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From the Gomberg radical to organic magnets

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Abstract. The synthesis and properties of triarylmethyl di- and polyradicals including perchlorinated ones are considered. The achievements in the design of magnetic clusters and organic magnets based on the Gomberg radical are described. Data on mixed-valence compounds containing triarylmethyl type radicals and carbanions as electroactive groups are given. The bibliography includes 117 references.

I. Introduction

Magnetism as a universal natural phenomenon is intensively studied by fundamental science. Magnetic phenomena are widely used in engineering. The traditional magnetic materials (ferro-, ferri- and antiferromagnets) contain metal atoms or ions with partially occupied d and f shells and represent metals, metal alloys and ceramics. In both fundamental and applied aspects, the interest of researchers is aroused by creation of an organic magnet, *i.e.*, an ensemble of organic molecules or macromolecules containing only light (non-metal) elements (C, O, H, N, S, *etc.*) and possessing spin ordering, *i.e.*, ferro- or ferrimagnetism. Various approaches to the design of organic magnets and achievements along this line have been summarised in reviews.[1–6]

This review considers the key methods for the synthesis and properties of di- and polyradicals and organic magnets based on the first experimentally detected (Gomberg, 1900) triphenylmethyl radical (TPMR). The chemical and spectroscopic properties of the Gomberg radical and other triarylmethyl type (TAMT) radicals have been described, for example, in a number of books.[7,8] The research area related to the molecular magnetism has developed so vigorously in recent years that it is difficult to cover it within one review. Works devoted to particular types of radicals are therefore required. For example, of the 373 references present in the recent review by Blundell and Pratt[6] dealing with organic and molecular magnets, only two references concern polymeric polyradicals. Somewhat more information on these species can be found in another publication.[4] A number of reviews by Rajca,[3,9–13] who is actively engaged in the synthesis of TAMT polyradicals, have been published; the recent review[13] deserves special mention.

The problem of the creation of organic magnets can be divided into the molecular and supramolecular aspects. In the molecular aspect, it is clear that organic paramagnetic compounds with unpaired electrons, stable radicals and carbenes should serve as the building blocks for organic magnets.

Currently, an enormous number of paramagnetic organic species are known, and ferromagnetic spin ordering in the crystal or in an amorphous solid, *i.e.*, the supramolecular aspect, remains the major problem. Indeed, according to Dougherty,[2] '...Nature favours antiferromagnetic coupling of two weakly interacting electrons'. However, several cases of ferro- and ferrimagnetism in the crystals of small radicals or organic charge transfer salts have recently been observed experimentally.[1–6] Two McConnell mechanisms demonstrating the possibility of through-space intermolecular ferromagnetic ordering of organic paramagnetic molecules (radicals and carbenes) have been considered in detail in reviews[1,4] which give references to original publications.

II. Exchange interactions in di- and polyradicals

Yet another approach to the design of organic magnets (alternative to the spatial ordering of small radicals) is the synthesis of polyradicals in which the intramolecular magnetic ordering of unpaired electrons occurs through chemical bonds. It is meant that pair exchange interactions between unpaired electrons are transferred through a system of conjugated π-bonds of a polymer. Since in some conjugated diradicals (including those stable under ambient conditions), very strong ferromagnetic coupling has been found,[3] this approach offers hope for the preparation of organic magnets with the Curie temperature equal to, or higher than, room temperature.

The descriptions of di- and polyradicals widely use[2,3] the notions 'ferromagnetic coupling unit' (FCU) and 'antiferromagnetic coupling unit' (ACU) (in some cases, they are referred to as the corresponding bridges). The simplest π-conjugated hydrocarbon diradical is trimethylenemethane (TMM) (**CU-1** structure in Fig. 1). In this diradical, two methyl radicals are attached to one end of the ethylene molecule (1,1-coupling) and the p orbitals with unpaired electrons are conjugated with the π-system of ethylene. The electron coupling is ferromagnetic, and TMM exists in a triplet ground state (T) with the full spin $S = 1$. In this case, ethylene acts as an FCU. Conversely, for the **CU-2** structure in Fig. 1 in which the radical centres are attached to different ends of the ethylene molecule (1,2-coupling), the ground state is singlet (S, $S = 0$) and in this case the double bond is an antiferromagnetic

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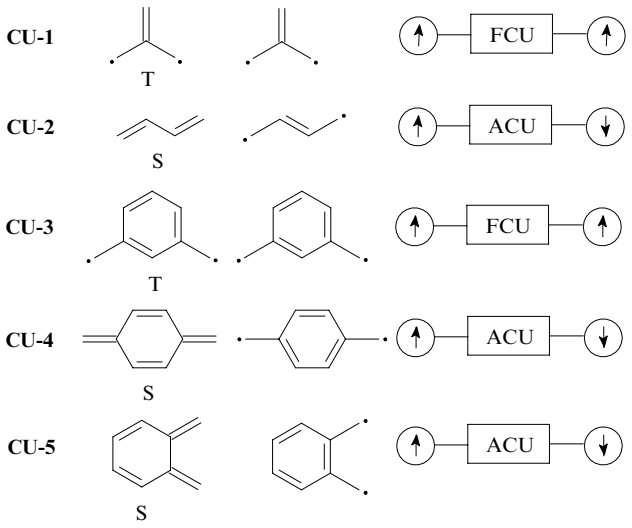


Figure 1. Structure (topology) of conjugated diradicals and spin coupling in them (see the text).

coupling unit. The exchange interaction of the unpaired electrons through a benzene ring also depends on the arrangement of the radical centres. The 1,3-coupling (*meta*-coupling) usually results in a triplet ground state of the molecule and a ferromagnetic coupling of electrons (**CU-3** structure in Fig. 1), whereas 1,4(*para*)- and 1,2(*ortho*)-coupling of the radical centres gives rise to a singlet ground state and, correspondingly, antiferromagnetic coupling of the unpaired electrons (**CU-4** and **CU-5** structures in Fig. 1).

It should be emphasised that the type of binding through phenylene units as well as the conjugation effect depend appreciably on the mutual arrangement of the orbitals bearing unpaired electrons and the plane of the benzene ring. Conformational distortions of the structure may result in a decrease in the exchange coupling and in the reversal of its sign, *i.e.*, a *meta*-phenylene unit may become an ACU, and a *para*-phenylene unit may be transformed into an FCU. Zang *et al.*[14] calculated the dependence of the singlet – triplet splitting energy and, hence, the exchange integral on the rotation angle of the p orbitals with unpaired electrons with respect to the plane of the benzene ring for the **CU-3** – **CU-5** units and gave references to the experimentally proven cases of sign reversal in the exchange coupling caused by steric distortion of the structure of the unit. Some examples of this sort are considered below.

A 'magnetic' polymer should, in a general case, be a macromolecule with a large number ($10^3 - 10^4$ or more) radicals that interact through coupling units, *i.e.*, a polyradical. Two differing in principle approaches for radical coupling within a conjugated polymer have been developed: in class I polyradicals, the radicals alternate with the coupling units, while in class II polyradicals, the radicals are attached to the conjugated polymer backbone (Fig. 2). The idea of using the conjugated polymer backbone as the common ferromagnetic coupling unit was first proposed by Ovchinnikov and co-workers [15] and subsequently developed by Nishide *et al.*[16]

The progress in the design of magnetic polymers may be evaluated using the average full spin S in the ground state of the macromolecule (for n ferromagnetically coupled spins equal to $1/2$, $S = n/2$).

III. Mesoscopic and monomolecular magnets. Spin clusters

On the one hand, researchers try to obtain magnetic molecules as large as possible (ideally, macroscopic, for example, as networks). On the other hand, it should be borne in mind that for the

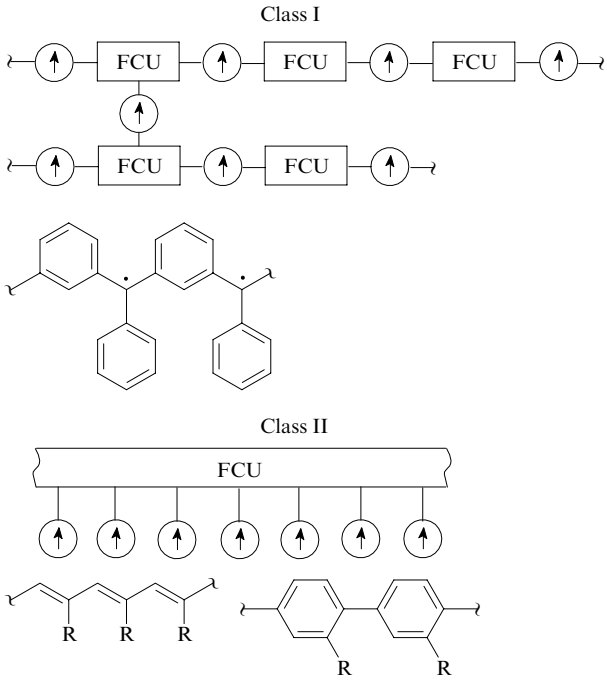


Figure 2. Two classes of polyradicals. R is a stable radical.

condensed phase, three main sorts of magnetic ordering (ferro-, antiferro- and ferrimagnetism) may be supplemented still by at least nine types (metamagnetism, 'seed' ferromagnetism, superparamagnetism, speromagnetism, asperomagnetism, helimagnetism, spin glass, mictomagnetism, sperimagnetism).[17] These sorts of magnetic order can apparently be also manifested in organic magnets, and one should, first, be ready to encounter them, and, second, to deliberately prepare compounds with these sorts of ordering. In particular, a new line of research closely connected with the superparamagnetism, called magnetic mesoscopics, has been actively developed in recent years;[18, 19] this deals with small magnetic particles with a size of $\sim 1 - 100$ nm containing $\sim 10 - 10\,000$ atoms. These mesoscopic magnets (or nanomagnets) are of obvious fundamental interest as regards transition from the magnetism of separate atoms to the collective magnetism (ferro, ferri, *etc.*) of amorphous and crystalline macrobodies. From the technology standpoint, the use of mesoscopic magnets is promising for increasing the density of magnetic data recording.

Now we consider briefly the magnetic properties of mesoscopic magnets, which are rather small single-domain particles and often behave as superparamagnets.[3, 18, 19] In small single-domain particles, magnetisation along the easy magnetisation axis is blocked: an energy barrier (E_A) to the rotation of the magnetisation vector appears due to the anisotropy energy. There are many types of magnetic anisotropy;[20] the most frequently encountered types are the crystallographic anisotropy caused mainly by the spin – orbit coupling and the shape anisotropy the microscopic cause of which is the long-range dipole – dipole coupling between the elementary magnetic moment carriers.[20]

Figure 3 shows the dependence of the energy (E) of a single-domain particle on the angle (Θ) between the magnetisation vector (M) and the easy magnetisation axis in the absence of a magnetic field and on its switching on. The field is oriented oppositely to the z axis, which is directed upward. The transition of a magnetic particle from the metastable state (the left minimum in Fig. 1*b*, $\Theta = 0$) to the equilibrium state ($\Theta = \pi$) requires overcoming an energy barrier the height of which decreases with an increase in the field and becomes equal to zero at the critical value $H_c = 2E_A/M$. At this instant, the particle is remagnetised, namely, the magnetisation vector is oriented along the external field. This process is called switching and the H_c is the switching

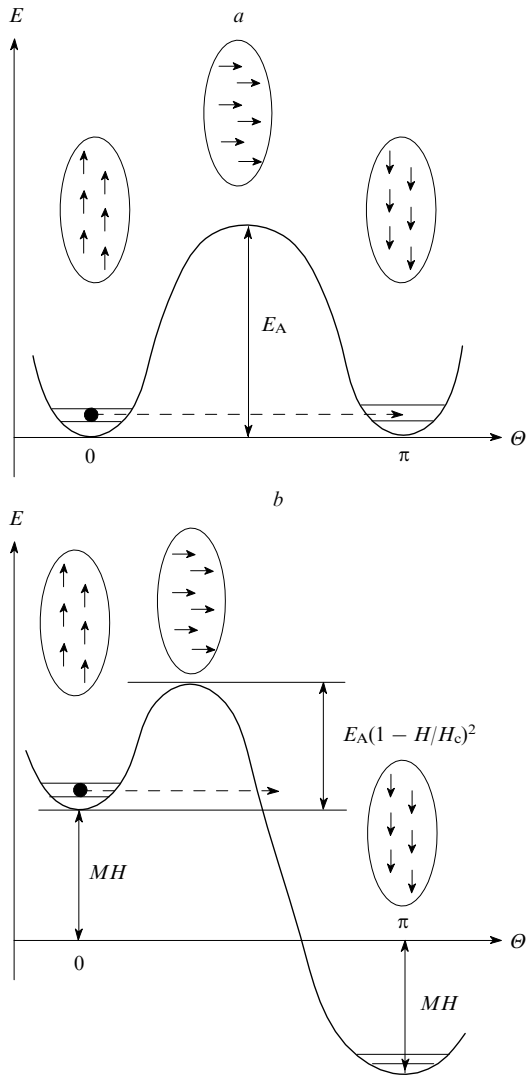


Figure 3. Energy barrier to remagnetisation of a single-domain particle of an oblong shape: (*a*) without an external magnetic field; (*b*) in an external magnetic field *H*.

field. This bistability of small magnetic particles can be used for data recording. The transition over the barrier is facilitated by thermal fluctuations of magnetisation, which are, in particular, interfering factors for data recording. Owing to the thermal fluctuations, magnetisation of a material consisting of small magnetic particles decreases with time, the relaxation rate decreasing with a decrease in temperature according to the Arrhenius law

$$\tau^{-1} = f_0 \exp\left(-\frac{E_A}{k_B T}\right),$$

where τ is the characteristic relaxation time, f_0 is the pre-exponential factor equal to $\sim 10^{-9}$–10^{-10} s^{-1} for typical magnetic particles, k_B is the Boltzmann constant, T is temperature.

It is noteworthy that the magnetisation vector may tunnel from one minimum to another upon quantum fluctuation, as shown by a dashed arrow in Fig. 3. These tunnelling transitions were actually detected experimentally; they are most clear-cut for a number of high-spin magnetic clusters that are considered below. This quantum effect is called macroscopic quantum tunnelling or magnetisation quantum tunnelling (MQT), its discovery being ranked among most prominent achievements of physics in the late 20th century. The violation of the Arrhenius law at low temperatures ($T \to 0$), in particular, reaching a constant relaxation rate, is a consequence of the MQT.

In 1993, Rajca realised the possibility and importance of investigation of the magnetism of high-spin organic molecules on a mesoscopic scale.[9] He noted that the spin–orbit coupling in carbon-centred radicals and carbenes is negligibly low, as follows from the small deviation of *g*-factors of these species from the *g*-factor of a free electron. Therefore, shape anisotropy is expected to be important for these species, and organic synthesis opens up extended opportunities for controlling this factor. For a particle with volume V, magnetisation I_s and the shape factor N, which is related to the demagnetisation factor ($0 \leqslant N \leqslant 2\pi$, $N = 0$ for a sphere, $N = 2\pi$ for an infinite rod), the energy barrier (in Kelvins) in the case of coherent rotation of the magnetisation is described by the formula

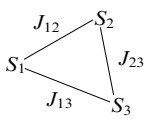
$$E_A = \frac{0.5 N I_s^2 V}{k_B}. \quad (1)$$

A calculation by this formula for triarylmethyl polyradicals with a moderately oblong shape (for example, an oblong ellipsoid of revolution with $a:b \approx 2$, $N \approx 3$) shows that about 200 ferromagnetically coupled spins (correspondingly, $S \approx 100$) are required to ensure a barrier of about 2 K.[21,22]

Nanomagnets can, in principle, be approached in two ways: 'top-down', *i.e.*, by grinding magnetic macrobodies, and 'bottom-up', *i.e.*, by synthesising large magnetic clusters. A magnetic, exchange or spin cluster is a set of several (two or more) spin centres connected by chemical or exchange interactions. Clusters in which magnetic transition metal ions (Fe, Mn, Cr, *etc.*) act as the spin centres are best known and best studied. The paramagnetic clusters are fairly convenient model systems in which all main physical interactions that form the properties of magnetic materials, including exchange interactions, are manifested for a limited number of atoms (ions) and, hence, they can be analysed more easily. Magnetic clusters, being adjacent to mesoscopic magnets, also represent a connecting unit between the microscopic and macroscopic magnetism. Extensive literature is devoted to various aspects of the physics and chemistry of inorganic exchange clusters; all relevant references can be found in books.[23–25] The traditional theoretical base for the description of magnetic and spectroscopic properties of exchange clusters comes from the Heisenberg–Dirac–Van Vleck model, which is often called for short the Heisenberg model. In this model, exchange interactions for polynuclear clusters are described by the Hamiltonian

$$\hat{H} = -\sum_{ij} J_{ij} \hat{S}_i \hat{S}_j,$$

where J_{ij} is the exchange parameter, which is positive in the case of a ferromagnetic spin coupling and negative in the case of antiferromagnetic coupling; $\hat{S}_i$ and $\hat{S}_j$ are operators of the coupled spins.



For example, for a trinuclear cluster of the spins S_1, S_2 and S_3, the Heisenberg Hamiltonian in the general case has the form

$$\hat{H} = -2J_{12}\hat{S}_1\hat{S}_2 - 2J_{23}\hat{S}_2\hat{S}_3 - 2J_{13}\hat{S}_1\hat{S}_3.$$

With known structure or symmetry of the polynuclear cluster, the number of independent exchange parameters in the Hamiltonian can be reduced, which substantially facilitates its solution. The corresponding Hamiltonian can be composed based on simple considerations almost for any system of exchange-coupled spins (paramagnetic ions, radicals, *etc.*).[23] The next stage, namely, the calculation of the spin level energies and derivation of the

theoretical equation for the magnetic susceptibility for rather simple clusters, is not faced with serious difficulties either. The limitations inherent in the Heisenberg model have been considered in detail in books. [23, 24]

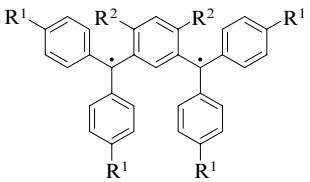
The research dealing with exchange clusters resulted in the development of single-molecular ensembles of paramagnetic ions, 'single-molecule magnets' (SMM). In 1980, Lis [26] reported the synthesis, structure and some magnetic properties of the nano-sized molecule $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$, which is usually designated as Mn_{12}. Each molecule contains a group of 12 manganese ions: four Mn^{4+} ions with the spins $S_1 = 3/2$ forming an internal tetrahedron and eight Mn^{3+} ions with the spins $S_2 = 2$ located outside the tetrahedron. The antiferromagnetic interactions of manganese ions with different oxidation states through oxygen ions give rise to a ferrimagnetic structure with the full spin of the molecule $S = 10$ ($8 \times 4/2 - 4 \times 3/2 = 10$). In 1993, it was found [27] that Mn_{12} has a substantial barrier of the magnetic anisotropy ($E_A = 60$ K) to the reversal of the magnetisation vector; this was manifested as a magnetic hysteresis loop at temperatures below 4 K. Since this type of hysteresis behaviour of these molecules is similar to the behaviour of small single-domain magnetic particles, the name 'single-molecule magnets' was proposed for them (as has been noted,[28] this name is not completely correct). This and similar molecular clusters demonstrate most clearly macroscopic quantum tunnelling mentioned above, as their chemical synthesis ensures the creation of ensembles comprising fully identical and equally oriented SMM.[6, 28]

The progress achieved in the preparation of mesoscopic magnets, magnetic clusters and SMM based on transition metal ions prompt the idea of preparing similar objects from organic radicals, the more so, that the synthesis of polyradicals having nanometre sizes is quite a realistic task.

IV. Triarylmethyl type di- and polyradicals

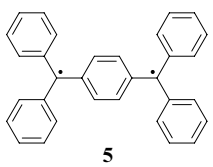
1. Diradicals

It is reasonable to consider first the diradicals obtained from the Gomberg radical in which the magnetic interactions of the unpaired electrons are manifested most clearly. The achievements in the synthesis of triarylmethyl diradicals and their properties have been discussed in a number of reviews and monographs (see, for example, the publications [3, 29, 30]). Table 1 presents the properties of hydrocarbon diradicals of the triarylmethyl type **1**–**18** including both the diradicals synthesised recently and those known long ago with known magnetic properties. Let us briefly discuss some of the diradicals. It is believed that for structures **5** (Thiele's hydrocarbon), **13** (Chichibabin's hydrocarbon, ChH) and **16** (Muller's hydrocarbon, MH), the singlet states exist as

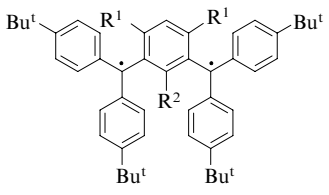


1–**4**

$R^1 = R^2 = H$ (**1**); $R^1 = Bu^t$: $R^2 = H$ (**2**), Me (**3**), Pr^i (**4**).

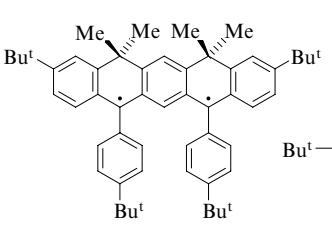


5

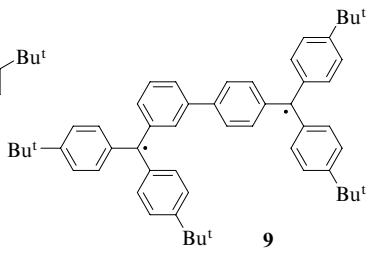


6, **7**

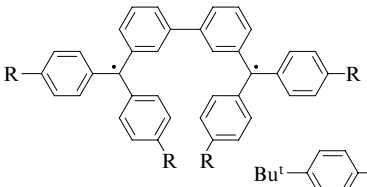
$R^1 = R^2 = Me$ (**6**),
$R^1 = CF_3$, $R^2 = H$ (**7**).



8

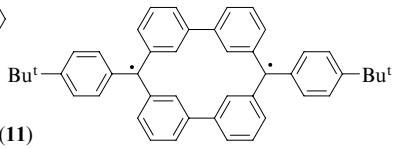


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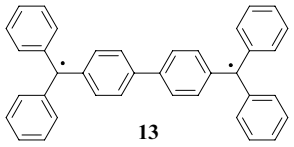


10, **11**

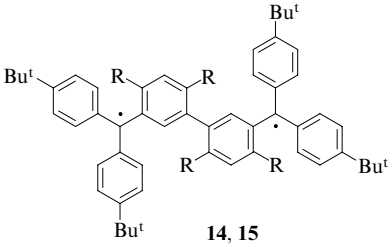
R = H (**10**), Bu^t (**11**)



12

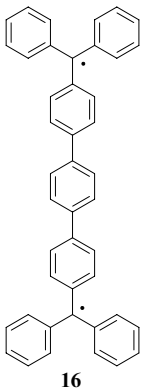


13

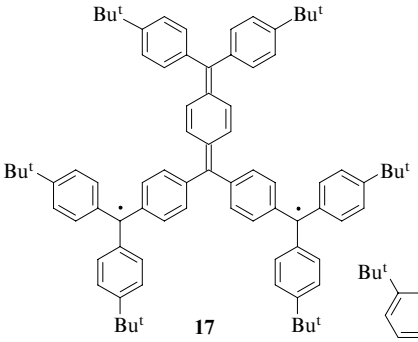


14, **15**

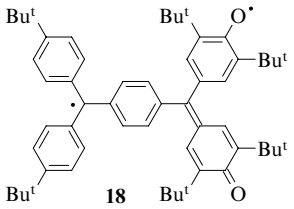
R = Me (**14**), Pr^i (**15**)



16

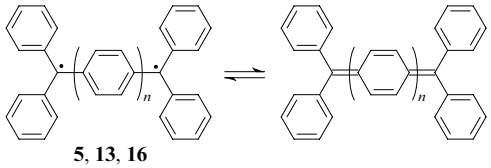


17



18

the corresponding quinonoid structures, which are in equilibrium with the triplet (diradical) states; for Thiele's hydrocarbon, the equilibrium is entirely shifted to the right due to the great energy difference between the singlet and triplet states and only the singlet state has always been observed.



5, **13**, **16**

n = 1 (**5**), 2 (**13**), 3 (**16**).

Table 1. Some properties of hydrocarbon diradicals of the triarylmethyl type.

Diradical	$10^3 \lvert D/hc \rvert$ /cm^{-1}; $10^3 \lvert E/hc \rvert$ /cm^{-1} (see [a])	Ground state [b]	Ref.
1	7.9; 0.7	T	31
2	6.6; ~0.8	T	32–34
3	8.7; ~0	T	33, 34
4	9.9; ~0	T (0.2)	32–34
5	–	S	7, 35
6	10.7; ~0	S (0.2)	33, 34
7	–	T	3
8	–	T	3, 36
9	2.5; –	T	37
10	4.9; ⩽0.3	T (0.3)	38
11	5.0; –	S (~0.1)	37
12	8.1; 0.8	S (~0.2)	39
13	16.6; 0.58	S (5.5)	40
14	~0	T (0.04)	41
15	~0	T (0.004)	41
16	3.5; ⩽0.2	S (0.9)	38
17	4.0; 0	T (> 0.05)	42
18	7.0; ~0	T	43

[a] D and E are zero-field splitting parameters; [b] in parentheses, the energy differences between the singlet and the triplet states $\lvert \Delta E_{ST} \rvert$ (kcal mol^{-1}) are given.

Analysis of the published data on the ChH casts some doubt in their interpretation. The solution of the famous diradical paradox formulated by McConnel [44] by no means completed the study of the ChH.[35,45,46] Sugimoto *et al.*[45] concluded that the data obtained by Brauer *et al.*[40] refer, most likely, to radical pairs rather than to the triplet state of the ChH molecules. In their opinion, zero-field splitting (ZFS) parameters for the triplet state of the ChH should be much lower than those measured by Brauer *et al.*;[40] hence, its signal should be difficult to observe against the background of a monoradical impurity. According to Sugimoto *et al.*,[45] this is the reason why no triplet EPR signals were detected for the ChH single crystals studied earlier.[35] Indeed, it can be seen in Table 1 that the zero-field splitting parameters for Chichibabin's hydrocarbon are markedly distinguished from the general trend. It is beyond doubt that this fact requires additional reasoning and new experiments dealing with the triplet state of the ChH.

Muller's hydrocarbon also call for additional investigation, as a number of reasons have been proposed attesting to its triplet ground state.[47] Determination of the ground state of the Schlenk–Brauns diradical (**10**) is also doubtful.[13]

Using diradical **6** as an example, one can see that structural distortions may transform even an obvious FCU (with *meta*-phenylene connection) into an ACU, and this should be taken into account in the synthesis of magnetic polymers. An assumption [34] that diradical **6** has a conformer with $\Delta E_{ST} \approx -0.02$ kcal mol^{-1} also deserves attention. This brings about the question of how the singlet state is realised for this and other diradicals in which the formation of a quinonoid structure is impossible and what is the electronic spectrum of these diradicals in the singlet state.

An approximately twice higher singlet–triplet splitting of the cyclophane diradical **12** compared to diradical **11** is probably due to the presence of two parallel 3,3′-biphenyl exchange routes in the former case, while in diradical **11**, only one route is present.[39]

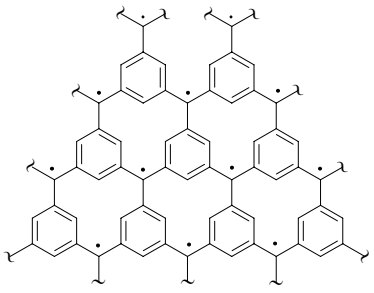
Diradical **17** is an analogue of the simplest and, hence, one of the best studied both theoretically and experimentally, π-conjugated organic diradical, trimethylenemethane (**CU-1**). This diradical is stable at room temperature and has a triplet ground state with a relatively strong ferromagnetic interaction, which makes it, in the opinion of Rajca *et al.*,[42] a promising structural block for organic magnetic polymers stable at room temperature.

A successful attempt [43] of the synthesis of combined diradical **18** comprising a triarylmethyl and a galvinoxyl radicals opens up the prospects for using other combinations of stable radicals, which may substantially extend the area of search for organic magnets.

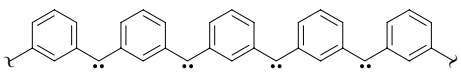
Modes of interactions of unpaired electrons in TAMT tri- and tetraradicals have been considered in reviews [3,13] and experimental data for these radicals are presented below.

2. Theoretical background for the development of magnets based on triarylmethyl type radicals

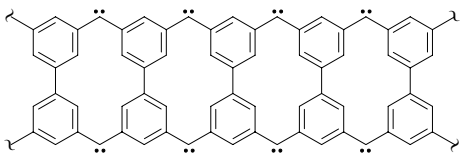
Judging by the number of references, an important role in drawing the attention of researchers to the design of organic ferromagnets belongs to the theoretical publication by Mataga.[48] He was the first to propose planar high-spin two-dimensional hydrocarbon structures constructed from triphenylmethyl radicals (**19**) or from triplet diphenylcarbenes (**20** and **21**) as potential precursors of organic magnets. It can be seen that coupling of the unpaired electrons in structures **19**, **20** and **21** occurs through the *meta*-position of the phenyl rings, as in the Schlenk diradical (**1**). The Leo triradical (**22**), which can be considered as a repeating unit for system **19**, should have $S = 3/2$, according to the known Ovchinnikov rule.[49] For structure **19**, the possibility of magnetic ordering at finite temperatures was demonstrated [50] in the framework of the Ising model; for an exchange integral of ~0.05 eV, the critical temperature should be ~1000 K. In an ensemble of one-dimensional chains of methyl radicals, the magnetic order can arise theoretically at a finite temperature only in the case where interchain exchange interactions are taken into account.[50] In a publication,[51] a critical review of the theoretical studies on linear organic ferromagnets is given and the possibility of stabilisation of the ferromagnetic ordering in linear chains of methyl radicals bound through the *meta*-positions of the phenyl rings is demonstrated using the density of states method. In the polymers where the methyl radicals are bound by *para*-phenylene bridges, the density of states method predicts pairing of the neighbouring spins to give quinonoid structures. For the polymer with quinonoid and benzenoid types of conjugation resulting from the pairing of spins, a high electrical conductivity upon doping has been predicted.[51]



19



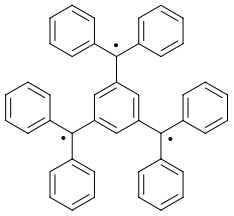
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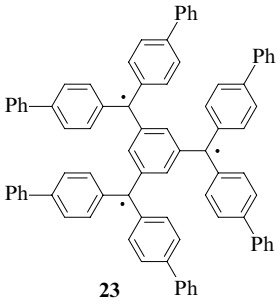
21

3. The Leo triradical and its analogues

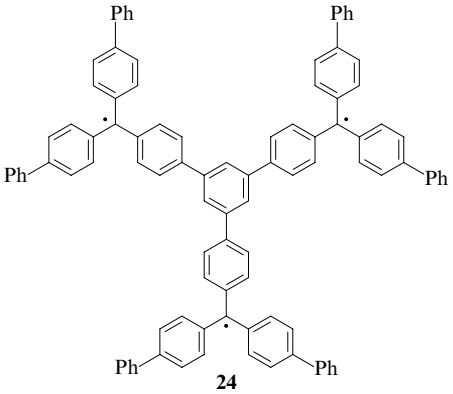
The first attempt to synthesise triradical **22** (without the purpose to design organic magnets) dates back to 1937. Subsequently, it was found that the Leo radical (**22**) exists in solution mainly as diamagnetic tetramers, monomeric species in the quartet state ($S = 3/2$) being present only in minor amounts.[52] Analogues of the Leo radical, compounds **23** and **24**, were prepared and shown, by EPR spectroscopy, to have the quartet ground state.[53, 54]



22



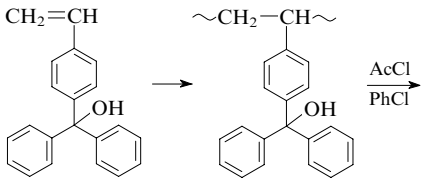
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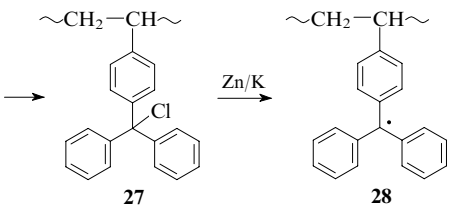
24

4. Triarylmethyl type radicals in polymers

The first successful experiments on the synthesis of polyradicals based on TPMR in polymers were reported by Braun *et al.*[55–58] and partially surveyed in a review [59] and a book.[60] Polymerisation of 4-vinyltriphenylmethanol (**25**) gave poly(*p*-vinyltriphenylmethanol) (**26**), which reacted with acetyl chloride in chlorobenzene to give poly(*p*-vinyltrityl chloride) (**27**). In order to obtain the expected poly(*p*-vinyltriphenylmethyl) radical (**28**), compound **27** was reduced with a zinc–potassium alloy.



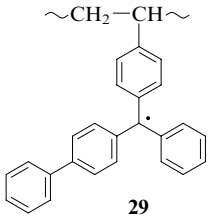
25 **26**



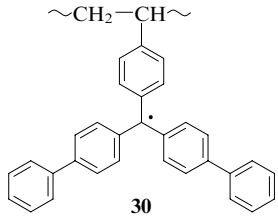
27 **28**

Polymer **26** and, correspondingly, polyradical **28** had a degree of polymerisation of 300–350. The highest yield (~10 radicals per molecule) was attained when the K/Na alloy was used. Polyradical **28** gave an EPR signal with poorly resolved hyperfine structure (HFS). Poor resolution of the spectrum was attributed to the interaction of radicals at their relatively high local concentration in macromolecular coils in combination with low splitting values for triphenylmethyl type radicals.

The same method was used to prepare poly(4-vinyl-4′-phenyltriphenylmethyl) radical (**29**) and poly(4-vinyl-4′,4″-diphenyltriphenylmethyl) radical (**30**). These polyradicals had degrees of polymerisation of 325 and 350 and were formed in yields of 40 and 100 radicals per molecule, respectively (in the reduction of polymers with the K/Na alloy at room temperature in benzene or THF).

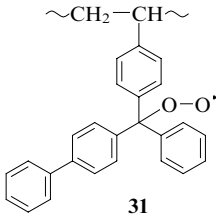


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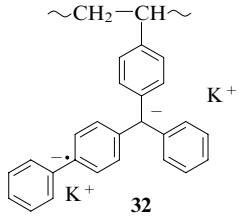


30

In the presence of oxygen, hydrocarbon radicals **28**, **29** and **30** form unstable peroxide radicals such as **31**; these readily react with the initial hydrocarbon radicals to give cross-linked polymeric radicals. For radicals **31**, a narrow smooth singlet was detected in the EPR spectrum (*g*-factor was not measured).



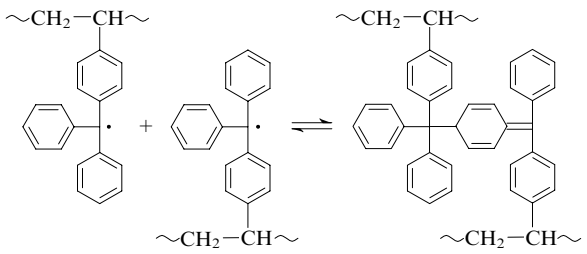
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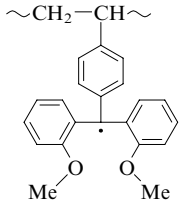
The use of the K/Na alloy results in high yields of radicals but leads to further reduction of the polymers to give carbanions; when the molecule contains biphenyl fragments, radical anions are formed, which can be detected by EPR and produce well-resolved spectra. The monomeric unit of polyradical **29** forms a doubly-charged radical anion, which can be represented as structure **32**. Unfortunately, Braun *et al.* did not report the electronic spectra of the polymeric radicals, carbanions or radicals but described only the changes in the solution colour during the reduction.

According to the views existing at that time, Braun believed in his early works that the radical centres of the polyradicals dimerise (both inside the coil and between the macromolecules) to give hexaphenylethane structures and that the dimers (non-radical species) and monomers (radicals) occur in equilibrium, which shifts, for example, toward the radicals as the temperature increases. This dimerisation equilibrium giving quinonoid structures can be depicted in the following way:[61]

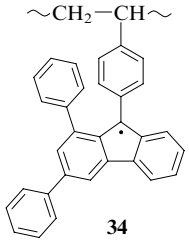


Dimerisation, resulting in a lower concentration of the radicals and giving rise to cross-linked polymers can be diminished by introducing bulky substituent into the *ortho*-position with respect to the unpaired electron. Polyradicals **33**–**37** were prepared [62] by a route similar to that described above, but chloro derivatives were reduced using mercury in order to stop the reaction after the formation of radicals. The least concentration of spins was found for polyradical **33**, because steric shielding by the methoxy groups

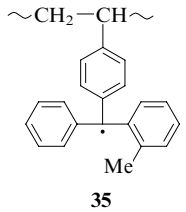
slightly influences dimerisation of the radical centres. This polyradical showed a resolved HFS in the EPR spectrum; this was attributed [62] to insignificant interaction of the radical centres due to their low concentration. The highest concentration of spins and the highest stability (the radical centres survived for at least several months) were found for polyradical **36**, which had a violet colour in benzene solution. The other hydrocarbon polyradicals obtained by Braun's research group were yellow or reddish. The high stability of polyradical **36** is due to pronounced delocalisation of the unpaired electron over the cyclopentadienyl ring and to steric shielding of the radical centre by five phenyl groups, which cannot fit in the plane of the pentadienyl ring due to the mutual repulsion of hydrogen atoms. The EPR signal for polyradical **36** is a smooth singlet only ~4 Œ wide, whereas for other polyradicals, the signal widths are ~10 Œ. Polyradical **37** was found to be 100% dissociated, fully non-cross linked and fairly stable.[62]



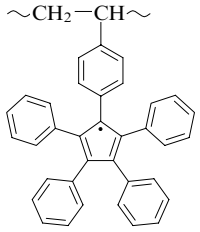
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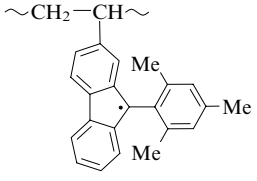
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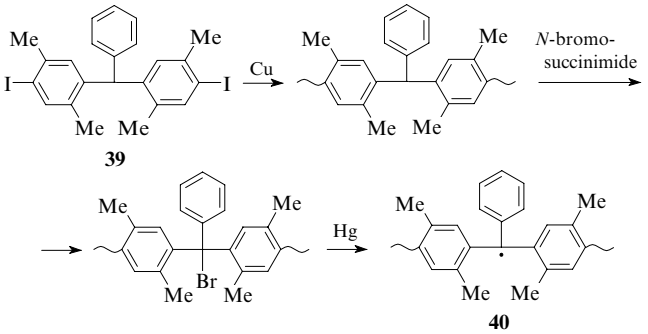


36



37

The polyradicals described above have unpaired electrons in the side chains of polymers. More interesting consequences of the interaction of radical centres in polyradicals should be expected for the case where they are located in the polymer backbone. Braun and Lehmann synthesised [63, 64] a number of polyradicals with triphenylmethyl type radical centers in the backbone. Bis(4-iodophenyl)phenylmethane (**38**) and bis(4-iodo-2,5-dimethylphenyl)phenylmethane (**39**) were prepared [63] and used as the starting compounds for the synthesis of polyradicals in which TPMR are linked by *p*-phenylene bridges. Compounds **38** and **39** were condensed according to Ullmann to give the corresponding polymeric hydrocarbons, which were then brominated with *N*-bromosuccinimide at the tertiary carbon atom. This was



39

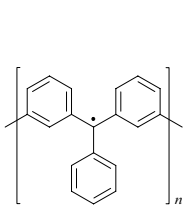
40

followed by generation of the triphenylmethyl type radicals. The bromo derivative obtained from compound **39** was reduced with mercury to the corresponding polyradical **40**.

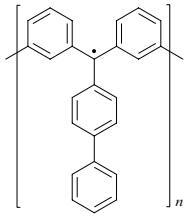
Analogous chemical transformations in the case of compound **38** resulted, as expected, in macromolecules **41** containing some triarylmethyl type radical centres apart from the quinonoid structures of the Chichibabin hydrocarbon type. A benzene solution of polymer **40** is yellow, the colour being due to the radicals, while a benzene solution of polymer **41** is deep-blue in thick layer and blue-green in thin layer. This colour was attributed [63] to quinonoid structures.

The EPR spectrum of a benzene solution of compound **40** is nearly a singlet (four HFS components can be distinguished) with a total width of 27.5 Œ; the EPR spectrum of a benzene solution of polymer **41** shows fairly well resolved 16 components with a splitting of ~1.5 Œ, the total width of the EPR signal being 29 Œ. For the polymers, precursors of polyradicals **40** and **41**, the number-average molecular masses (M) and the average degrees of polycondensation (P) were determined by osmometry: for compound **40**, M = 2300, P = 7; for compound **41**, M = 3970, P = 15. Polycondensation of compound **39** was accompanied by an undesirable side reaction, *viz*, cross-linking of fragments through the methyl groups.

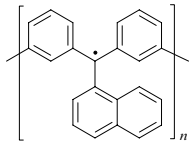
In order to avoid side reactions and annihilation of neighbouring radicals in the polymer, Braun and Lehmann synthesised,[64] by a similar route, polyradicals **42** – **44** in which the radicals are bound through the *meta*-positions of the phenyl groups.



42

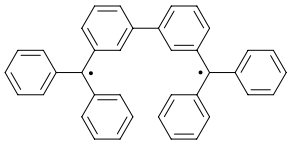


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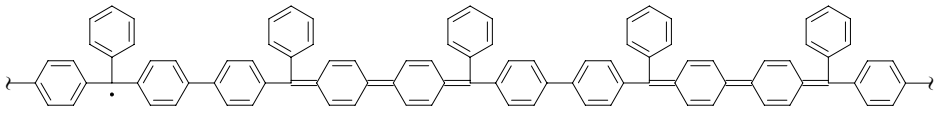
44

This gives a polymer with paramagnetic structures such as the Schlenk – Brauns hydrocarbon (**10**) in which, in the Braun's opinion, no formation of a quinonoid structure is possible.



10

The polymeric precursors of polyradicals **42** – **44** had average degrees of polymerisation of 5 – 8 and average molecular masses of 1640 – 1940. The EPR signal of polyradical **42** in a benzene solution has an overall width of ~31 Œ and splits into (at least) 19 lines; the colour of the solution is dark yellow. The EPR signal of the solution of polyradical **43** in benzene has an overall width of ~30 Œ and a poorly resolved hyperfine structure; the solution is violet. The EPR spectrum of a benzene solution of polyradical **44** has a total width of ~31 Œ and a poorly resolved hyperfine structure, and the solution is red-brown. In the absence of air, benzene solutions of polyradicals are stable for more than a month even in the light. On contact with oxygen, the solutions are rapidly decolourised and no longer give EPR signals. Braun and



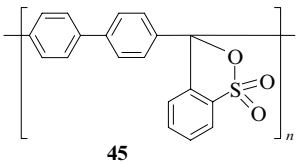
41

Lehmann [64] were unable to detect spin coupling in the polyradicals, which would produce broadening of the EPR spectra.[65]

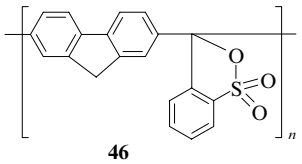
Thus, Braun's research group synthesised at least 13 polyradicals of the triarylmethyl type. Among compounds with radical centres in the side groups usually characterised by higher degrees of polymerisation (up to 350) than polyradicals with backbone radical centres, the highest concentration of radicals (nearly 100%) was found for compounds **36** and **37**. In the case of polyradicals with radical centres in the backbone, the degree of polymerisation was, most often, 5–8 and only in the case of compound **41**, it reached 15, *i.e.*, actually the obtained compounds were oligomers, and the yield of radicals in them was not estimated. Usually, the colour was indicated for polyradicals, but, unfortunately, in none of the cases, was the electronic spectrum reported. For all the obtained polyradicals, EPR spectra were recorded. No clear-cut manifestation of coupling (exchange, dipole–dipole, *etc.*) between neighbouring spins was noted for the polyradicals, except for some broadening of the spectral components, resulting in the loss of resolution. Usually, the EPR spectra of the polyradicals resembled the spectra of low-molecular-mass models, differing only in a poorer resolution. However, the loss of resolution in the EPR spectra may also be due to an increase in the viscosity of polymer solutions.

Film-forming cardo polymers, poly(arylenesulfophthalides) (PASP), are quite attractive for the generation of TAMT polyradicals and quinonoid structures; the synthesis and properties of these polymers have been reported.[66]

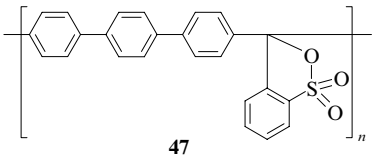
Poly(biphenylenesulfophthalide) (**45**), poly(fluorenylenesulfophthalide) (**46**) and poly(terphenylenesulfophthalide) (**47**) have been studied; alkaline hydrolysis of compound **45** gives polymer **48**.[67]



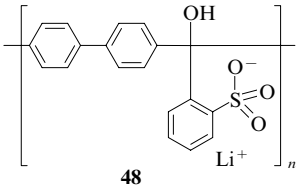
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46



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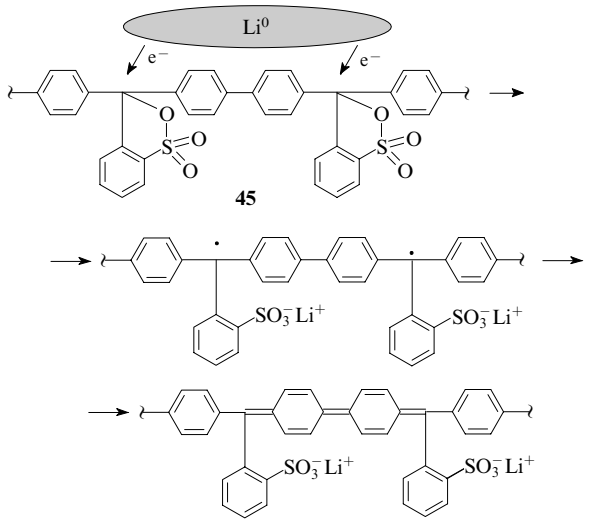
48

We have shown that the action of various physical and chemical factors on these polymers results in generation of the TAMT radicals and the quinonoid structures derived from them. First, the formation of TAMT radicals upon the thermolysis of polymers **45** and **48** was established.[68,69] The highest concentrations of the radicals ($\sim 10^{20}$ spin g^{-1}) were achieved for compound **48** at 280 °C and for compound **45** at 320 °C. At this concentration, one unpaired electron per ~20 polymer units is present. Upon thermolysis of polymer **48**, coupling of neighbouring TAMT radicals was observed as the formation of blue colour centres with an absorption band at 595 nm, which is attributable to the quinonoid structures like the Chichibabin hydrocarbon.

Quantum chemical PM3 calculations for the model diphenylsulfophthalide (DPSP) molecule show the presence of low-energy vacant orbitals and relatively large positive adiabatic electron affinity (1.76 eV), which should be favourable for the capture of electrons by the sulfophthalide ring. Indeed, DPSP is easily reduced by hydroxide ions on alkaline hydrolysis in DMSO to give triphenylmethyl radicals, as was detected [70] by EPR and electronic spectroscopy. The TAMT radicals and the derived quinonoid structures are also formed on the alkaline hydrolysis of PASP,[71] and in the complex system, PASP–aniline–cyclohexanone,[72] in which the mechanism of their formation is still unknown.

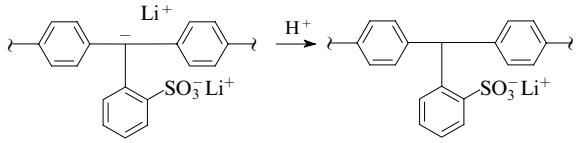
As expected, the reduction of these polymers with alkali metals proved to be an appropriate method for radical generation. The reduction of both dilute ($\sim 10^{-3}$ mol litre^{-1}) solutions of polymers **45**–**47** [73,74] and concentrated (~0.1 mol litre^{-1}) solutions of polymer **45** [75] in DMSO with metallic lithium at room temperature has been studied by spectroscopic methods. The results (for compound **45** as an example) can be summarised as follows.

1. The transfer of an electron from the lithium atom to the sulfophthalide ring having high electron affinity results in its dissociation to give a triarylmethyl radical and a salt group (distonic radical anion). The weak absorption band at 410 nm and a singlet in the EPR spectrum with $g = 2.0028$ and $\Delta H = 10$ Œ were assigned to the TAMT monoradicals. The neighbouring TAMT radicals give rise to the ChH type quinonoid structures responsible for the strong absorption bands at 568 and 350 nm.



2. The reduction of the quinonoid structures and triarylmethyl radicals gives rise to carbanions responsible for an absorption band at 640 nm.

3. This is followed by protonation of the carbanions to give the major final reduction product.



The reduction process of compound **45** comprises a sequence of electron and proton transfer reactions, resulting in a mixture of the intermediate and final products listed above. The ratio of the formation rates of these products ensures a high yield of the ChH type quinonoid structures. The predominant formation of one final reduction product (protonated salt form) attests to a single major reaction route.

The reduction of polymer **46** also gives TAMT radicals and ChH type quinonoid structures. The reduction of compound **47** with lithium does not give quinonoid structures but results in a high content of TAMT radicals (~100%) in the polymer backbone. This fact confirms good prospects of PASP for the synthesis and study of high-spin polyradicals. In the case of polymer **47**, the absorption bands at 430 nm (allowed transition) and 638 nm

(forbidden tranition) in the electronic spectrum and a singlet with $g = 2.0028$ and $\Delta H \approx 10$ Œ in the EPR spectrum were assigned to the TAMT radicals.

The possibility of reduction of films of polymer **45** and three poly(arylene phthalides) in the liquid ammonia–sodium system has been demonstrated.[76] Polyarylene phthalides are PASP-related polymers in which the labile sulfophthalide rings were replaced by more stable phthalide rings. The sulfophthalide and phthalide rings in these polymers are cleaved by solvated electrons to give TAMT radicals and quinonoid structures of the ChH type, which is confirmed by EPR and electronic spectroscopy. Poly(arylenephthalides) react with the NH_3 + Na system more slowly and the radical products of this reaction are less stable than in the case of compound **45**. Apart from TAMT radicals, the reduction of poly(diphenylenesulfophthalide) affords paramagnetic species that produce a singlet EPR signal with $g \approx 2.0028$ and $\Delta H \approx 4-5$ Œ, while the reduction of poly(diphenylenephthalide) yields paramagnetic species responsible for a singlet EPR signal with $g \approx 2.0047$ and $\Delta H \approx 4$ Œ.

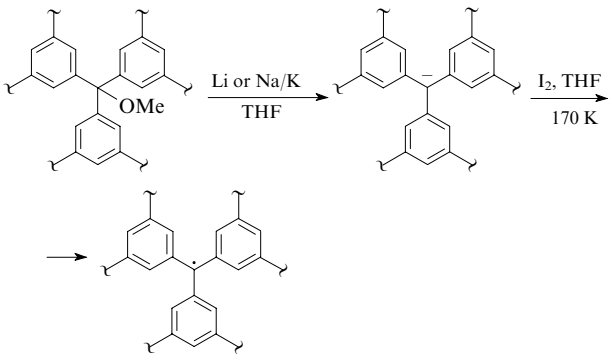
Low-temperature (77 K) γ-radiolysis of films of polymers **45**–**47** also gave rise to EPR singlets with $g = 2.0028$ and $\Delta H \approx 10$ Œ and electronic absorption bands at ~410–430 nm; it is beyond doubt that they refer to the TAMT radicals. In view of the radiolysis mechanism and the properties of PASP, it can be assumed with a high degree of probability that the TAMT radicals are formed upon dissociative capture of secondary electrons by the sulfophthalide ring. Whereas the reduction of compounds **45** and **46** yields mainly quinonoid structures derived from TAMT radicals, radiolysis of these polymers gives rise to single TAMT radicals, which is apparently due to the deficiency of secondary electrons under radiolysis conditions, *i.e.*, the probability that two secondary electrons occur in neighbouring sulfophthalide rings of the macromolecule is low.

It would hardly be possible to obtain practically valuable magnets from the linear polymers [poly(arylenesulfophthalides) and poly(arylenephthalides)] we consider. Nevertheless, the synthesis of relatively stable di- and polyradicals in these polymers is quite realistic. Good solubility in polar solvents and the possibility of their synthesis directly in the polymer films are promising properties of the polyradicals in PASP. Study of the properties of these radicals would evidently contribute to the views on the coupling of unpaired electrons in high-spin systems.

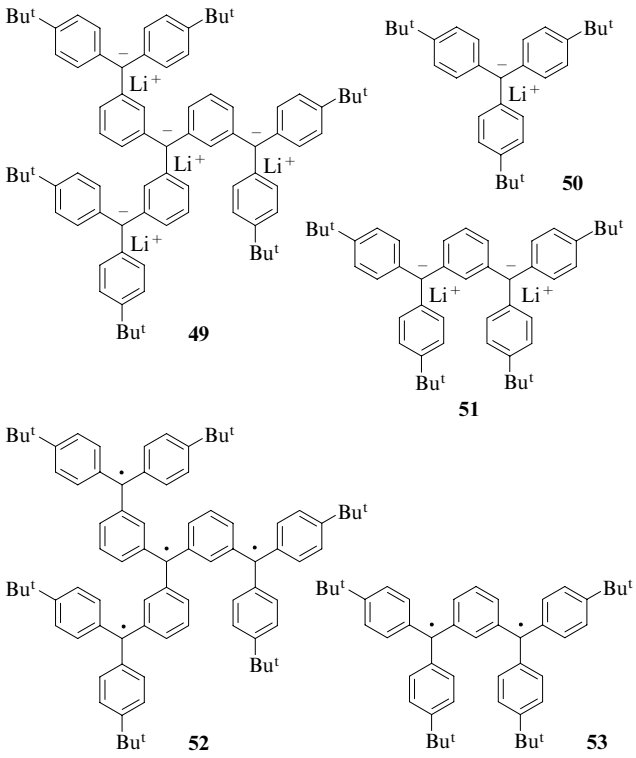
5. The latest achievements in the synthesis of triarylmethyl type polyradicals

a. Carbanionic method of synthesis

Apart from the diradicals mentioned above, Rajca's group (University of Nebraska, Lincoln) prepared a large number of polyradicals based on the Gomberg radical in which record values of the total spin were repeatedly attained. A 'carbanionic' method for the synthesis of triarylmethyl type polyradicals was developed.[32, 77] According to this method, an appropriate polyether is prepared and reduced with an alkali metal in an ether type solvent (most often, THF) to the polyanion, which is then oxidised with iodine to the polyradical.



The synthesis and the properties of polyanions **49**–**51** were reported,[77] and the preparation and some properties of tetraradical **52** and diradical **53** were described.[32] Subsequently, Rajca used this method relying on Mataga's ideas on polyradical polymers to synthesise the first plastic magnet in the world.

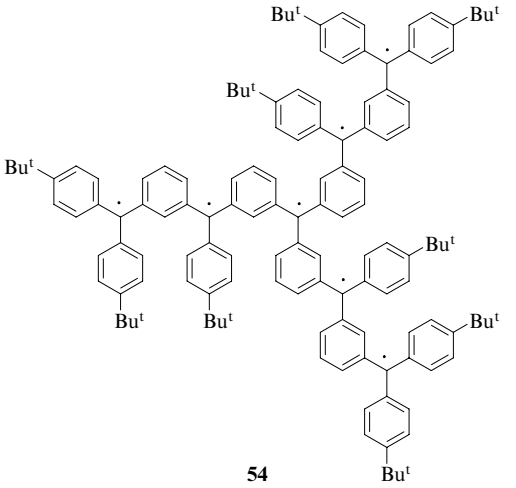


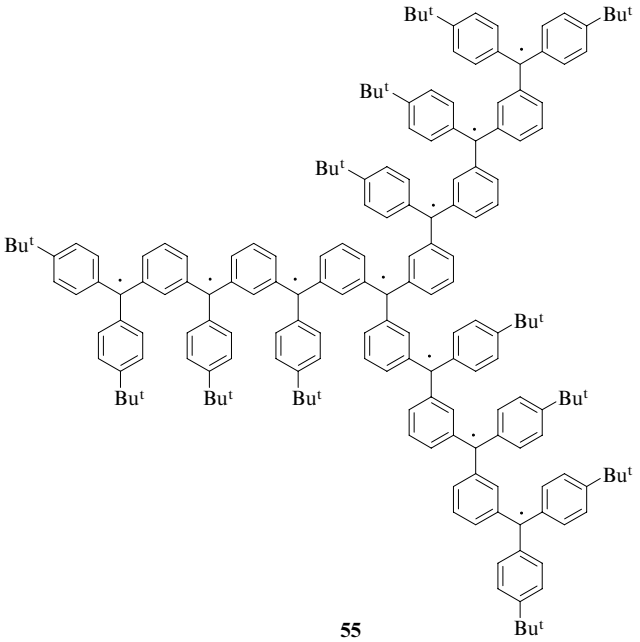
b. Star-shaped and dendritic polyradicals. The role of defects

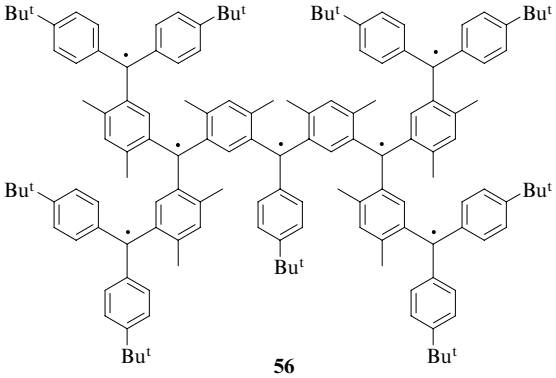
Star-shaped homologues of tetraradical **52**, namely, heptaradical **54** and decaradical **55**, having the highest spin states (7/2 and 5, respectively) among the radicals known at that time, have been synthesised.[78] EPR studies (at 100 K) and magnetic susceptibility measurements by NMR (at 150 K) showed that the heptaradical with $S = 7/2$ and the decaradical with $S = 5$ were the predominant species. The magnetic susceptibility measurements on a SQUID magnetometer gave lower values, $7/2 > S > 5/2$ [radical **54** in 2-methyltetrahydrofuran (MTHF) at $T \geqslant 5$ K] and $S = 4$ (radical **55** in THF at $T = 10$ K). Presumably, the lack of a noticeable amount of other paramagnetic species (thermal population of low-spin excited states) implies that both polyradicals have high-spin ground states with a strong intramolecular ferromagnetic coupling. Low-temperature magnetic susceptibility measurements for these polyradicals show weak intermolecular antiferromagnetic coupling at $T \leqslant 5$ K for heptaradical **54** and at $T \leqslant 20$ K for decaradical **55**. In the study cited, the decrease in the spin has not yet been attributed to the inevitable presence of defects in polyradicals.

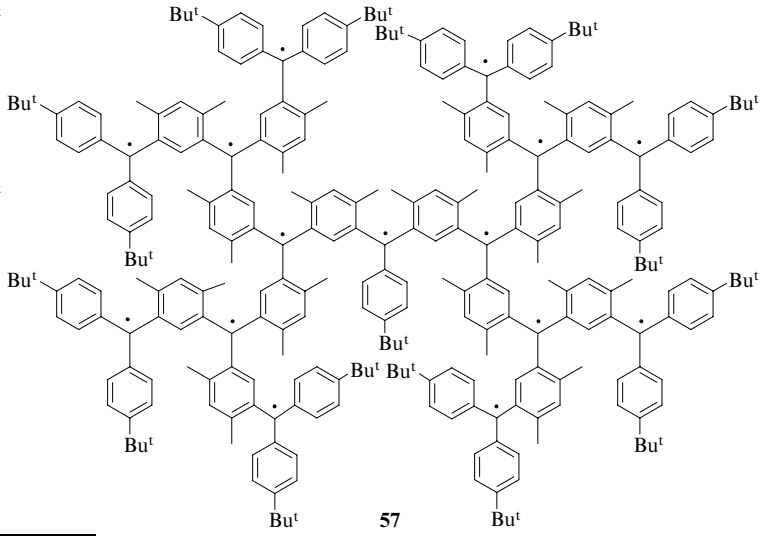
Owing to lower sensitivity to defects, dendritic molecules should surpass the usual linear macromolecules as regards the spin order. Nevertheless, dendritic heptaradical **56**, pentadecaradical **57** and polyradical **58** with 31 radical centres synthesised by Rajca and co-workers had average total spins of only 3, 7/2 and 5/2, respectively, instead of the expected 7/2, 15/2 and 31/2.[21, 22]

Among other reasons, the lower spins may be due to either chemical defects (an atom or a chemical group instead of the unpaired electron) or topological defects (interruption of the ferromagnetic coupling caused by unfavourable spatial arrangement of orbitals with neighbouring unpaired electrons). Generally, the common spin coupling is highly sensitive to both types of defects, as they break the exchange interaction paths. For example, an internal defect present in pentadecaradical **57** divides it into three non-interacting parts with lower total spins, which markedly









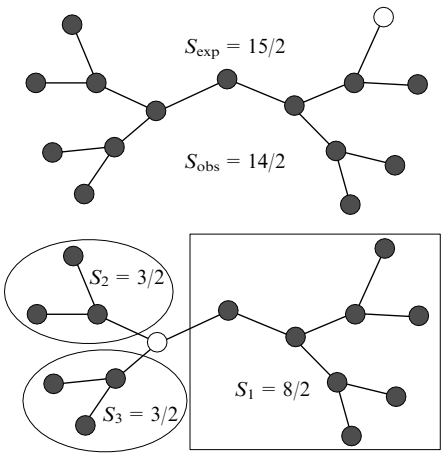


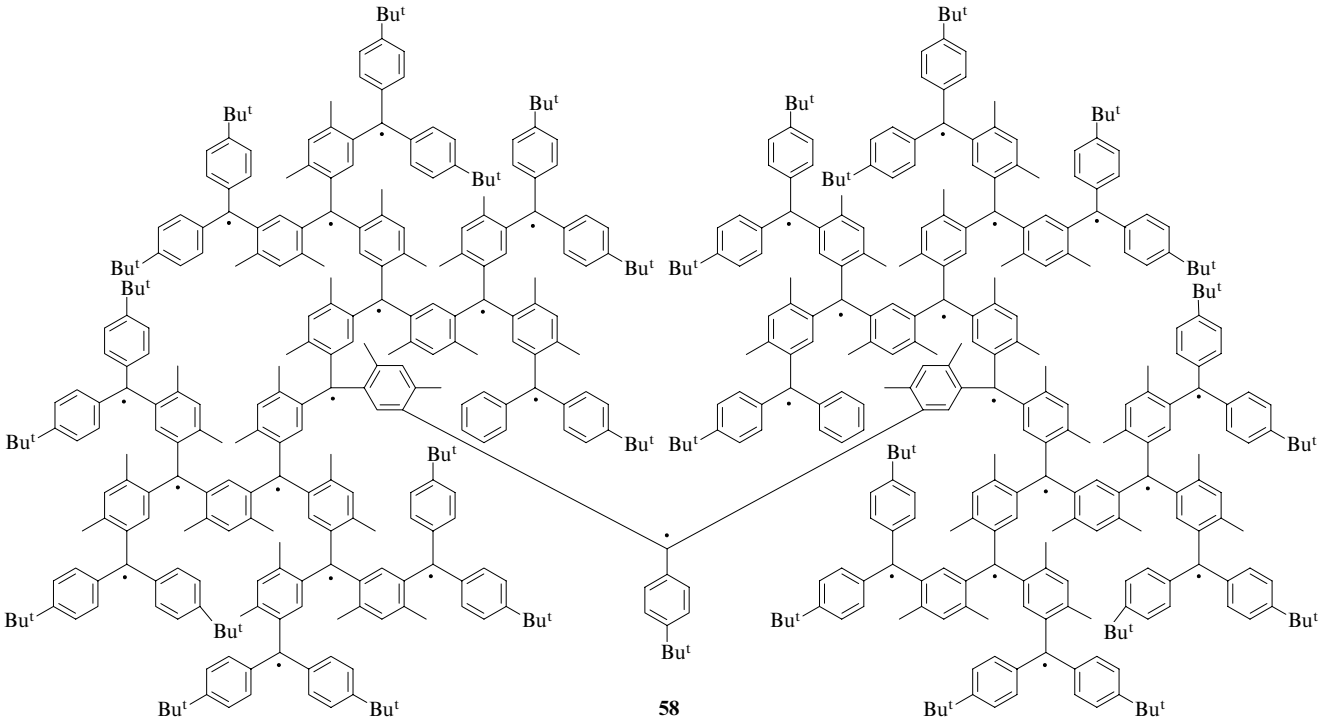
Figure 4. Effect of the defects on the total spin S of dendritic pentadecaradical **57**.
Light circles are defects; dark circles are unpaired electrons; lines are ferromagnetic coupling units.

decreases the effective total spin of the whole polyradical (Fig. 4). The peripheral defects have a less pronounced effect on the total spin.

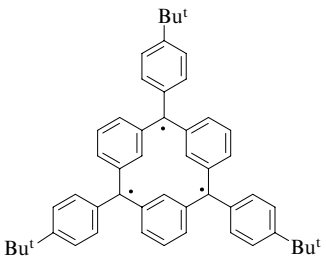
c. Macrocyclic polyradicals

Rajca decided to avoid the problem of defects by designing polyradicals of the macrocyclic calixarene type, which should have low sensitivity to spin defects owing to multiple paths of spin coupling. The calix[3]arene triradical **59** and calix[4]arene tetraradical **60** were synthesised.[79] It is clear that in the presence of one defect in the ring, exchange interaction between the spins is retained. It was found that triradical **59** readily dimerises, probably, due to insufficient steric shielding. The steric shielding in calix[4]arene **60** was sufficient for its stabilisation, and out-of-plane distortions were slight, which allowed the ferromagnetic spin coupling to be retained. It was concluded[79] that these macrocycles may be suitable as building blocks for polyradicals with low sensitivity to defects.

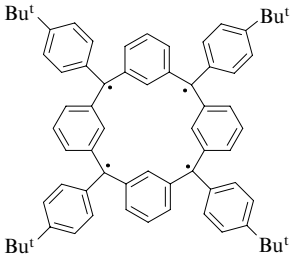
Highly annulated polymacrocyclic systems are rather difficult to synthesise; however, Rajca's group have obtained, for example, trimacrocyclic tetradecaradical **61** and demonstrated that both π-conjugation and ferromagnetic spin coupling are retained in this



58

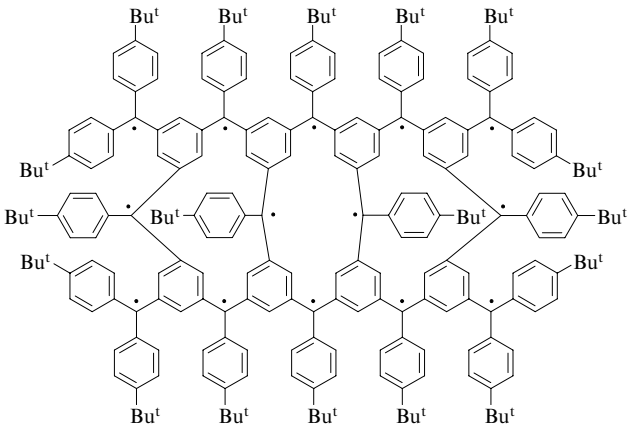


59



60

species even in the presence of defects.[80] A study of this polyradical in the THF-d_8 – MTHF system by SQUID magnetometry gave $S = 6.2$, which is lower than the theoretical value of 7 expected for a strong ferromagnetic coupling of 14 unpaired electrons.

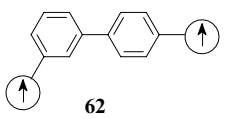


61

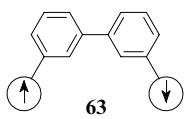
An analysis of the products obtained by quenching of the polycarbanion corresponding to polyradical **61** with methanol showed that the insertion of approximately one deuterium atom per polyradical from the solvent (THF-d_8) is one of the reasons for the appearance of defects and the decrease in the spin. A study of the temperature dependence of the magnetisation showed that the ferromagnetic coupling between the spins is relatively weak, probably, due to the out-of-plane distortion of the π-system. It is noteworthy that structure **61** can also be represented in a different way (see Section IV.5.d); the picture given here better represents the strain of the system, while the other representation is more economic and reveals more clearly the three rings. In another publication,[80] where Rajca summarised all his experimental results, he concluded that successful design of 2D and 3D ferromagnets requires that three factors be taken into account: π-conjugation; binding that complies with ferromagnetic coupling; and steric shielding for radical stabilisation. The strategy of organic synthesis should meet these conditions.

d. Spin clusters based on triarylmethyl type radicals

In principle, any polyradical can be considered as a spin cluster, as was actually done by Rajca in his early works where he analysed the spin states of the synthesised TAMT di- and polyradicals using the Heisenberg Hamiltonian. Subsequently, it has been proposed[81,82] to design high-spin organic polyradicals as simple spin clusters consisting of high-spin modules with strong intramodule ferromagnetic coupling J' connected to each other by relatively weak inter-module ferromagnetic coupling J, the J value being comparable in magnitude with the thermal energy, *i.e.*, $J' \gg J \approx kT$. This splitting into modules and the introduction of a hierarchy of exchange interactions markedly simplified the problem of determination of the energy spectrum of the cluster (polyradical) and, hence, analysis of its magnetic characteristics (magnetisation, susceptibility, *etc.*). To construct high-spin clusters from the macrocyclic and dendritic blocks proposed previously in which 1,3-phenylene or benzene-1,3,5-triyl units were used as 'strong' FCU, Rajca chose biphenyl-3,4′-diyl bridges **62** as an alternative to *meta*-phenylene bridges. In a study of the properties of diradical **9**, it was found that units **62** are ferromagnetic with weak coupling capable of additional stabilisation of radicals.[37] The properties of diradical **11** imply that the biphenyl-3,3′-diyl bridge **63** is an antiferromagnetic coupling unit, which, however, can also be used to construct ferrimagnetic high-spin clusters.

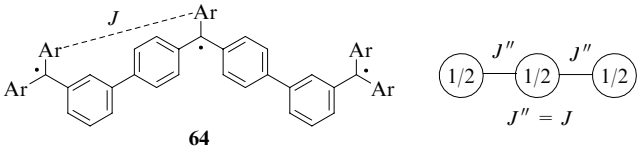


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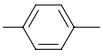


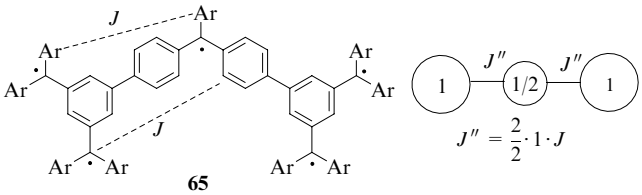
63

Using the Suzuki cross-coupling,[83] Rajca and co-workers synthesised[82] spin clusters **64**–**67**, in which the intra-module ferromagnetic coupling through 1,3-phenylene units was much stronger than the inter-module coupling through biphenyl-3,4′-diyl (or biphenyl-3,5,4′-triyl) units. An estimate based on the hyperfine coupling in the triphenylmethyl and (biphenyl-4-yl)diphenylmethyl monoradical gives $J:J' \approx 1:6$. In addition, Rajca carried out energy scaling for the inter-module ferromagnetic coupling J'' in each cluster, according to the approach described earlier.[84] This scaling takes into account the number of coupling paths (1 path for biphenyl-3,4′-diyl and 2 paths for biphenyl-3,5,4′-triyl units) and the fraction of directly interacting spins from neighbouring modules. Polyradicals **64**–**66** have only one site where a single defect can interrupt the spin coupling, whereas polyradical **67** has two such sites. This can potentially be a hexadecaradical with $S = 8$; according to magnetic measurements, the spin value was high, $S = 7.2$, *i.e.*, the yield of generation of unpaired electrons for this polyradical reached 98%. Subsequently, using the Negishi cross-coupling reaction,[85] polyradical **68** with the total spin $S = 10$ was synthesised.[86]

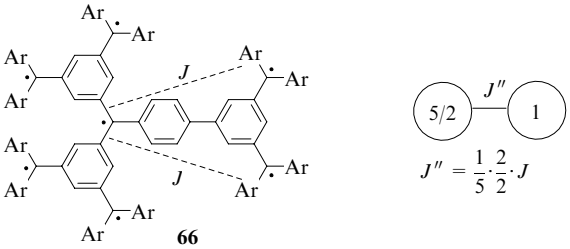


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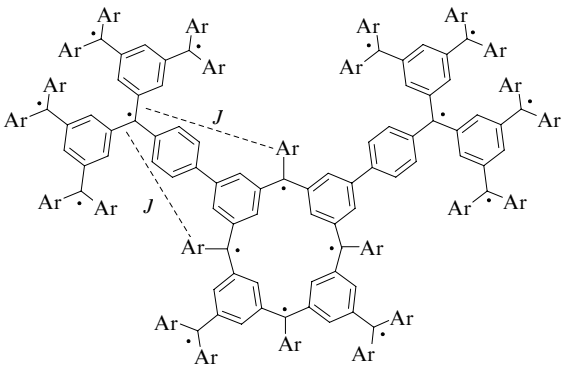
Hereinafter, Ar = Bu^t .



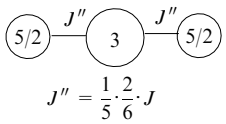
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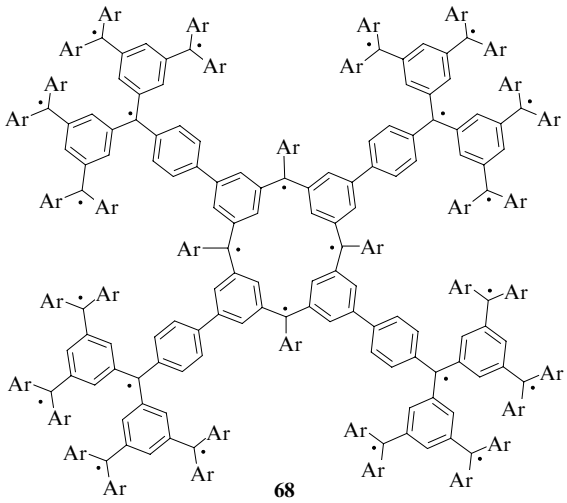


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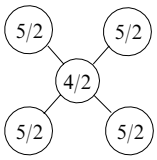


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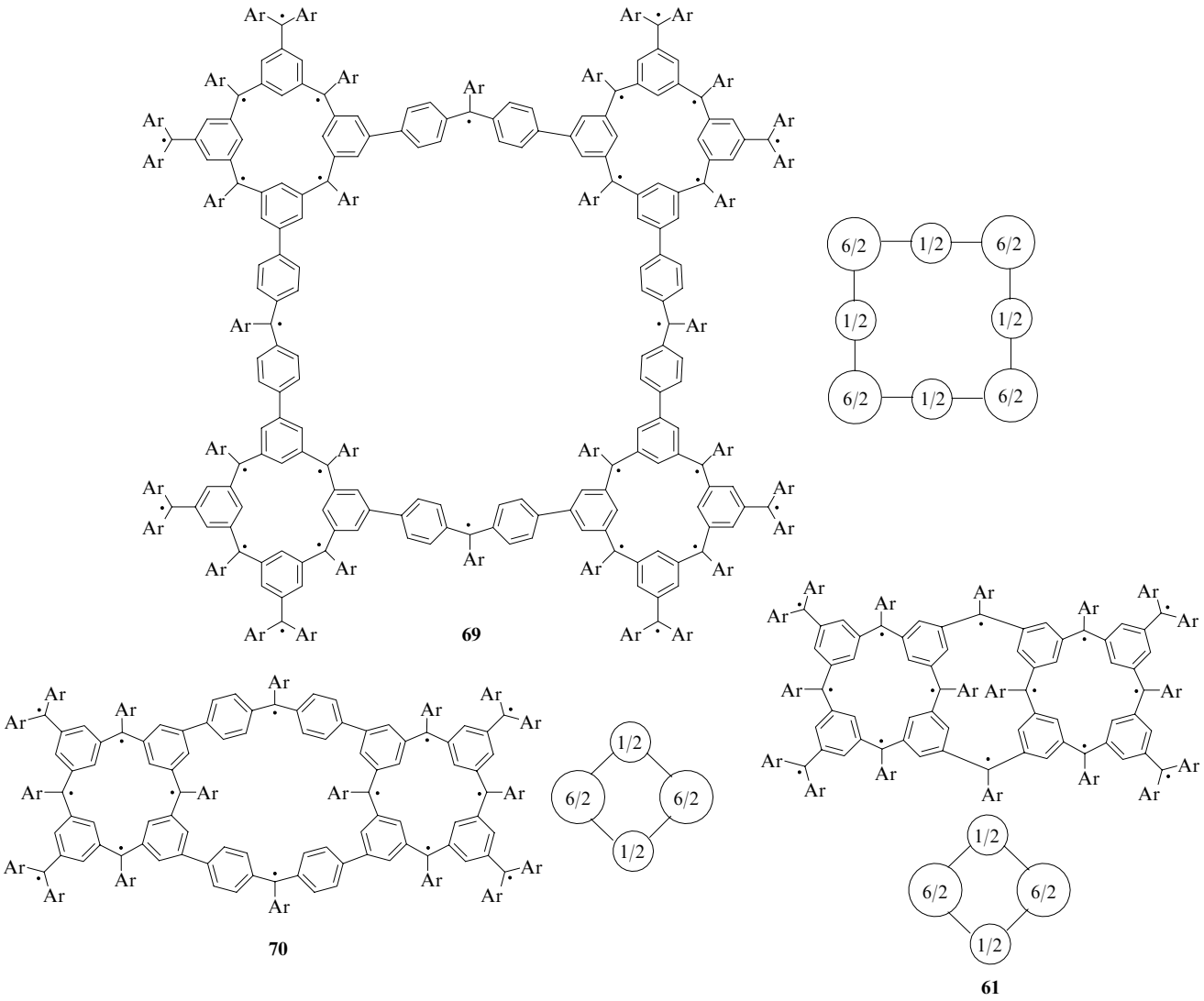
68



Four dendritic branches and the macrocyclic core of this polyradical form a ferromagnetically coupled pentamer, four terminal modules of which have $S = 5/2$, while the central fragment has $S = 2$. Theoretically, the total spin of polyradical **68** should be equal to 12. The dependence of magnetisation M on the H/T value (H is the magnetic field strength, T is temperature) gives $S \approx 10$ at 5 K. At that time (1998), this was the record-breaking value of the total spin.

More recently, spin clusters **61**, **69**–**74** based on TAMT radicals were synthesised and the properties of these clusters and the corresponding polyether precursors were studied.[87–89]

The polyether precursors of the polyradicals were obtained by a multistep block-synthesis in which the key step was the Negishi cross-coupling of four monofunctional dendritic blocks with modules and a tetrafunctional calix[4]aryl-containing macrocyclic core for (compounds **68** and **72**), of difunctional calix[4]arene-containing macrocycles (for annulated structures **61**, **69** and **70**) and of mono-, di- and tetrafunctional calix[4]arene-containing macrocycles with (aryl)bis(4-halophenyl)methoxymethyl linking units (for polyradicals **71**, **73** and **74**). The target polyethers were isolated from the reaction mixtures by chromatography. The corresponding polycarbanions were then synthesised and oxidised to polyradicals in THF-d_8. The polyradicals thus formed were classified as spin clusters, their structures are given near the formulas. Some properties of these clusters and the starting polyethers are summarised in Table 2. The saturation magnetisation and the magnetic susceptibility values for all polyradicals reported in the studies cited[87–89] indicate that ~40%–60% of unpaired electrons are present at low temperatures ($T = 1.8$–5 K) and confirm the presence of high-spin ground states. Analysis of the S values and the mole fractions of the unpaired electrons (M_{sat}) suggests that ferromagnetic coupling predominates in these polyradicals. Nevertheless, significant antiferromagnetic coupling is also present and, together with chemical defects, it decreases the S and M_{sat} values with respect to the theoretical ones. It is believed that detailed interpretation of magnetic measurements becomes more complicated due to the possible presence of conformations with different exchange (ferro or antiferro) interactions, different methods of averaging for the measured values (S, M_{sat} and χT) and the possibility of incomplete transfer of the sample mass during experiments. In some cases (for polyradicals **68** and **72**), the magnetic data are described satisfactorily by the Heisenberg model for magnetic interactions in the cluster. For polyradical **70**, the magnetic characteristics

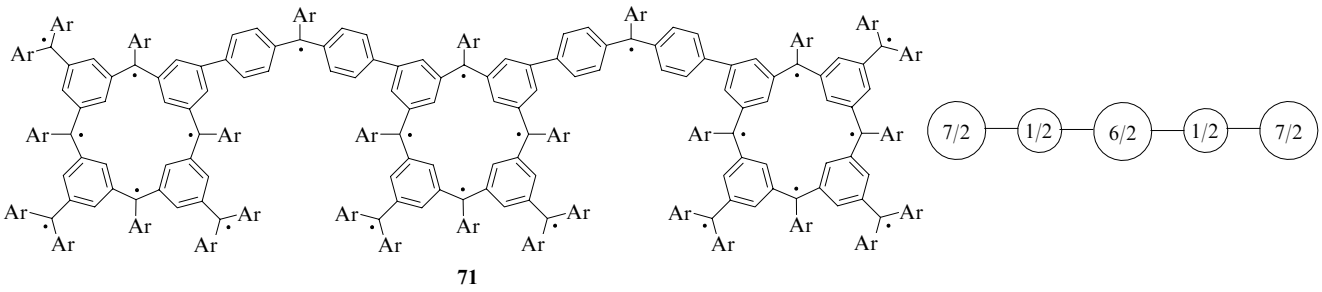


varying with temperature also comply with the model based on the Heisenberg Hamiltonian; however, this model is no longer applicable to the description of low-temperature data varying with the magnetic field. In relation to spin trimer **73** and pentamer **71**, a two-parameter percolation model of organic spin clusters with a chaotic distribution of chemical defects and alternation of ferro-

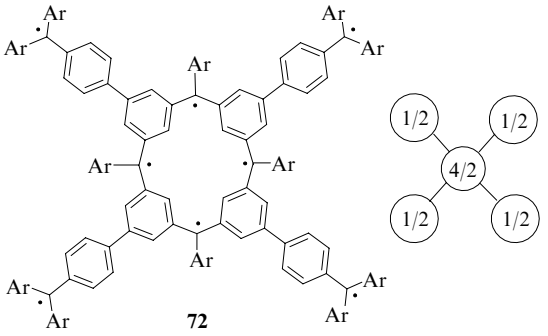
Table 2. Some physicochemical and magnetic characteristics of spin clusters and their polyether precursors.

Cluster	$[M-OMe]^+$ /Da	R_g /nm [b]	S_{exp} [c]	S_{theor} [d]	M_{sat} /μ_B [e]	χT_{max} /emu K mol^{-1} (see [f])	M_w /kDa [g]	J/k /K [h]	Ref.
68	7001	1.5	10	12 (24)	0.5–0.7	35–45	–	7	86, 88
69	~7780	1.7	~10	14 (28)	~0.56	~46	10.5	–	89
70	3874	–	~6–7	7 (14)	~0.6	~16	4.9	12 (−9)	89
71	6117	1.3	7–9	11 (22)	~0.6	~30	7.5	–	87
72	–	–	3.6–3.8	4 (8)	0.81	7.3	–	34	88
73	4165	1.2	5–6	7.5 (15)	0.6	15–16	~5	–	87
74	10022	1.8	11–13	18 (36)	0.4–0.6	21–86	12	–	87
78 [i]	–	3.2	~18	>28 (>56)	~0.5	~2	29–33	–	89

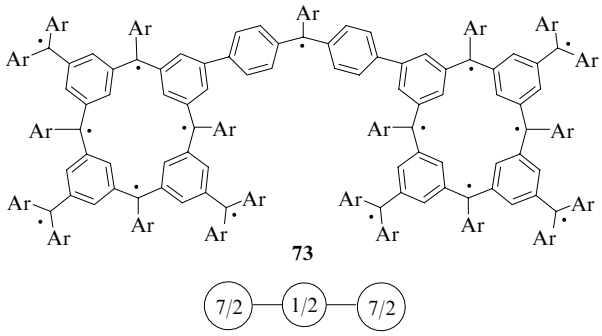
[a] $[M-OMe]^+$ is the mass of the positive ion formed upon abstraction of one ether group in the fast atom bombardment mass spectrum of the polyether; [b] R_g is the rotation radius of the polyether molecule determined in small angle neutron scattering (SANS) experiments; [c] S_{exp} is the average total spin of the polyradical determined mainly from representation of the SQUID magnetometry data by a linear combination of the Brillouin functions; [d] S_{theor} is the maximum possible total spin of the polyradical under ferromagnetic coupling of unpaired electrons, the values in parentheses represent the numbers of possible triarylmethyl fragments in the polyradical, *i.e.*, the greatest number of unpaired electrons; [e] M_{sat} is the saturation magnetisation (a 1 μ_B value corresponds to one unpaired electron per triarylmethyl fragment); [f] χT_{max} is the maximum value of the product of the magnetic susceptibility into temperature in the χT *vs*. temperature curve; [g] M_w is the weight average mass of the polyether determined by gel permeation chromatography with large angle light scattering; [h] J/k is the spin–spin coupling constant corresponding to pair interaction of spin cluster components in the Heisenberg model; for polyradical **70**, the possibilities of both fully ferromagnetic and fully antiferromagnetic coupling (data in parentheses) were considered; [i] for information about this compound, see Section IV.5.e.



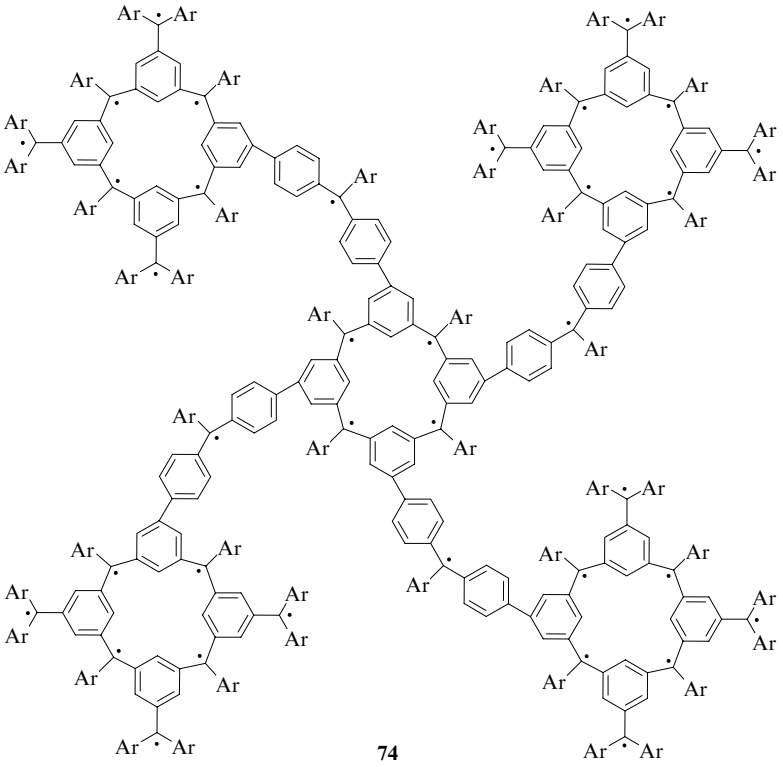
71



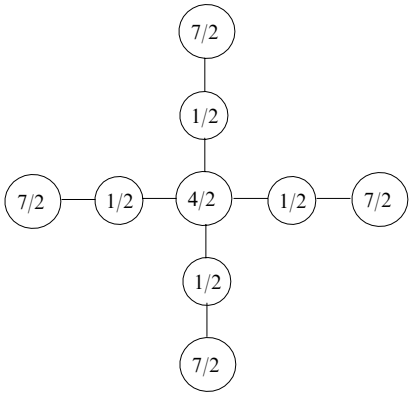
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73



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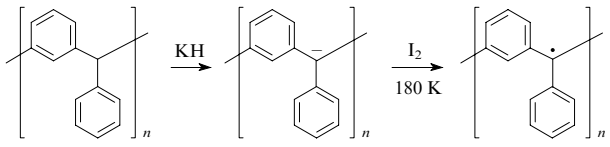
magnetic and antiferromagnetic coupling has been developed.[87] This model ensures a quantitative agreement between the experiment and the theory both for the clusters in question and for other spin clusters studied previously.[87–89]

The value $S = 13$ achieved for nonamer **74** is now the record value for organic molecules.

For polyradical **68** (with the average spin $S = 10$), the size and the shape were estimated by the SANS method (see Table 2); the barrier to magnetisation reversal [Eqn (1)] determined by the shape anisotropy is rather low (about 0.001 K). It has been assumed[87] that macromolecular polyradicals with S values of about $10^3 - 10^4$ similar to polyradical **68** as regards the shape and spin density distribution would behave as SMM at easily attainable temperatures $T > 2$ K.

e. Polymeric polyradicals of the triarylmethyl type

It is clear from the preceding sections that Rajca's group achieved great progress in the synthesis of diradicals and clusters; however, the synthesis of macromolecular polyradicals like the Mataga polymer **19** still remained the main goal of researchers. In 1993, high-spin linear polymer **75** was obtained.[90]

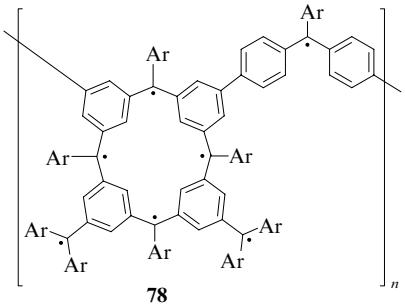


76 **77** **75**

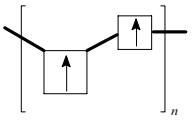
Polyradical **75** was generated by the carbanionic method from polyarylmethane polymer **76** containing ~30 triarylmethane centres per macromolecule. The EPR spectrum of compound **75** recorded in MTHF or THF at 4 K in the region of $\Delta m_s = 1$ is a singlet; a weak signal is observed at $\Delta m_s = 2$, which implies the presence of high-spin species with $S \geqslant 1$. Magnetisation measurements for solutions of polyradical **75** at 10 K give $S = 2$, which indicates ferromagnetic interaction of at least four unpaired electrons, although some length distribution of exchange-coupled segments exists most likely in the polymer chain. The interruption of spin interactions in the chain is due to defects, which may be caused by partial protonation of polycarbanion **77**, its oxidation, intra- or intermolecular cross-linking of polyradical **75**, *etc*. This case clearly demonstrates the sensitivity of linear chains to chemical defects; it is this fact that stimulated Rajca to turn subsequently to dendritic and macrocyclic polyradicals. It was also found that at 5 and 2 K, $S < 2$. The decrease in the 'effective' spin of the polymer at low temperatures was attributed to the antiferromagnetic coupling between polymer chains. The same coupling results in a negative deviation of the plot for the product of magnetic susceptibility and temperature *vs*. temperature from a straight line at $T < 10$ K. This was the only attempt of Rajca's group to synthesise a linear one-dimensional triarylmethyl type polyradical.

A ferromagnetic – ferrimagnetic coupling scheme based on the non-equivalence of spin modules in the clusters has been used [89] to prepare two high-spin polymers **78** and **79** containing calix[4]arene macrocycles.

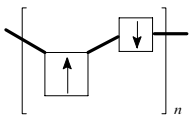
Polymer **78** in which macrocycles with $S = 3$ are linked by bridges with $S = 1/2$ can be regarded as a 'quasi-linear' chain of inequivalent spins with $S = 3$ and $S = 1/2$. It was found that polyradical **78** obtained from polyether with $M = 30\,000$ is characterised by an average S 18 at low temperatures. This value differs substantially from S of about 50 – 60, which would be expected if all the unpaired electrons were involved in ferromagnetic coupling and if no chemical defects were present. However, $S \approx 18$ is still higher than the best value $S \approx 5$ attained for other high-spin organic polymers. Some characteristics of polymer **78** are also presented in Table 2.



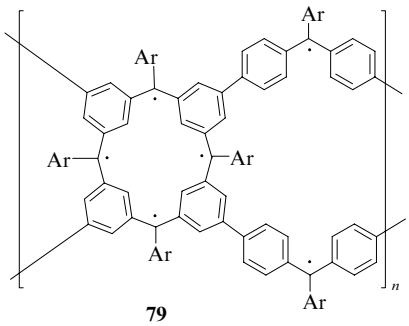
78



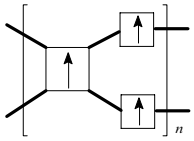
Ferro $S = 3.5\,n$



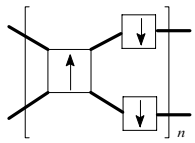
Ferri $S = 2.5\,n$



79



Ferro $S = 3\,n$



Ferri $S = n$

f. The first plastic magnet

Similarly to polymer **78**, the cross-linked polymer **79** can be considered as a network of non-equivalent spins, in particular, macrocyclic modules with $S = 2$ and linking modules with $S = 1/2$. The polyradical **79** synthesised [91] from the soluble fraction of the polyether with $M = 300\,000 - 500\,000$ has on average $S \geqslant 40$. The S value for polymer **79** obtained from insoluble polyether fractions which form a gel with THF-d_8 depends on the polymerisation time after gelation. If polymerisation stops near the gelation point (10 – 30 min), polymer **79** has $S = 600 - 1500$; for longer polymerisation times (5 h), the values $S = 3000 - 7000$ were attained.[92] It was found that at low temperatures, ~50% of unpaired electrons are present. This fact is consistent with the views on inevitable presence of chemical defects and with the scheme of combination of ferro- and ferrimagnetic coupling. It should be borne in mind that structure **79** is rather arbitrary, as macrocyclic modules may form diverse structures during condensation and detailed analysis of the final insoluble polymer is almost impossible. In particular, polyradicals **61**, **69** – **74** have been considered [87 – 89] as possible fragments of a plastic magnet **79**.

Conjugated organic polymer **79** was the first to exhibit magnetic properties other than merely paramagnetism. The magnetic ordering in this polyradical is switched on at ~10 K; for a typical sample with $S = 5000$, a sharp increase in the magnetisation (by two orders of magnitude) is observed. Below 10 K, magnetisation increases very rapidly with strengthening of the applied magnetic field and almost reaches saturation at relatively low fields. The saturation magnetisation for polymer **79** is ~10 emu g^{-1}, which is close to the paramagnetic saturation magnetisation for the poly(arylmethyl) polyradicals prepared previously. At a zero and low magnetic fields (about the Earth magnetic field), magnetic blocking was found, *i.e*., a substantial barrier to the magnetisation reversal was observed. Magnetic susceptibility studies in alternating fields gave a barrier of ~15 K and showed that very high magnetic moments ($S \approx 5000$) are frozen at low ($\leqslant 10$ K) temperatures with some degree of ordering (cooperativity). Generally, the magnetic properties of polymer **79** can be classified as being intermediate between the properties of non-conducting spin glasses and blocked superparamagnets but they are closer to spin glasses.[92] As regards the magnetic behaviour, polymer **79** resembles known organic low-molecular-mass magnets, although the temperature of ordering in the polymer is higher.

6. Perchlorinated triarylmethyl type di- and polyradicals

Ballester [93, 94] has shown that perchlorinated di- and triphenylmethyl radicals synthesised by his group are fully monomeric both in solution and in the solid state and have high thermal stability and unique chemical stability, due to the essential localisation of the unpaired electron on the central carbon atom and considerable steric shielding of this atom. The first perchlorinated diradicals **80** [94] and **81**,[95] which are as chemically inert as the monoradicals, were also obtained.

The electronic spectrum and the EPR spectrum of compound **80** do not virtually differ from the corresponding spectra of the perchlorinated TPMR; in particular, the EPR spectrum of this diradical does not manifest the magnetic dipole – dipole coupling. Thus, the radical centres in diradical **80** do not interact with each other, despite their relative geometric proximity. This fact can be attributed [96] to the perpendicular arrangement of the benzene rings in the biphenyl bridge and, correspondingly, complete elimination of the conjugation between the unpaired electrons. Apparently, the localisation of unpaired electrons highly pronounced for perchlorinated radicals also plays a role, because partially chlorinated diradical **82** in which the benzene rings in the bridge are also nearly perpendicular has a singlet ground state (Table 3) and its EPR spectrum does exhibit [97] magnetic dipole –

Table 3. Some properties of perchlorinated and mixed di- and triradicals of the triarylmethyl type.

Diradical	$10^3 \lvert D/hc \rvert$ /cm^{-1}; $10^3 \lvert E/hc \rvert$ /cm^{-1}	Ground state [a]	Ref.
80	–	–	94
81	–	–	95
82	7.2; ⩽0.3	S	97
86	⩽10; ~0	–	98, 99
87	⩽3; ~0	–	98, 99
meso-**88**	15.2; 5.1	T (>0.2)	100
(D,L)-**88**	8.5; ⩽0.3	T (>0.2)	100
89 [b]	16.5; 4.7 (A)	T	100
	7.4; ~0 (B)	T	
	9.2; ~0 (C)	T	
90 [b]	3.6; ~1 (A)	Q	101
	5.0; ~0 (B)	Q	
91	5.5; 0	T (0.02)	102

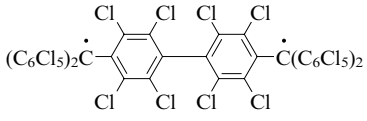
[a] The energy differences between the singlet and the triplet states $\lvert \Delta E_{ST} \rvert$ (kcal mol^{-1}) are given in parentheses. [b] Letters A – C designate different conformers of these radicals.

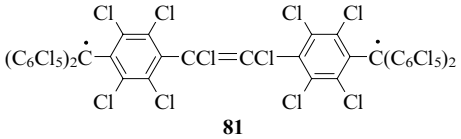
dipole interaction for thermally excited molecules in the triplet state.

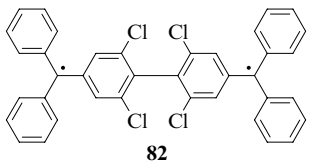
The interaction between the 'halves' of diradical **82** is also manifested in a bathochromic shift of the absorption bands in its electronic spectrum with respect to the spectrum of the model monoradical. In the vinylene perchlorinated diradical **81**, the steric restrictions are less pronounced (the benzene rings in the bridge are not perpendicular) and in this case, spin – spin exchange can be observed as a twofold decrease in the coupling constant of the unpaired electrons with the ^{13}C nuclei.

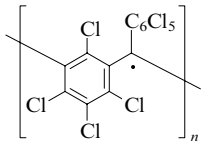
Naturally, Ballester's followers (Veciana's group) proposed [98, 100, 103] a strategy for the synthesis of linear and dendritic perchlorinated polyradicals of types **83** – **85** as a possible base of organic magnets.

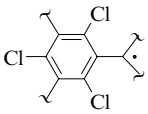
Radicals **86** – **90** have been synthesised and studied by spectroscopic and magnetic methods (see Table 3). Mixed diradicals **86** and **87** in which perchlorinated triphenylmethyl radical centres are connected by hydrocarbon bridges retained the thermal and chemical stability typical of perchlorinated radicals but the intramolecular magnetic dipole and exchange interactions of the unpaired electrons in them proved to be fairly weak.[98, 99] The nature of the ground state for diradical **87** has not been elucidated;[98] for diradical **86**, the ground state is singlet, however, according to another publication,[99] the nature of the ground state cannot be regarded as definitely established for both diradicals. The greater D value and the greater bathochromic shifts of the absorption bands in the electronic spectrum of diradical **86** compared to diradical **87** are believed [98] to be due to more pronounced delocalisation of unpaired electrons with *para*-bridg-

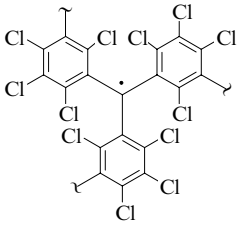

80

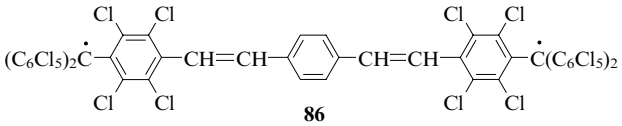

81

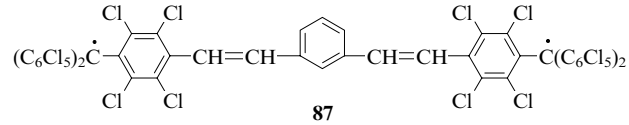

82

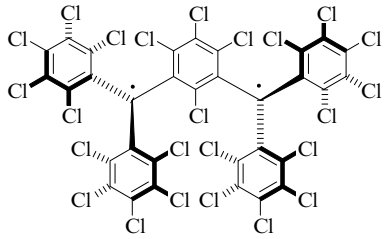

83

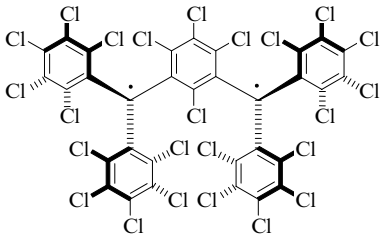

84

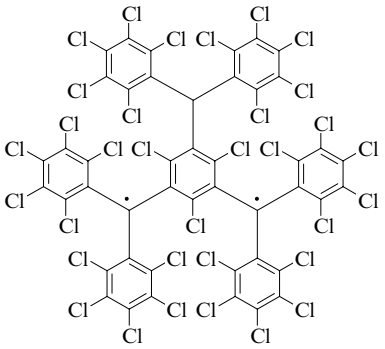

85

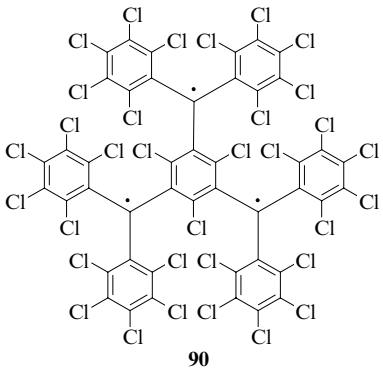

86

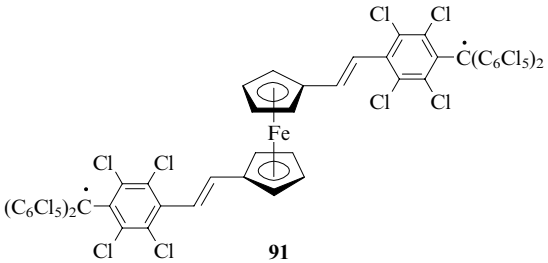

87


(D,L)-**88**


meso-**88**

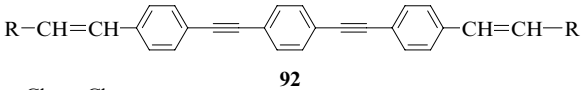

89


90

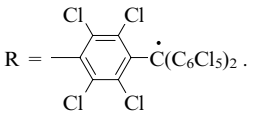

91

ing. The weak spin coupling in these diradicals is obviously due to the large length of the bridges, which actually comprise three benzene rings and two double and four single bonds. In the AM1-optimised structures of the diradicals, the through-space and through-bond distances between the radical centres are 18.8 and 24.1 Å, respectively for diradical **86** and ~16 and 22.7 Å, respectively, for diradical **87**. It is worth noting that the distance between the spins determined from the parameter D in the point dipole approximation is 19 Å for diradical **86** and 22 Å for diradical **87**, *i.e.*, electron delocalisation in the *para*-coupled divinylphenylene bridge reduces the effective separation of spins in **86**.[99] Subsequently, diradicals **88**, **89** and triradical **90** in which the unpaired electrons were located much more closely to each other than in **86** and **87** have been prepared.[100, 101] Radicals **88**–**90** were prepared by oxidation with chloranil of the corresponding carbanions, which were generated by treatment of hydrogen-containing precursors with $Bu^n_4N^+OH^-$. The presence of bulky *ortho*-chlorine atoms in the di- and triradicals thus formed brings about great steric restrictions to the rotation of pentachlorophenyl groups, which results in coexistence of various stereoisomers separated by high energy barriers (~24 kcal mol^{-1}). Full stereochemical analysis of compounds **88**–**90** was carried out; signals of separate conformers were identified in the experimental EPR spectra. Interpretation of the spectra was possible by virtue of isolation of the conformers by chromatography or recrystallisation. EPR spectroscopy and magnetic susceptibility and magnetisation measurements have shown that all conformers of these radicals have high-spin ground states, which are separated from the low-spin excited states by energy barriers substantially exceeding 200 cm^{-1}. For example, diradical **89** has a triplet ground state and is stable in air up to 250 °C. Thus, intramolecular exchange interactions in these radicals are ferromagnetic, *i.e.*, in this case, the perturbation by electronegative heteroatoms, the loss of planarity and symmetry changes have only a slight influence on the exchange interaction. It was concluded [100, 101] that the topological model developed for planar and unsubstituted alternant hydrocarbons may be applicable to highly distorted and substituted systems. However, as we have demonstrated above for the hydrocarbon diradical **6**, this is not always the case. Later, the limitations of this conclusion have been manifested in an attempt to synthesise a perchlorinated tetraradical (see below).

Veciana's group has synthesised and studied [102] diradical **91** consisting of two perchlorinated triphenylmethyl radicals linked by a ferrocene-1,1′-diyldivinyl bridge. A study of the temperature dependence of the intensity of the EPR signal of this diradical showed that it has a triplet ground state; the triplet–singlet splitting was determined using the Bleaney–Bowers equation.[104] Rather unexpectedly, weak antiferromagnetic coupling was manifested even in diradical **92** (Ref. 105) in which the distance between the radical centres reaches ~4 nm.

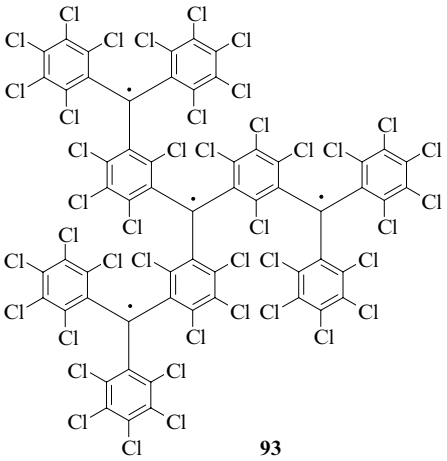


92



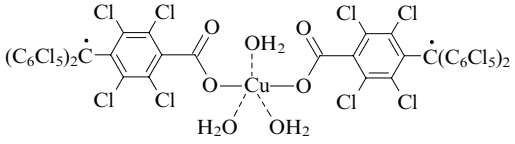
Attempts to synthesise perchlorinated polyradicals with $S > 3/2$ have faced so far inextricable difficulties due to steric overcrowding of polychlorinated compounds. The precursor of the dendritic perchlorinated TAMT tetraradical **93** was synthesised with great difficulty;[103] however, the attempts to obtain appreciable amounts of the tetraradical from this precursor have failed due to the formation of numerous chemical defects.

Subsequently, these results were critically re-evaluated [106] and it was concluded that a tetraradical in the chemical sense, *i.e.*, as a species containing four unpaired electrons, was actually synthesised in a high yield, but its quintet state with $S = 2$ was not manifested due to the magnetostructural (topological) defects, *i.e.*, transformation of a large portion of *meta*-phenylene FCU into ACU, which took place due to steric crowding of molecules **93**. This is why magnetic measurements for these compounds reveal mainly (96%) triplet species with $S = 1$ (Ref. 106).



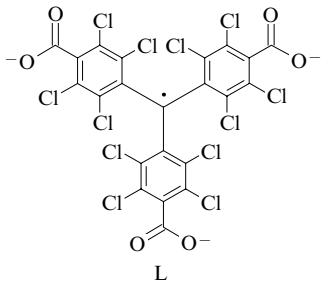
93

Unfortunately, the works on the synthesis of perchlorinated polyradicals have not been further developed as yet. Instead, another line of the use of polychlorinated stable radicals in the design of new magnetic materials is being actively developed. According to one more approach existing in the design of molecular magnets,[107] paramagnetic metal ions are combined with purely organic radicals, most often, iminoxyl radicals, as ligands. Four copper(II) complexes containing perchlorotriphenylmethyl radicals with carboxyl substituents as ligands have been prepared.[108] Magnetic susceptibility and magnetisation measurements for all complexes have shown the presence of fairly strong antiferromagnetic coupling between Cu(II) ions and two coordinated radicals. For example, for complex **94**, presentation of the magnetic data in the three-spin linear model gave $J/k_B = -24.9$ K.



94

Moreover, perchlorotriphenylmethyl radicals with three carboxyl groups as substituents were used to create [109] a polymeric magnetic nanoporous material $[Cu_3L_2(py)_6(EtOH)_2(H_2O)]_n$ in which the presence of large pores with linear dimensions of ~3 nm was combined with ferrimagnetic ordering at low temperatures (the structure of ligand L is shown below).



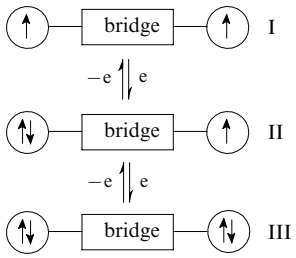
L

7. Mixed-valence compounds based on triarylmethyl type radicals

As shown above, almost all methods for the preparation of TAMT di- and polyradicals are related to the reduction of molecular precursors and oxidation of the resulting carbanions. These reactions often yield mixed-valence organic compounds in

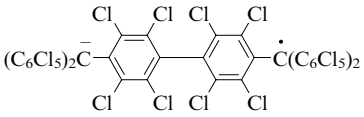
which intramolecular electron transfer (IET) is possible. The problem of intramolecular electron transfer in mixed-valence compounds and examples of this transfer in coordination and purely organic compounds have been discussed in a review.[110]

The transition from the diradical to doubly charged anion (and back) upon consecutive addition (abstraction) of electrons can be represented as follows:

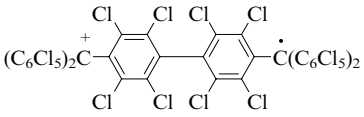


In the case of carbon-centred radicals in compound II on the left (anion), carbon is tetravalent while on the right (radical) it is trivalent, *i.e.*, this is a mixed-valence compound.

Ballester *et al.*[96,111] prepared the reduced (**95**) and oxidised (**96**) forms of diradical **80**, which retained the thermal and chemical stability.



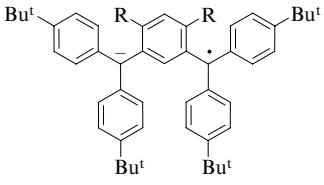
95



96

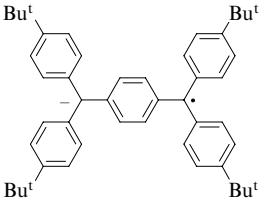
The twofold decrease in the ^{13}C coupling constants in the EPR spectra of compounds **95** and **96** with respect to the spectra of mono- and diradical shows the spin and charge delocalisation on an EPR time scale, *i.e.*, in these mixed-valence compounds, the perpendicular arrangement of the benzene rings in the biphenyl bridge does not prevent electron delocalisation.

A study of the HFS of the EPR signals of radical anions **97a** and **98** in the temperature range of 100–300 K indicates[112] that the unpaired electron spin density in the 1,3-coupled radical anion is localised on one triarylmethyl fragment, while in the 1,4-coupled radical anion it is delocalised over two triarylmethyl fragments. It was concluded that the arylmethyl fragments are strongly coupled through 1,4-phenylene and weakly coupled through 1,3-phenylene. The problem of the nature of the absorption bands in the electronic spectra of compounds **97a**,**b** at 740 and 770 nm, respectively, remains open, although it cannot be ruled out that they refer to electron transfer bands. Some properties of radical anions **97** and **98** are presented in Table 4.



97a,**b**

R = H (**a**), Pr^i (**b**).



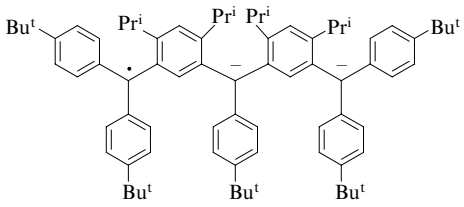
98

A question has been raised[113] of how an electron added to a chain of exchange-coupled (ferro- or antiferromagnetically) spins affects the interaction of the remaining unpaired electrons. This type of anionic defects can evidently occur in 'incompletely oxidised' polyradicals obtained from polyanions. To answer this question, oligomeric radical anions **99**–**102** were specially prepared and studied (Table 5).

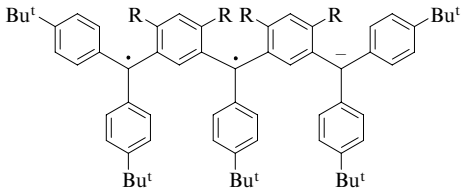
Table 4. Properties of radical ions based on triarylmethyl type diradicals.[112]

Compound	Ground state	a_H /Œ (see [a])	λ_{max}/nm
97a	D	2.65 (6H)	740
		1.15 (5H)	
		2.85 (1H)	
97b	D	–	770
98	D	1.3 (12H)	–
		0.65 (8H)	–

[a] Hyperfine coupling constant in the EPR spectra.

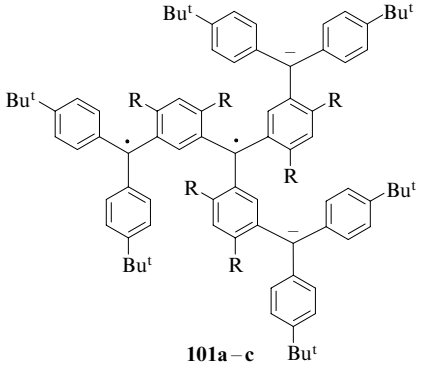


99



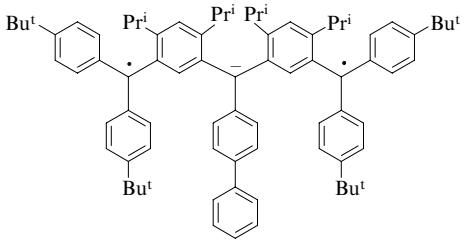
100a–**c**

R = H (**a**), Me (**b**), Pr^i (**c**).



101a–**c**

R = H (**a**), Me (**b**), Pr^i (**c**).



102

First, it was found that in all these compounds, the charge and the spin are localised on particular triarylmethyl fragments, as in compound **97a**. Second, it was demonstrated that if the charge (electron pair) is localised on a terminal fragment (compounds **100**, **101**), ferromagnetic coupling of the remaining unpaired

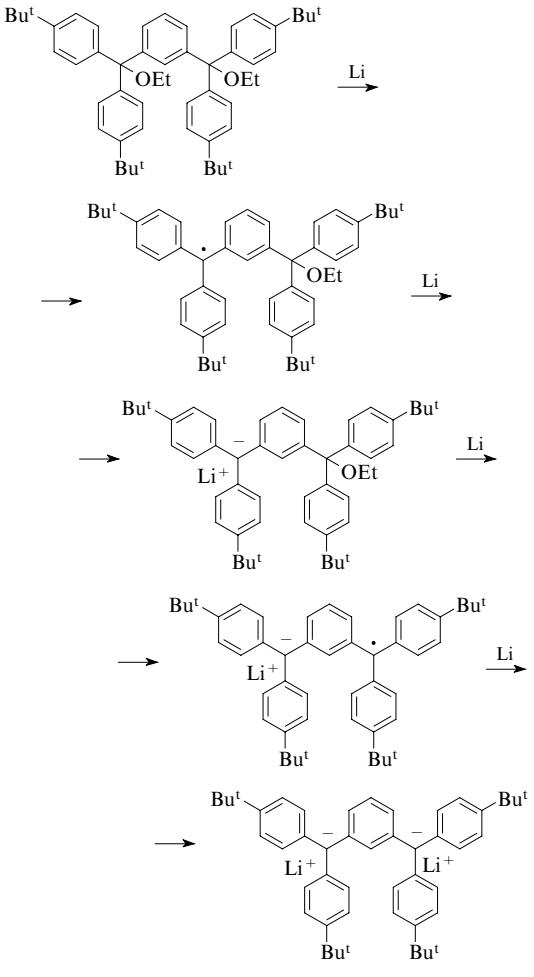
Table 5. Model oligomeric radical anions of the triarylmethyl type.[113]

Compound	$10^3 \lvert D/hc \rvert$ /cm^{-1}	Ground state [a]	λ_{max} /nm
99	–	D	–
100a	6.9; 5.0 (2 isomers)	T	–
100b	8.6	T	–
100c	9.6	T	~350 ~465
101a	7.1; 5.2	T	–
101b	9.5	T	–
101c	9.4	T	–
102	2.7	S (0.018)	~350 ~370 (shoulder)

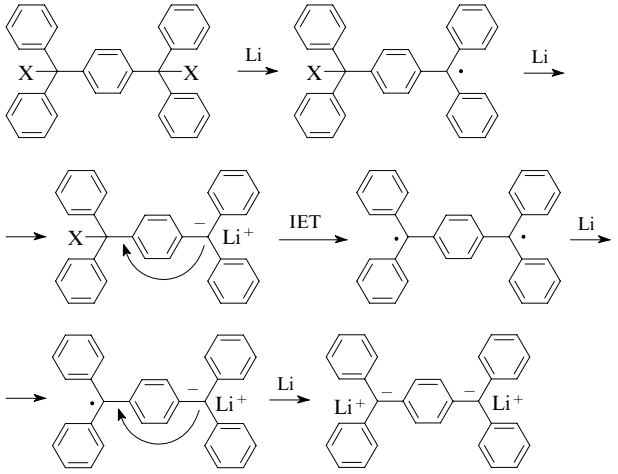
[a] The $\lvert \Delta E_{ST} \rvert$ value (kcal mol^{-1}) is given in parentheses.

electrons is retained. However, if the charge is concentrated on the central fragment (compound **102**), the remaining unpaired electrons are involved in antiferromagnetic coupling. Thus, spin coupling can be controlled by controlling charge localisation. Having summarised his own results and Ballester's data on radical ions **95** and **96**, Rajca put forward a hypothesis [3] that ferromagnetic or antiferromagnetic coupling in the starting polyradicals leads to electron localisation or delocalisation, respectively, in the obtained radical ions.

In view of the electron localisation in the 1,3-coupled compounds, Rajca proposed [112] the following mechanism for their reduction with metallic lithium:



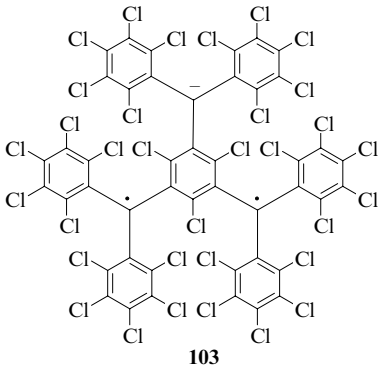
Presumably, intramolecular electron transfer processes would play an important role in the reduction of 1,4-coupled compounds.



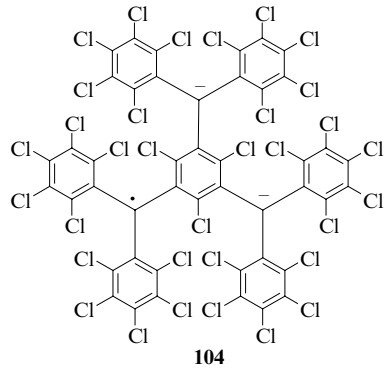
X is an electron-withdrawing leaving group.

This scheme does not show the formation of the quinonoid structure from the diradical. For the radical anion, the IET results in spin and charge delocalisation over two positions. Note that this scheme does not contradict the putative mechanism of the electroreduction of dihalo-*p*-xylenes.[114] In particular, the IET should apparently be taken into account when investigating the reduction of poly(arylenesulfophthalides) and poly(arylenephthalides) containing biphenyl-4,4′diyl and fluorenediyl bridges.

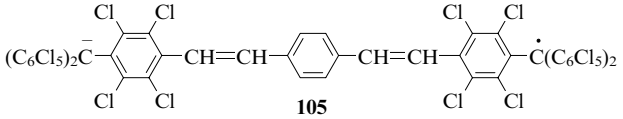
The IET processes were found for compounds **103**–**105** (Table 6) in which the perchlorinated triphenylmethyl carbanion acts as the electron donor, while the perchlorinated triphenylmethyl radical is the electron acceptor.



103



104

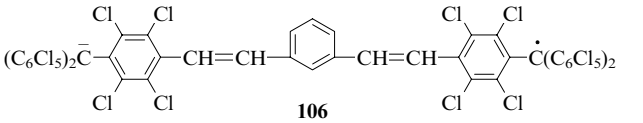


105

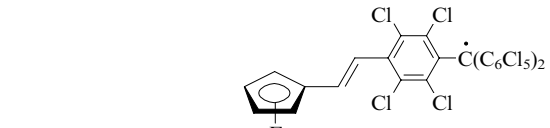
Table 6. Properties of the radical anion systems based on perchlorinated triarylmethyl type radicals.

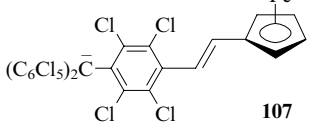
Compound	Ground state	a_H and a (^{13}C) /Œ	λ_{max} /nm	λ_{ET} /nm	V_{ab} /cm^{-1}	Ref.
103	T	–	368 508	~2900	320	115
104	D	–	368 508	~2900	390	115
105	D	1.9 (1H)	–	1400	121	99
106	D	1.8 (2H) 0.6 (2H)	– –	none	–	99
107	D	–		none	–	116
108	D	1.6 (1H) 29.3 (C_α)	– –	none	–	103, 116

In the near-IR region, broad intensive electron transfer bands typical of mixed-valence compounds were observed.[110] With known peak position (λ_{ET}) and the extinction coefficient at the peak, one can find the electron coupling parameter V_{ab} using the Hush formula. Compound **103** is the first example of a purely organic mixed-valence compound in which intramolecular electron transfer was found in addition to the high-spin ground state. In the case of compound **105**, a thermally activated IET was also observed [99] by EPR in the temperature range of 200 – 300 K, the activation barrier being 0.117 eV. For radical anions **106** – **108**, no intramolecular electron transfer was found.

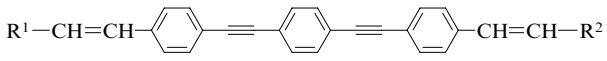


106

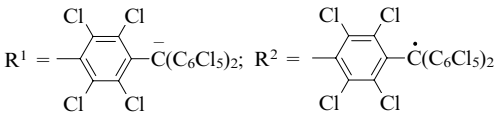




107



108



It can be seen from a comparison of compounds **105** and **106** that a *p*-phenylene fragment present in the bridge facilitates the electron transfer, while a *m*-phenylene fragment hampers the electron transfer, which is consistent, to some extent, with Rajca's data presented above. It is noteworthy that the problem of intramolecular electron transfer is tightly connected with the search for appropriate molecular wires for the various molecular devices;[110, 116] meanwhile, the bridges in compounds **103** – **105** can be regarded as molecular wires.

V. Conclusion

Polymeric polyradical **79** can apparently be considered to be the world first polymeric organic magnet. It took almost a hundred years to create such a magnet based on the first discovered stable hydrocarbon radical (the Gomberg radical). Generally, the achievements of Rajca's research group represent an example of deliberate consecutive work and the use of the whole power of the advanced methods of organic chemistry and physical techniques for substance investigation; however, these would be impossible without the preceding research into the TAMT mono-, di- and polyradicals.

Of course, Rajca's plastic magnet has only feebly pronounced magnetic properties and is far from being suitable for practical purposes. However, the ordering temperature of ~10 K is relatively high for organic magnets and confirms the great potential of the macromolecular approach to their design. The unavoidable presence of chemical and topological defects in the TAMT polyradicals also precludes the formation of ensembles of identical single-molecule magnets from these polyradicals. It is clear that the design of practically useful magnets requires the use of more stable radicals and the existence of magnetic ordering at room (or higher) temperature. A consistent application of Rajca's strategy to the synthesis of inert perchlorinated TAMT polyradicals may give organic magnets stable at room temperature; however, no data concerning any studies along this line are available to date.

As we have seen, the unsolved problems remain also in the studies of TAMT diradicals, even the best known ones such as the Chichibabin, Muller and Schlenk – Brauns hydrocarbons.

As regards the problem of organic magnets as a whole, it is quite possible that practically valuable organic magnets will be obtained in a quite unexpected way, for example, in the way the magnetic order was found at room temperature for the tetracyanoethylene complex with polyaniline.[117] However, it must be remembered that the magnetic properties of organic compounds are often due to ferromagnetic impurities (known examples can be found in a review [1]).

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