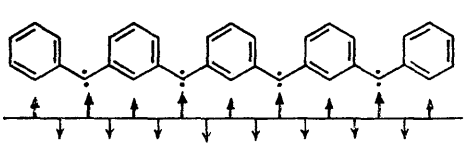
stabilises the low-spin singlet state ($S = 0$), i.e. the exchange interaction of the electrons arranges the electron spins within the molecule in an antiferromagnetic manner. A combination of the *meta—meta* type stabilises the low-spin state, but a combination of the *meta—para* type, i.e.



stabilises the high-spin ($S = 2$) quintet state of this dicarbene.[7]

We shall now turn to the problem when and under what conditions and in what systems is the exchange interaction positive and stabilises the high-spin electronic state of the molecule and when is it negative and even a molecule with a large number of unpaired electrons is in a low-spin state; in the former case, a ferromagnetic arrangement of all the spins in the molecule takes place, while in the latter case an antiferromagnetic arrangement obtains. It would seem that it is possible to count on an exact answer from the rigorous quantum chemistry of the molecule, but theory frequently falls out of step (we have seen an example above), the reason being that spin molecules are systems with open shells for which an exact calculation is unreliable (particularly when one is dealing with small differences between the energies of spin states). There is, however, a simple way of predicting the sign of the exchange interaction and the spin state based on a simple valence bond scheme and on the ideas of spin delocalisation and spin polarisation; as a result of delocalisation, the spin is distributed throughout the molecule and spin polarisation induces a negative spin density at certain points within the molecule, i.e. the local spin at these points is oriented against the total spin. (An example is provided by the allyl radical $\dot{C}H_2 - CH = CH_2$ in which the spin is distributed on the terminal carbon atoms and its density is positive—~0.45 on each; however, on the central atom the spin polarisation induces a negative spin density of about −0.01.) If the spin densities of both electrons in a two-spin system (for example in a π-electron biradical) alternate rigorously as regards sign (in other words, the two spins are separated by a negative spin density), a triplet state obtains, but if the distribution of spins in the molecule results in the appearance of direct spin contacts (i.e. there are no regions of negative spin density between them), the low-spin state is stabilised.

We shall demonstrate this rule in relation to the polycarbene synthesised by Iwamura and co-workers:[8,9]

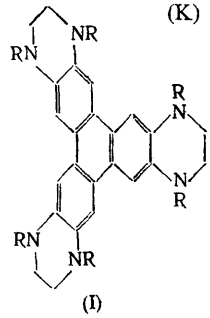


Five phenyl rings are linked by carbene fragments at the *meta*-positions. The signs of the spin densities are indicated below: the bold arrows denote positively oriented spins and the thin arrows denote negatively oriented spins. Evidently the signs of the local spins alternate rigorously: the contacts between positive spins are formed solely via atoms with negative spins. Clearly a high-spin state of this carbene should be achieved. Indeed the spin of this molecule is $S = 4$ and the ground state has the nonet multiplicity ($2S + 1 = 9$)[8] and all 8 unpaired electrons are arranged in a ferromagnetic manner.

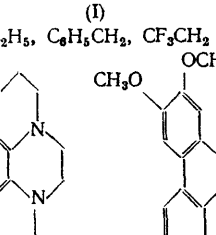
Using this rule, it is easy to demonstrate that the binitrenes or bicarbenes discussed above are high-spin species when they are combined via a *meta—para* junction but are low-spin species if the

combination of the nitrene or carbene groups is of the *meta—meta* or *para—para* type. These predictions agree with experiment. It is easy to extend these rules to any case of polyconjugated multispin systems and to predict when the multispin system will be in a high-spin state and when it will be in a low-spin state. In other words, it is possible to show when the multispin molecule will be "ferromagnetic" and when it will be antiferromagnetic (strictly speaking these concepts are macroscopic and refer to a crystal or an amorphous body, but we shall sometimes apply them also to molecules). These features and rules are useful in predicting the synthesis of high-spin molecules as potential precursors of organic ferromagnetics.

Among the high-spin molecules, charged species are known. Thus the cyclopentadienyl and pentachlorocyclodienyl cations are triplet species,[10,11] although their stability is low. On the other hand, the pentaphenylcyclopentadienyl cation has a singlet ground state.[12] Interest in organic ferromagnetics has stimulated the search for and the synthesis of stable high-spin cations. The hexachlorobenzene cation is known to be in a triplet state but is unstable.[13] Breslow and co-workers[14,15] synthesised aromatic hexazo-molecules of the type

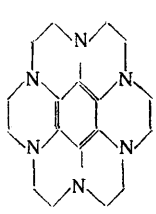


(K)

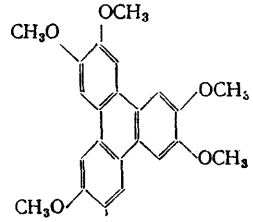


(I)

R=C_2H_5, $C_6H_5CH_2$, CF_3CH_2 etc.

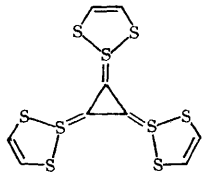


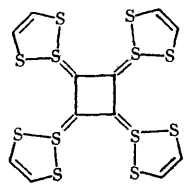
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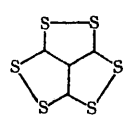


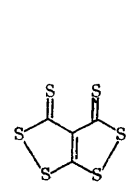
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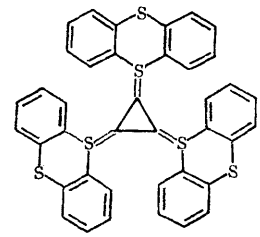
whose dications are stable triplet species. Compound (I, R = C_2H_5) has been designated[14,15] by the abbreviation HET (hexaethyltriphenylene) and compound (II) has been designated by HOC (we shall make use of these abbreviations below). Chiang et al.[16] synthesised hexamethoxytriphenylene (HMT) (III), whose dication is also a stable triplet species. Readily oxidised sulphur-containing molecules of the type





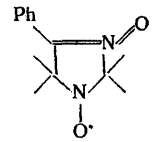






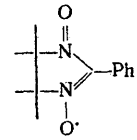
have been synthesised and it is expected (and the first confirmations have already been obtained) that their dications are high-spin triplet species, which may be suitable for the creation of organic ferromagnetics.[17,18]

Mixed organometallic high-spin complexes have already been synthesised. Thus in the complex $3Cu(hfacac)_2.2L$, where hfacac = perfluorinated acetylacetonate and L = nitroxyl, with two complex-forming groups, i.e.



the exchange interaction of the electrons of the metal ion and the ligand is positive (~ 12 cm^{-1}) and stabilises the high-spin state of the complex.[19]

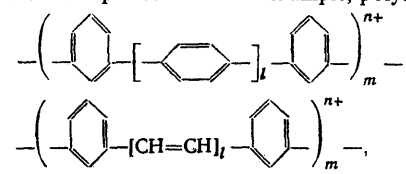
In the complex of the nitroxyl radical



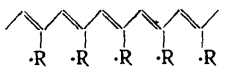
with $Mn(hfacac)_2$, six Mn^{2+} ions and six ligand radicals form a ring with ferromagnetic intramolecular interaction of all the unpaired electrons; it stabilises the high-spin state of the complex with the total spin $S = 6(5/2) + 6(1/2) = 18$.[20,21] In the complex $[Cr_4S(O_2CCH_3)_8(H_2O)_4]_2.H_2O$, the Cr_4S cluster has a spin $S = 6$ in the ground state.[22] In the complexes $Mn_{12}O_{12}(O_2CCPh)_{16}(H_2O)_4$ and $Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4$, the cluster nucleus contains the Mn_4^{4+} and Mn_8^{3+} ions with a positive exchange interaction, which stabilises the high-spin state of the cluster with a spin $S = 14$.[23]

Finally, macromolecules (linear or two-dimensional networks) with a high density of paramagnetic centres are multispin species with the largest number of spins. Spin-labelled polymers with a high concentration of paramagnetic labels—nitroxyl and verdazyl radicals (in the limit one paramagnetic fragment per monomer unit)—have been synthesised. These polymers and their magnetic properties are described below in Section V; organometallic multispin macromolecules and the magnetic properties of the corresponding polymers are discussed in Section VI.

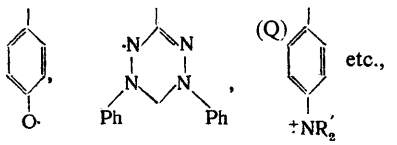
For the purpose of synthesis, hypothetical structures have been proposed for linear multispin molecules in which a "ferromagnetic" exchange interaction of the spins and the stabilisation of the high-spin state are expected.[24–26] For example, polycations of the type



in which the blocks comprising poly-*p*-phenylenes or polyenes are joined via phenyl rings, should be high-spin species. The polyene macromolecules



where R are the radical fragments



should also be ferromagnetic (according to the predictions formulated above). On the basis of the same principle, it is possible to suggest a series of other "ferromagnetic" macromolecules for synthesis.

Mataga[27] was the first to propose the hypothetical structures of high-spin planar two-dimensional hydrocarbons made up of triplet diphenylcarbenes combined into a single conjugated system via the *meta*-positions in the phenyl rings (actually the polycarbene with a spin $S = 4$, examined above, is a fragment of such a structure and has been synthesised in accordance with Mataga's principle). Another two-dimensional structure, which he also proposed, is based on the triphenylmethyl radical as the main structural element; the interaction of unpaired electrons is effected via the *meta*-positions in the phenyl rings. Mataga regarded both systems as potential precursors of organic ferromagnetics.[27]

A number of interesting linear and two-dimensional conjugated systems have been proposed by Ovchinnikov;[24] they include a hypothetical boron-substituted graphite—a high-spin system which is a possible precursor of a ferromagnetic. The same worker proposed a general theory and formulated a simple rule which permits the prediction of the spin of such polyconjugated high-spin molecules. The experimental data concerning the construction of organic ferromagnetic polymers on the basis of multispin molecules will be examined below (see Section V).

III. The ideas and theoretical foundations of "organic" ferromagnetism

In organic spin molecules, the unpaired electrons populate the highest of the occupied molecular orbitals and are localised on the "surface" of electron shells. The exchange intermolecular interaction of unpaired electrons is therefore negative and antiferromagnetic, orienting the spins of neighbouring, even high-spin molecules in opposition to one another. The key problem in "organic" ferromagnetism is how to overcome this difficulty; the attainment of ferromagnetism through antiferromagnetic interactions—this is the paradoxical formulation of the problem.

Several ideas for the resolution of this paradox have been proposed and we shall now consider them. The first was formulated as early as 1963 by McConnel.[28]

As we have already seen above, two mechanisms are significant in the propagation of the spin in the molecule—spin delocalisation and spin polarisation. The interplay of these mechanisms make the distribution of the unpaired electrons in a spin molecule non-uniform not only in magnitude but also as regards sign: at certain points within the molecule, the spin density is negative, i.e. a local (partial) spin is oriented in opposition to the total spin of the unpaired electron. The regions of positive spin density in the molecule frequently alternate with regions of negative spin density. Suppose that in a crystal or glass the spin molecules can be organised in a remarkable manner such that the regions of positive spin density of one molecule are in contact with the regions of negative spin density of another and this order is retained throughout the given volume. It is readily seen that in such a system the negative intermolecular (interspin) exchange generates two spin subsystems: positive spin densities oriented on one side and negative spin densities oriented on the opposite side (as in a ferromagnetic). However, the positive spin densities are much greater than the negative spin densities and the overall spin corresponds to a ferromagnetic arrangement, the substance becoming an organic ferromagnetic.

We shall refer to this route to ferromagnetics as the McConnell mechanism and the regions of intermolecular contact in which the positive spin densities of one molecule are combined with the negative spin densities of another will be referred to as the McConnell islands. There is direct evidence for this mechanism—both theoretical and experimental. A calculation has been carried out for the allyl + methyl radical pair in terms of the geometry illustrated in Fig. 1.[29] In case *a*, the methyl radical approaches one of the terminal carbon atoms of the allyl radical (the π-electron spin density on these atoms is positive and amounts to ~0.49 on each), while in case *b* the methyl radical approaches the central atom (the spin density on this atom is negative, amounting to −0.01). The McConnell island arises only in case *b*—this is the region where the positive spin density of the methyl radical is in contact with the negative density of the central atom of the allyl radical.

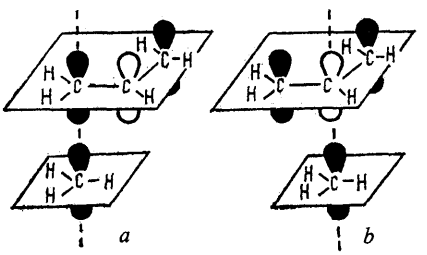


Figure 1. Schematic illustration of the disposition of the partners in the allyl + methyl radical pair: (*a*) the methyl group approaches the terminal carbon atom of the allyl group, where the spin density is positive; (*b*) the methyl group approaches the central atom of the allyl group with a negative spin density.[29]

Fig. 2 presents the dependence of the exchange interaction on the distance between the radicals. In case *a*, the exchange interaction is negative, there is a singlet ground state, and the orientation of the spins in the pair is antiferromagnetic. In case *b* (where there is a McConnell island), the exchange interaction is positive and stabilises the high-spin triplet state, while the orientation of the spins in the pair corresponds to ferromagnetism. The simplicity of the system for which the calculation has been made and the identity of the approximations used in the calculations in both versions, *a* and *b*, as well as the independence of the principal results of the method of calculation ensure the reliability of the result.

Another piece of evidence is experimental.[30]

Substituents (triplet phenylcarbenes) were introduced into the phenyl rings of paracyclophanes fixed in space by chemical—CH_2CH_2—bridges in different positions within the ring: pseudo-*ortho*- (Fig. 3*a*), pseudo-*meta*- (Fig. 3*b*), and pseudo-*para*- (Fig. 3*c*). It is readily seen that, when the unpaired π-electron migrates from the carbene to the phenyl ring of the cyclophane, the distribution of its spin density in the pseudo-*ortho*- and pseudo-*para*-structures creates McConnell islands—spin densities of one sign in one phenyl ring of cyclophane are located opposite the spin densities of the reverse sign in another ring. In the pseudo-*meta*-structure, there are no McConnell islands—spin densities of the same sign are in contact. In exact correspondence to this property, the arrangement of spins in the pseudo-*ortho*- and pseudo-*para*-structures is ferromagnetic (quintet ground state, $S = 2$), while in the pseudo-*meta*-structure it is antiferromagnetic (singlet ground state). These results were also reproduced for cyclophanes whose phenyl rings are fixed in space by—$CH_2CH_2CH_2$—bridges.[6]

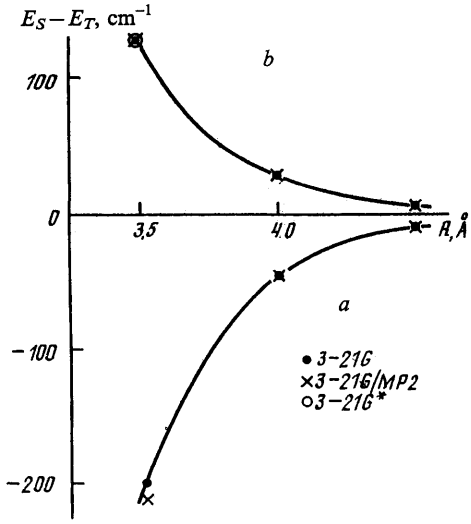


Figure 2. The exchange interaction (singlet–triplet splitting) in the allyl + methyl radical pair as a function of the distance R between the partners for the two types of their mutual approach (*a* and *b*). Circles—results of the calculation in terms of three different approximations; continuous lines—their exponential representations.[29]

These two simple and elegant proofs reliably justify the McConnell mechanism of the route to organic ferromagnetics.

The second idea was also put forward by McConnell in 1967[31] and referred to the possible ferromagnetism of a special class of compounds—the radical-ion salts of the type ...$D^+A^-D^+A^-D^+A^-$... constructed as quasi-one-dimensional spin chains of the donor radical-cations D^+ alternating rigorously with the acceptor radical-anions A^-. It was suggested that virtual excited states of the D^+A^- pair may exist, stabilising its high-spin triplet state and ensuring a ferromagnetic arrangement of the spins in the quasi-one-dimensional chain. An admixture of such excited states can arise as a result of the virtual forward charge transfer ($D^+ + A^- \rightarrow D^{2+} + A^{2-}$), the reverse charge transfer ($D^+ + A^- \rightarrow D^0 + A^0$), or a disproportionating charge transfer ($D^+ + D^+ \rightarrow D^{2+} + D^0$). If any one of the charge transfer states (D^{2+}, D^0, or A^{2-}, A^0) is singlet, the singlet spin state of the D^+A^- pair, to which corresponds an antiferromagnetic arrangement of the spins in the chain, is established. If even one of the species D^{2+}, D^0 or A^{2-}, A^0 is a high-spin triplet molecule (and this is its ground state), then the virtual charge transfer will stabilise the high-spin state of the D^+A^- pair and will give rise to a ferromagnetic arrangement of the spin chain.

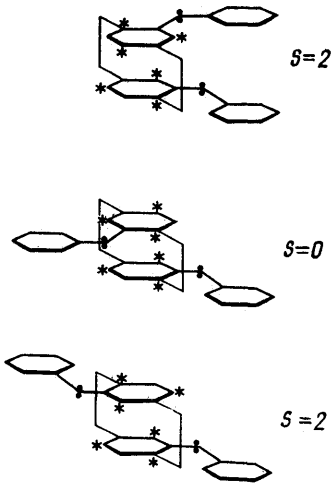


Figure 3. The structures of paracyclophane dicarbenes—pseudo-*ortho* ($S = 2$), pseudo-*meta* ($S = 0$), and pseudo-*para* ($S = 2$).[30]

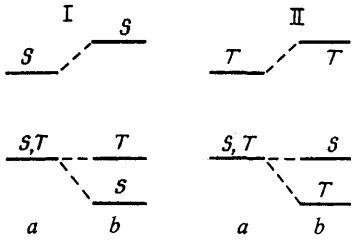


Figure 4. The energy levels of the D^+A^- pair without taking into account the virtual charge transfer (*a*) and the change in the energy levels when account is taken of the virtual charge transfer (*b*). Case I corresponds to the stabilisation of the singlet state of the pair and case II corresponds to the stabilisation of the triplet state.

The energy level schemes for these versions are illustrated in Fig. 4. The normal state of the D^+A^- pair is degenerate (the difference between the energies of the singlet S and the triplet T may be neglected), but the virtual charge transfer in the excited state of

the pair reduces the energy of the singlet (if the transfer takes place with participation of the singlet state of one of the D^{2+}, A^{2-}, D^0, and A^0 species) and of the triplet (if even one of the D^{2+}, A^{2-}, D^0, and A^0 species has a high-spin triplet ground state). The schemes in Figs. 4*a* and 4*b* correspond to the first and second versions respectively. The reduction of energy as a result of the admixture of the excited state of the pair (virtual charge transfer) can be estimated in terms of the perturbation theory; it is a quantity of the order of magnitude of $t^2/\Delta E$, where ΔE is the excitation energy of the pair and t is the charge transfer integral.

This simple idea was specified in detail by Torrance et al.,[32] was expanded by Breslow and Le Page,[15] and was generalised by Miller and Epstein.[33]

In order to generate ferromagnetism by means of this mechanism, it is necessary that one of the partners (but not both) should have a degenerate and partly occupied molecular orbital; an appreciable charge transfer is needed, i.e. an appreciable admixture of the excited state of the D^+A^- pair, in order to stabilise its ferromagnetic and antiferromagnetic states; the molecules must be highly symmetrical without any structural or electronic defects (of the type of the Jahn–Teller effect), which remove the degeneracy already in the ground state.

There is no direct evidence for this mechanism of the generation of ferromagnetism, although most of the studies (both experimental and theoretical) have been devoted to the development of precisely this field. Highly symmetrical molecules, producing excellent readily crystallisable radical-ion salts, have been specially synthesised in conformity with this mechanism; furthermore, among them are there also those which produce doubly charged high-spin cations ideally corresponding to the conditions for charge transfer and the stabilisation of the ferromagnetic state [of the type $(HET)^{2+}$ and $(HOC)^{2+}$; see Section II]. However, ferromagnetics were never obtained (with the exception of metallocene salts—this will be discussed later in Section IV). Here one should recall that, regardless of the search for ferromagnetism, an enormous number of radical-ion salts (including organic superconductors) are known, but they all become antiferromagnetic at low temperatures (like other organic paramagnetic materials). One-dimensional spin chains are known to be unstable in such salts (Peierls instability): the chain breaks up into pairs with a strong interaction within the pair and a weak interaction between the pairs. This suppresses the virtual charge transfer (and yet ferromagnetism requires a collective charge transfer throughout the sequence of ions in the chain, since otherwise a complete arrangement of all the spins is not achieved). The Peierls instability is in fact the cause of the conversion of highly conducting radical-ion supports (organic metals) into dielectrics and can prevent the possible transition of the chain to the ferromagnetic state. Incidentally, the theory of spin waves in radical-ion chains has been thoroughly developed and predicts the antiferromagnetism of these chains (in agreement with experiment).

The third idea[34] is the cocrystallisation of low-spin and high-spin molecules (for example monoradicals and biradicals with spins of 1/2 and 1). If their chemical structures are almost identical, one may expect a regular alternation of the two types of molecules in the crystal. Negative intermolecular exchange arranges the spins of neighbouring species in opposition and generates two spin sublattices: the spins of molecules of one kind are oriented in one direction and those of molecules of the other kind are oriented in the opposite direction. The overall ferrimagnetic arrangement of the spins is illustrated schematically in the two-dimensional version in Fig. 5. This idea was confirmed experimentally in relation to organic metallic polymers (see Section VI); it gives rise to a simple route to the ferromagnetic arrangement of multispin molecules (at any rate it is now not more complex than the arrangement of the McConnell islands).

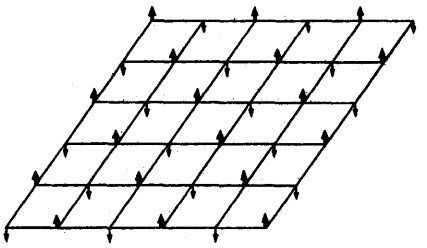


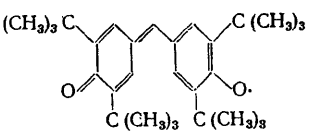
Figure 5. Two-dimensional ferrimagnetic spin lattice.

We shall now proceed to the analysis of experimental studies carried out in connection with the search for organic ferromagnetics.

IV. Molecular crystals

The magnetic properties of stable organic radicals of different classes and their relation with the structure of the crystals have been described systematically and surveyed.[35] Their common property is paramagnetism which obeys the Curie–Weiss temperature law with a negative Curie–Weiss point corresponding to the antiferromagnetic interaction of the spins. Indeed, at low temperatures the crystalline radicals become antiferromagnetics. Compression of the crystals does not alter the negative sign of the exchange interaction and merely enhances the antiferromagnetism, shifting the Curie–Weiss point to higher temperatures.[36]

There are several exceptions to this general rule, among which only two are trustworthy. This concerns a phenoxyl radical (the galvinoxyl) radical, i.e.



and its deuterio-analogue (the central CH group has been replaced by the CD group).[37,38] The high-temperature crystalline phase of the galvinoxyl ($T \geqslant 85$ K) is paramagnetic but shows signs of ferromagnetism (a positive Curie–Weiss temperature of 19 K).[38] Below 85 K, there is a phase transition and there is a new low-temperature phase, this time antiferromagnetic. In mixed crystals with the added phenolic precursor of galvinoxyl (its crystallisation is of the same type as that of its radical), the phase transition is suppressed and the higher the content of the phenol in the crystal the lower the temperature at which the high-temperature ferromagnetic phase is retained.[39–41]

In mixed crystals of galvinoxyl with its phenol, direct evidence was also obtained for the ferromagnetic interaction between the radicals in the high-temperature ferromagnetic phase. For high

dilutions with the phenol [low (1–10%) contents of the radical], EPR signals characteristic of triplet states (including forbidden transitions at $g = 4$) were observed in the mixed crystals.[41] It follows from the temperature variation of the intensity of these signals that there is a triplet ground state and the latter was referred to a radical pair with a positive, ferromagnetic interaction of the spins $J \simeq 1.5 \pm 0.7$ meV (approximately 30 cal mol^{-1}).

For high contents of the radical in the mixed crystals, triplets, quadruplets, etc., i.e. radical clusters, appear together with the isolated radical pairs. There is of course a distribution with respect to the sizes of these clusters, which is generated in the lattice by the insertion of phenol molecules between the radicals. It has actually been possible to estimate the sizes of the clusters.[41] Thus in a mixed crystal with ~20% of phenol the dependence of the magnetisation $M(H)$ on the magnetic field is described satisfactorily by the Brillouin function $B_J(x)$:

$$M(H) = M_S B_J(x), \text{ where } x = Jg\mu_B H/kT,$$

whence it was found that the average size of the ferromagnetic cluster corresponds to six radicals; its spin is $S = 3$ and it has a septet ground state ($2S + 1 = 7$).[40]

Thus the high-temperature phase of galvinoxyl is ferromagnetic not only as regards macroscopic features (positive Curie–Weiss temperature) but also as regards molecular features: the exchange interaction in the radical pairs and in the radical clusters is also positive and ferromagnetic, stabilising the high-spin states of the pairs and clusters. This means that the high-temperature phase of galvinoxyl can be regarded as the first organic ferromagnetic.

The low-temperature phase of this radical is antiferromagnetic—this follows also from the negative Curie–Weiss temperature and from EPR data. EPR signals corresponding to triplet states were also found in this phase, but it follows from the temperature variation of their intensity that these triplets are thermally excited and that there is a low-spin singlet ground state corresponding to the antiferromagnetism of this phase. The exchange interaction of the radicals in the antiferromagnetic phase is fairly intense (about 45 meV).[41]

The question arises of the cause of the anomalous ferromagnetism of galvinoxyl among radicals. The crystal structure of its high-temperature ferromagnetic phase is illustrated in Fig. 6.[42] The lattice is monoclinic and there are four molecules in the unit cell. The planar molecules are arranged in layers; one-dimensional chains of radicals are formed along the c axis of the crystal. They are "skewed" in such a way that opposite the –CH= groups of one radical there are the phenyl rings and oxygen atoms of another radical at a very short distance. In other words, the regions with negative spin density (in galvinoxyl, this is the –CH= group) are in contact with regions where the spin density is predominantly positive (oxygen atoms and phenyl rings). These are McConnell islands and are apparently the cause of the ferromagnetic arrangement of the spins[43] in the high-temperature phase of galvinoxyl.

Naturally, this is only a hypothesis, but it is difficult to find an alternative. It will be extremely important to establish the crystal structure of the low-temperature, antiferromagnetic phase of galvinoxyl. If it is such that there are no McConnell islands, this will be evidence in support of the proposed explanation of the ferromagnetism and even in support of the entire concept of McConnell islands.

We shall now deal with the search for other molecular ferromagnetics. As already mentioned (see Section II), polycarbene has a high-spin molecule but the hopes that after the accumulation of such molecules at sufficient concentrations signs of a ferromagnetic behaviour of the system would appear proved vain.[7]

When polycarbenes were generated in frozen glasses, in a host (benzophenone) single crystal in which the molecules of polyazide (a precursor of polycarbene) were incorporated, and also in polyazide crystals, the accumulation of polycarbenes was always accompanied by the appearance of signs of antiferromagnetic behavoiur (negative Curie–Weiss temperature.[8] This means that the intermolecular exchange interaction of even the high-spin molecules is antiferromagnetic (as in solid oxygen).

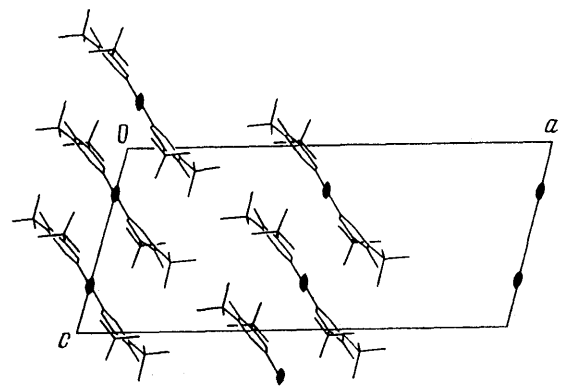


Figure 6. The crystal lattice of galvinoxyl.[42]

As already mentioned above, the search is directed principally towards the synthesis of radical-ion salts in which the conditions for the virtual charge transfer, stabilising the ferromagnetic arrangement of the spins, are achieved (see Section III). Among the large number of such salts of the type $D^{+\cdot}A^{-}$, where the donor D consists of HOC, HET, and HME molecules (see Section II), while the acceptor A consists of TCNQ, TCNE, $TCNQF_4$, and hexacyanotrimethylenecyclopropane molecules, no signs of ferromagnetism were observed; on the contrary, all the salts were clearly antiferromagnetic.[15,16,32] However, all the conditions satisfying McConnell's second idea are in fact brilliantly fulfilled in precisely these salts—they crystallise as ideally ordered alternating chains of cations and anions and the virtual charge transfer $D^{+\cdot} + A^{-\cdot} \rightarrow D^{2+} + A^{2-}$ gives rise to the doubly charged cation D^{2+} in the triplet, high-spin state (see Section II) and it should therefore stabilise the ferromagnetic state of these salts. Thus the idea of the virtual charge transfer as a means of ensuring the ferromagnetism of radical-ion salts has not so far been justified.

A remarkable exception to this series of failures is certain radical-ion salts of the decamethylferrocenium radical-cation $[Fe(C_5Me_5)_2]^{+\cdot}$ with the radical-anions $(TCNE)^{-\cdot}$, $(TCNQ)^{-\cdot}$, and $[C_4(CN)_6]^{-\cdot}$. They have been synthesised and investigated by Miller, Epstein, Reiff, and co-workers[44–49] and although they contain an iron atom, they should be regarded as true molecular ferromagnetics because their ferromagnetism is associated with the unpaired electron in the highest occupied molecular orbitals of the ferrocenium ion.

The above ferrocenium salts form ideal one-dimensional spin chains of alternating cations and anions. The ferromagnetic properties are manifested most strikingly by the salt

$[Fe(C_5Me_5)_2]^+(TCNE)^-$: the Curie–Weiss temperature is 30 K, the saturation magnetisation of the polycrystalline material at 2 K in magnetic fields $H > 300$ Oe is 11000 e.m.u. mol^{-1} (this is comparable to the magnetisation of metallic iron under normal conditions), and sextets characteristic of a ferromagnetic appear in the ^{57}Fe Mössbauer spectra near 9 K.[45] Spontaneous magnetisation ($m \simeq 2000$ e.m.u. mol^{-1}) appears in a zero magnetic field at $T < 4.5$ K. In a single crystal, when the magnetic field is oriented along the axis of the one-dimensional arrangement of cations and anions, the saturation magnetisation is 16000 e.m.u. mol^{-1}; this is greater by 36% than for metallic iron (when calculated per atom) and agrees with the theoretical magnetic saturation moment in the ferromagnetic arrangement of the spins of the cation ($S = 1/2$, $g = 4$) and the anion ($S = 1.2$, $g = 2$). There is also a hysteresis loop with a coercive force of 30 Oe at 4.2 K and 1000 Oe at 2.0 K.[47]

It follows from the temperature variation of the magnetic susceptibility χ, the magnetisation M, and the field dependence $M(H)$ that above 16 K the magnetic properties are best described by the one-dimensional Heisenberg exchange model with $J = 19$ cm^{-1}, while at $T < 16$ K the substance is closer to a three-dimensional ferromagnetic.

The magnetisation of the salt $[Fe(C_5Me_5)_2]^+(TCNQ)^-$ in fields $H < 1.6$ kOe is characteristic of an antiferromagnetic, but for $H > 1.6$ kOe it increases abruptly and rapidly attains saturation, which is characteristic of a ferromagnetic. This is a feature of a metamagnetic—a layered magnetic (of the type of $FeCl_2$) in which the intensity of the exchange interaction within the layer exceeds that of the exchange interaction between the layers. A number of inorganic metamagnetics are known but among organic substances this is the first example.

The creators of this class of organic ferromagnetics explain the origin of their ferromagnetism within the framework of the hypothesis of the virtual charge transfer (McConnell's second idea), although the first idea is in this instant much more reasonable.[43]

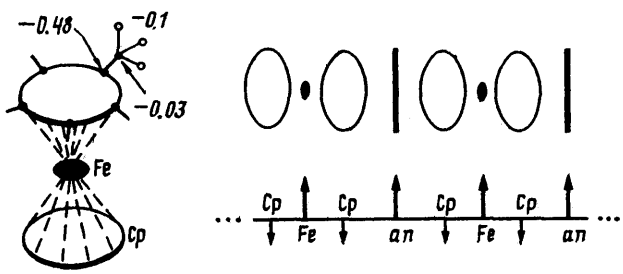
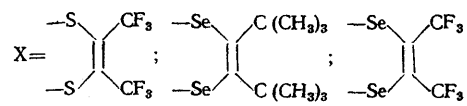


Figure 7. Schematic illustration of the spin distribution in the ferrocenium cation (on the left) and the arrangement of spins in a one-dimensional chain of a ferrocenium salt (on the right). Fe = iron atom; Cp = cyclopentadienyl ring; an = anion. The numerals denote the $^{13}C-H$ hyperfine interaction constants (in gauss).[50]

Fig. 7 illustrates schematically the arrangement of the radical-cations $[Fe(C_5Me_5)_2]^+$ and the radical-anions $(TCNQ)^-$ in a regular one-dimensional chain and, also schematically, the spin distribution in the radical-cation known from the contact paramagnetic NMR shifts for this radical-cation.[50] The π-electron spin density in the ring of the radical-cation is positive, while on the methyl groups along the perimeter of the ring the spin density is negative. McConnell islands can exist between the methyl groups of the ring of the radical-cation (negative spin density) and the CN groups of the radical-anion on which a positive spin density is localised. The McConnell islands are responsible for the alternating arrangement of the positive and negative spin densities illustrated in Fig. 7 and leading to the ferromagnetic arrangement of the spins and to ferromagnetism.

Within the framework of this concept, it is possible to explain the change in magnetic properties when the radical-anion or the metal ion is replaced in radical-ion salts of this type. Thus the salt $[Fe(C_5Me_5)_2]^+[C_4(CN)_6]^-$ is ferromagnetic, while the salt $[Fe(C_5H_5)_2]^+[C_4(CN)_6]^-$ is merely paramagnetic and shows no signs of ferromagnetic properties. It is known that the signs of the spin densities in the ligands C_5H_5 and C_5Me_5 are different and the replacement of the C_5Me_5 ligand by C_5H_5 therefore breaks up the McConnell islands, which entails the disappearance of ferromagnetism. The replacement of the $[C_4(CN)_6]^-$ paramagnetic radical-anion in the salts by the diamagnetic $[C_3(CN)_5]^-$ anion or of the paramagnetic radical-cation $[Fe(C_5Me_5)_2]^+$ by the diamagnetic cation $[Co(C_5Me_5)_2]^+$ also abolishes the McConnell islands and the substituted salts do not therefore show signs of ferromagnetism. In contrast to the ferromagnetic salt $[Fe(C_5Me_5)_2]^+[C_4(CN)_6]^-$, the salt $[Ni(C_5Me_5)_2]^+[C_4(CN)_6]^-$ is antiferromagnetic; the cause is similar because the signs of the spin densities in the C_5Me_5 ligand at the Fe and Ni ions are different (this is known from NMR[51]) and there are therefore no McConnell islands and no ferromagnetism in the nickel salt. We may note that all these substitutions should not affect the ferromagnetism if its origin were associated with the virtual charge transfer.

The first discoveries of molecular ferromagnetics among ferrocenium salts stimulated an extensive search for analogues. Thus radical-ion salts in which the anion is provided by the complex salt NiX_2, where

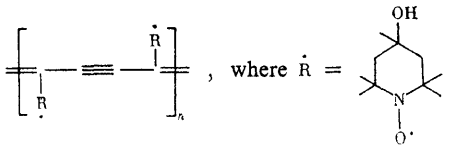


have been synthesised on the basis of $Fe(C_5Me_5)_2$. These molecules are packed in crystals in stacks with a remarkable two-dimensional architecture and the Curie–Weiss temperature is positive (about 1 K), which indicates weak signs of ferromagnetism but explicit ferromagnetics have not so far been found among these substances.[52]

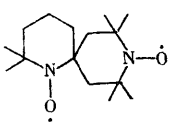
V. Organic polymers

Ovchinnikov and co-workers[53,54] achieved impressive results in the preparation of ferromagnetic organic polymers. The thermal or photochemical polymerisation of the spin-labelled diacetylene $\dot{R}-C\equiv C-C\equiv C-\dot{R}$, where $\dot{R}$ is a nitroxyl radical, yielded a polymer in which 0.1–0.3% of the overall mass consisted of particles which could be separated magnetically and whose magnetisation reached ~ 1 G g^{-1}. The Curie point is 420–460 K and sometimes higher, i.e. the ferromagnetism persists up to anomalously high temperatures adjoining the limiting temperature of the chemical stability of the polymer. The crystal structure of the

initial diacetylene[55] prevents its topochemical polymerisation, typical for the majority of diacetylenes. However, one can assume that oligomeric blocks of the type



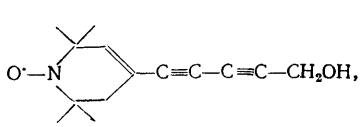
exist in the polymer. The two spin systems—one belongs to the principal polyene chain (in which the concentration of unpaired electrons is as usual high) and the other belongs to nitroxyl fragments—are independent, i.e. the exchange interaction between them is negligible. This follows from the fact that even in the initial monomer the paramagnetic fragments are independent (the EPR spectrum of the biradical consists of a triplet and is typical of a nitroxyl monoradical) and there is no exchange between the unpaired electrons through the π-system. Even in a biradical with the paramagnetic centres in close proximity, i.e.



the exchange energy is $J \ll 15$ Oe (i.e. $J \ll a$, where a represents the hyperfine electron–nuclear interaction involving the ^{14}N nucleus).[1] The low value of J is due to the barrier set up by the σ-bonds which separate the two π-electron systems.

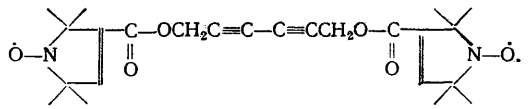
The very weak exchange interaction of the two spin systems ($J \lesssim 10^{-7}$ eV) is inconsistent with the high-temperature ferromagnetism of the polymer (there is an energy deficiency by 7–8 orders of magnitude), which means that it is not the cause of the ferromagnetism. It may be that McConnell islands are present in the structure of Ovchinnikov's ferromagnetic polymer, but it would then be necessary to assume that structures with such islands are very rigid, are not disrupted by molecular motion, and persist even at 450–500 K, where the polymer itself already undergoes chemical degradation. This is naturally a large claim for which there is no proof. At any rate, the origin of the ferromagnetism of the spin-labelled polydiacetylene remains puzzling. The structure of the polymer is just as puzzling: it is insoluble and amorphous and the type of polymerisation and the chemical mechanism of the propagation of the polymer chain are unknown; it is only known that polymerisation entails the destruction of the paramagnetic centres of the nitroxyls (sometimes to an extent up to 80%), possibly as a result of addition to multiple bonds.[56] Polymerisation can be induced by the shear deformation of the monomer under high pressure conditions (1.2 GPa, 40° and 270° shifts), which affords a dark-brown powder (resembling that formed on thermal polymerisation), but it shows no signs of ferromagnetism.[55]

The polymerisation of another spin-labelled diacetylene has been reported:[57]



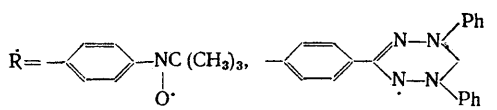
In contrast to the previous monomer, it is capable of topochemical polymerisation and its structure is much more definite. The polymer contains about 3% of a ferromagnetic fraction with a saturation magnetisation of 0.3 G cm^3 g^{-1}.[57]

Japanese workers[58] reproduced Ovchinnikov's polymer and in addition synthesised a polymer from another spin-labelled diacetylene:



Its magnetic properties are similar to those of Ovchinnikov's polymer (coercive force 300 G, saturation magnetisation ~0.2 e.m.u. g^{-1} at 30 K, residual magnetisation 2.5×10^{-2} e.m.u. g^{-1} (although the exchange interaction between the two spin systems—polyene and nitroxyl—is in this case still weaker (because the σ-bond barrier between these systems is much higher).[58]

Iwamura and Murata[6] synthesised spin-labelled polyacetylenes in another way—by the catalytic polymerisation of acetylenes CH≡CR, where



in the presence of the $WCl_6/SnPh_4$ catalyst. In the former case, the average number of monomer units in the macromolecule was 180, while in the latter case it was 210 and the fraction of radical spins preserved in the "living" units was 25–30%. The polymer was paramagnetic and showed no signs of ferromagnetism.[6]

In flexible-chain polymers spin-labelled with nitroxyls [styrene–maleic anhydride copolymer, poly(glycidyl methacrylate), polyfulvene, etc.], a ferromagnetic fraction (3–5%) was also found.[59] The ferromagnetic grains "follow" the magnet. After the subsequent division in two, one of the halves attains ferromagnetism, while the other loses it. The destruction of nitroxyl radicals (by thermolysis or by treatment with acids) does not destroy the ferromagnetism, i.e. there is no direct relation between paramagnetism and ferromagnetism.

The magnetisation of the flexible-chain ferromagnetic polymers is 10^{-1}–10^{-2} G g^{-1} and the Curie point is at 350–400 K. Measurements have been made of the amounts of metal ions present as an impurity (10^{-1}–10^{-2}%) and it was shown[59] that the experimentally measured magnetisations do not as a rule exceed the magnetisations calculated on the assumption that the iron ion impurities are combined into clusters consisting predominantly of α-iron. However, one cannot conclude from this that the impurity iron ions are reduced to metallic iron which is responsible for the ferromagnetism. It may be that the metal ions arrange the paramagnetic fragments of macromolecules into ferromagnetic organometallic structures (as a result of an interaction of the metal–ligand type). A similar possibility was incidentally discussed as early as 1963 by Blyumenfel'd[60] in connection with the previously discovered ferromagnetism of DNA and other biopolymers. The ferromagnetism of organic structures is naturally induced by iron impurities, but one cannot reduce it to trivial ferromagnetic contaminations (inclusions); iron ions or clusters are linked to the main organic structure in such a way that together they generate a single ferromagnetic system.[60] It is likely that these ideas will now become again of current interest.

Weak ferromagnetism is frequently observed in degraded or carbonised polymers (including cellulose) and in polymers subjected to strong shear deformation at high pressures. It has a number of unusual features (non-reproducibility, irreversible disappearance in

time, etc.) and has therefore generated much scepticism. Its origin is obscure. It can be associated with the reduction of traces of metal ions by chemical reactions induced by degradation or mechanodegradation, but one cannot exclude (although this is unlikely) the possibility of the formaton of structural clusters with McConnell islands. At any rate, the question whether or not purely organic ferromagnetic polymers without ferromagnetic metal impurities can be created remains open.

We may note a further three cases of the observation of ferromagnetism in organic polymers. The pyrolysis of polyacrylonitrile at 350 °C is accompanied by the appearance of a weak ferromagnetism (the magnetisation is 0.3–0.5 G g^{-1}), while its heat treatment at high temperatures (up to 900 °C) affords a material (pyropane) with a magnetisation of 15 G g^{-1}.[61] It consists of amorphous graphite (~80%) and an aromatic polymer (10–12%) and contains a highly crystalline phase (8–10%), which can be separated magnetically and has a magnetisation of about 150 G g^{-1} and a density of 3 g cm^{-3} (we may recall that the magnetisation of metallic iron is 200–215 G g^{-1}). The iron content in pyropane is $(1-3)\times10^{-4}$% and that in the magnetic phase is 1×10^{-2}%, which is too negligible to permit the assumption that the ferromagnetism of pyropane is due to the impurity. The idea of an intermediate graphite–diamond system in which each second carbon atom in the graphite-like lattice plane has an unpaired electron has been proposed.[61] Such an idealised structure has a theoretical magnetisation of 230 G g^{-1} and a spin concentration of about 10^{23} cm^{-3}, which is completely unusual for organic structures.[61] It has been concluded that pyropane approaches this idealised graphite–diamond structure. However, later other data indicated that the content of iron in the magnetic phase of pyropane 8% instead of 10^{-2}%,[57] but even this is too low to account for the ferromagnetism of pyropane.

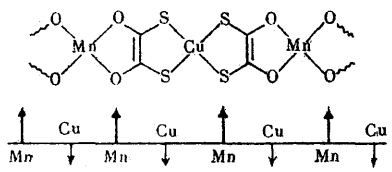
It has also been noted that, when pyropane is ground in a ball mill, its magnetisation increases with a simultaneous rise in the iron content[57] (the spheres in the ball mill were probably metallic, although this is not reported; however it is known that on treatment in a ball mill with steel or magnetite spheres, even wood filings become ferromagnetic).

Torrance[32,62] reported that the reaction of symmetrical triaminobenzene with iodine in different solvents and even in the vapour phase results in the formation of a black, insoluble polymer of unknown structure, which sometimes contains up to 2% of a ferromagnetic fraction with a magnetisation of the order of 10^{-2} G g^{-1}. It vanishes irreversibly only at ~700 K; there is also a weak hysteresis loop.[62] The results are random and non-reproducible; the polymer contains traces of iron, but, according to the author's claim,[62] its amount is smaller by a factor of 15 than that required for the "impurity" explanation of the ferromagnetism.

Finally, Japanese workers[63] have reported the appearance of ferromagnetism (0.2–0.6 G g^{-1}) in resins based on condensed polynuclear aromatic compounds. There are two remarkable features of this ferromagnetism. Firstly, it arises only on UV irradiation of the resins, i.e. on generation of radicals, and, secondly, it appears only in resins based on *meta*-substituted aromatic compounds but is absent from polymers based on *p*-xylylenes. The possibility of "native" ferromagnetism as a result of the generation of McConnell islands on photolysis have been postulated. However, a trivial explanation cannot be ruled out either: although the authors claim that there were no metals in the resins, there is a possibility that traces of metal ions were reduced to ferromagnetic chemical forms under the influence of photochemical reactions.

VI. Organometallic polymers

This class of ferromagnetics is based on multispin organometallic macromolecules in which the spins belong to paramagnetic ions. The first example of macromolecules of this type is provided by the mixed bimetallic dithiooxalate polymeric complex of manganese and copper:[64]

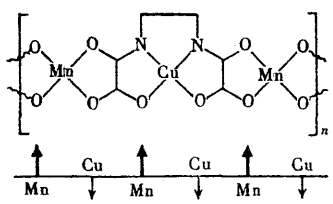


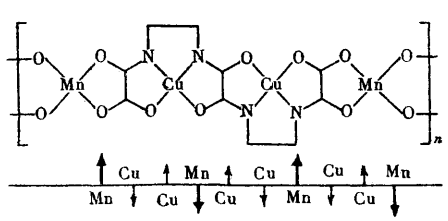
The alternating copper and manganese ions are joined together by organic ligands in such a way that each copper atom is at the centre of a planar square made up of four sulphur atoms, while each manganese atom is at the centre of a plane made up of five oxygen atoms, two pairs of which belong to two dithiooxalate ligands and the fifth is the oxygen atom of an attached water molecule.

The isolated macromolecule has a planar zig-zag shape in which the exchange interaction of the metal ions via the organic ligand is negative and arranges the spins of the ions antiferromagnetically (as shown below, underneath the chemical formula of this macromolecule). However, since the spin of the Mn^{2+} ion ($S=5/2$) is greater than that of Cu^{2+} ($S = 1/2$), the spin chain proves to be ferrimagnetic, its magnetisation increasing with decrease in temperature (when the exchange energy J_{intra} is comparable to or exceeds kT).

In the crystal, these high-spin macromolecules are arranged in parallel in stacks: an Mn^{2+} ion opposite another Mn^{2+} ion and a Cu^{2+} ion opposite another Cu^{2+} ion. The intermolecular exchange interaction arranges the spins of neighbouring ions in an antiparallel fashion, so that the overall high spin of one macromolecule is compensated by the spin of a neighbouring molecule. Therefore at T_c = 7.5 K, where $J_{inter} \simeq KT_c$, the polymer passes to the antiferromagnetic state.[64]

Kahn and co-workers[65,66] have made the greatest advances on the way to organometallic polymers. They synthesised bimetallic crystallising linear multispin macromolecules from the 1,3-propylenebisoxamate dianion:





The arrangement of spins in these macromolecules is indicated under the formulae. In both cases, the intermolecular exchange interaction between the ions is negative and arranges them

antiferromagnetically. In the first case, the macromolecule is of the high-spin type and ferrimagnetic (the overall spin of the Cu^{2+} ions does not compensate for the total spin of Mn^{2+}). However, in the crystal the intermolecular exchange interaction is negative and again the high spin of one macromolecule is compensated by the oppositely oriented spin of a neighbouring molecule, so that the crystal, made up of high-spin macromolecules, become antiferromagnetic overall at low temperatures. In the second case, the change in the sequence of ions in the chain can result in the complete compensation for the spins and the macromolecule is of the low-spin antiferromagnetic type.

The arrangement of the spins in a pair of neighbouring macromolecules with a regular alternation of Cu^{2+} and Mn^{2+} ions is illustrated in Fig. 8*a*; their compensation is evident. However, if one macromolecule is displaced relative to another by a distance equivalent to "half a ligand" (under these conditions the Cu^{2+} ions of one molecule are placed opposite the Mn^{2+} ions of another and conversely), then the arrangement of the spin changes sharply and becomes ferrimagnetic: the Mn^{2+} spins are oriented in one direction and the small Cu^{2+} spins are oriented in another (Fig. 8*b*). Such arrangement of spins had in fact been predicted previously (Fig. 5).

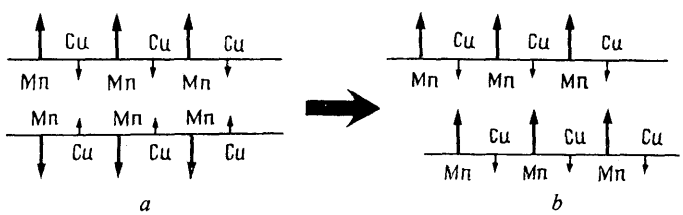
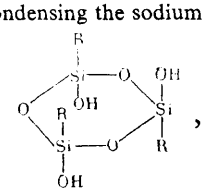


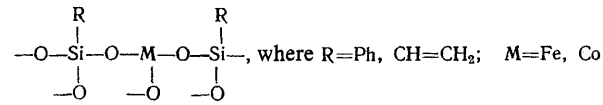
Figure 8. The transformation of the antiferromagnetic arrangement of the spins of two organometallic molecules into a ferrimagnetic arrangement by the "shift" of one macromolecule relative to the other.

The "half-ligand" shift of the macromolecule has been achieved experimentally[66] by replacing the $CH_2CH_2CH_2$ group connecting the nitrogen atoms in the ligand by the $CH_2CHOHCH_2$ group. The resulting organometallic polymer did indeed prove to be a low-temperature ferromagnetic with typical properties, including a hysteresis group.[66] The same workers obtained a similar ferromagnetic on the basis of another ligand—the oxamidobisbenzoate dianion.[67]

In essence, all these polymers are polymeric complexes of organic ions with organic ligands which were synthesised by methods of inorganic chemistry. Procedures are also being developed to produce ferromagnetics based on organometallic polymers with paramagnetic metal atoms bound covalently in the main polymer chain. A notable example is provided by polymetallosiloxanes,[68] which were obtained by condensing the sodium salt of cyclotrisiloxane, i.e.


, where R = Ph, CH=CH$_2$,

with metal salts ($FeCl_3$, $CoCl_2$, etc.) in anhydrous solvents. They contain the fragments


, where R=Ph, CH=CH$_2$; M=Fe, Co

with alternating—SiOM—and—SiOSi—bridges, as well as siloxane rings, open chains, and cross-linked structures. Polymer fractions with an M : Si ratio ranging from $10^{-3}-10^{-2}$ to 1.5 can be isolated by fractional precipitation. In the fractions with a high M : Si ratio, the—$MO(SiOSiO)_nM$—molecular fragments with high values of n are replaced by short fragments with $n = 1$ and even $n = 0$ (—MOM—).

In order to convert such paramagnetic polymers into ferromagnetics, it is necessary to achieve an exchange interaction between the metal atoms. There are various ways of doing this: by shortening the bridges between the atoms, making them "conducting" to the exchange interaction; by creating new additional bridges; and finally by removing the organic bridges altogether and joining together the paramagnetic atoms.[68] All these versions are being actively developed. The simplest is attained in the high-temperature pyrolysis of ferropolysiloxane. A considerable proportion of the organic component of the molecule is then removed and a ferromagnetic composite material with a magnetisation of 10—50 G g^{-1} is produced (depending on the metal content and the pyrolysis temperature). It contains iron silicide and carbide phases, amorphous silicon dioxide, and carbon, as well as 300—350 Å α-ion clusters.[68] As regards their dynamic properties, these high-temperature ferromagnetics belong to the rigid class: in the wavelength range 0.8—30 cm, their magnetic permeability is close to unity and the tangent of the magnetic loss angle is negligible. This aspect of the chemical construction of ferromagnetics is closely related to the modern materials science of metal-filled polymeric composites.

VII. Conclusion

The principal achievements of the science of organic ferromagnetics are the recognition and understanding of the physical principles of their construction and the chemical pathways leading to it; there exists reliable theoretical and experimental evidence showing that these procedures are realistic; finally, the first "genuine" organic ferromagnetics exist.

Problems and difficulties can be clearly seen; the main one is the problem of the molecular organisation of multispin and high-spin molecules in a "solid state" order such that a ferromagnetic arrangement of the spins is ensured. This problem is soluble (we have seen brilliant examples of such solutions), but requires serious intellectual efforts.

One must clearly recognise also the deficiencies of organic ferromagnetics as potential magnetic materials. They all arise from the fact that organic molecules contain a lot of "dead weight"—a ballast consisting of spinless groups and fragments which results in a low spin density, i.e. a small number of spins per unit volume of the substance. Thus metallic iron contains 4×10^{23} spins per cm^3 while their number in an organic ferromagnetic is smaller by 1—2 orders of magnitude. This gives rise, firstly, to low magnetisations (smaller by 1—3 orders of magnitude than in iron) and, secondly, to low exchange energies (because of the large interspin distances), resulting

in low temperatures of transition to the ferromagnetic state (in other words, "genuine" organic ferromagnetics should be as a rule low-temperature materials); thirdly, the dipole interaction of the spins is also weak and this hinders the formation of a domain structure and spontaneous magnetisation. Finally, one should bear in mind the chemical instability of organic materials, the "ageing" of magnetic materials based on them as a function of time, and the restricted operational usefulness of such materials under severe thermal conditions or in oxidising media. Organic ferromagnetics are hardly likely to have superior static magnetic properties compared with classical metallic ferromagnetics but they can possess unusual dynamic properties—magnetic and dielectric losses and their frequency dependence.

From technical standpoints, the polymeric organic ferromagnetics are naturally the most attractive, although there is no certainty that such polymers can exist in the absence of impurities or traces of metals.

The problem of ferromagnetic impurities and inclusions (especially for low magnetisations) is most acute for polymers. The problem is tricky for the following reasons. On the one hand, impurities are discouraging, creating the impression of a "non-genuine" ferromagnetic, and destroy the stimulus to scientific research. On the other hand, if impurities are incorporated in an organic structure and organise its paramagnetic component (spin labels, polyconjugated systems, etc.) into a ferromagnetic order, we have a success, an achievement. It is then necessary to learn how to control this process—how to introduce such impurities into such polymers and in a way ensuring the maximum "synergism" of the organic and inorganic components in the generation of ferromagnetic organo-metallic structures. Here there is only one procedure—quantitative comparison of impurities with magnetisation. The problem is not yet clear: in some cases the impurities are sufficient to ensure the observed ferromagnetism, whilst in others their content is insufficient by 1–2 orders of magnitude. However, the unreliability of the analyses for metallic impurities and the non-reproducibility of the results leave open this part of the problem of organic ferromagnetics (although it is entirely clear how it could be "closed").

At the present level of knowledge, mixed organometallic ferromagnetics merit most attention, although overall the entire field of organic ferromagnetics merits vigorous development. Nor can one ignore its useful forays into adjoining fields, in particular into the chemistry of multispin and high-spin molecules as the potential elementary basis of the future molecular electronics.

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