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New Data on Biradicals

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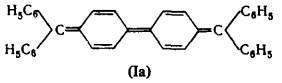
Data on biradicals, including both the results of studies by pre-1947 methods (static magnetic susceptibility, ortho-para conversion of hydrogen, etc.) and the results of studies on biradicals by electron spin resonance are reviewed. Biradicals of various types are discussed—biradicals in the singlet ground state which pass to a triplet state on excitation and biradicals in the triplet ground state which arise in consequence of the degeneracy of higher occupied levels, the presence of an insulating group between the monoradical components, atropisomerism, etc. A complete compilation is also given of all the data on biradicals with heteroatoms. The application of the electron spin resonance method to biradicals permitted an approach to the problems of the interaction of unpaired electrons in these systems. The theory of such interaction and the form of the spectra which should be obtained in its presence and absence are discussed. However, many studies on this interaction have proved erroneous because the data obtained did not refer to the substances to which the observed spectra were attributed but to the products of their further reactions—the formation of di- and poly-mers. These problems are not usually discussed in sufficient detail in physical papers on biradicals, while in the present review special attention has been given to them.

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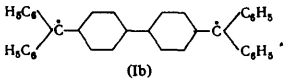
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I. INTRODUCTION

Advances in the modern theory of organic compounds include significant progress in the solution of the problem of biradicals. These are compounds, the molecules of which have, in contrast to monoradicals, an even number of electrons (so structures can be written for them with all electrons paired), but which nevertheless exhibit the properties of radicals, in this case "double" radicals. This term includes substances of three different types. The first includes ordinary molecules with a singlet ground state which can exhibit the properties of radicals because of the possibility of transition to an excited triplet state, so that there is an appreciable concentration of molecules in the triplet state in equilibrium with those in the singlet ground state. Such an approach to biradicals of this type made it possible to resolve the old controversy about whether compounds such as Chichibabin's [frequently spelt Tschitschibabin's (Ed. of Translation)] hydrocarbon have a quinonoid or benzenoid structure:

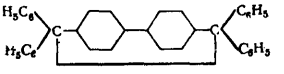


(Ia)

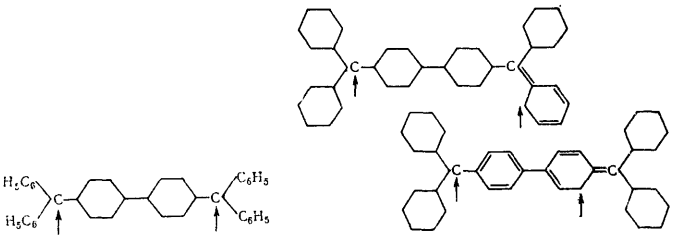


(Ib)

All the structures with the overall spin $S = 0$ (Ia) and others such as, for example,



have been represented in the singlet state, while the triplet state can be described as the superposition of the structures



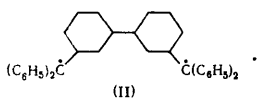
etc. For compounds of this class, the problem consists mainly in the detection of the triplet state and the explanation of the reasons for the relative ease of transition to the latter.

In any molecule with an even number of electrons a transition to the triplet state is possible in principle when the overall spin is equal to unity, i.e. there are two unpaired electrons. However, in the vast majority of organic compounds the excitation to the triplet state requires a very considerable energy and the equilibrium fraction of triplet molecules is low. The substances which exhibit the properties of biradicals are those in which the triplet state is separated from the singlet ground state by a relatively small energy difference. An attempt to account for such relations between the energies of substances of this type was made by Dyatkina and Syrkin [1] on the basis of calculations by the MOH method†. The authors postulated a correlation of the energy difference between the highest occupied and lowest free one-electron levels with the energy of excitation from the singlet to the triplet state. Strictly speaking these quantities cannot be regarded as identical. Calculations of the energy differences between the singlet and triplet states of the molecule as a whole require that the interelectronic repulsion be taken into account. Nevertheless the hypothesis of a parallel variation of the energies of the one-electron transition and the

† MOH—the molecular orbital method in Hückel's approximation.

energy of excitation to the triplet state agrees satisfactorily with the findings that the tendency towards the transition to the biradical state and the fraction of the biradical form in equilibrium clearly increase as the energy of the one-electron transition decreases.

The second type of biradicals constitute substances the molecules of which have a triplet ground state because of the degeneracy of the upper occupied levels, as should happen in cyclobutadiene and *meta*-quinonedimethane and substances such as the hydrocarbon of Schlenk and Brauns (II):



(II)

Cyclobutadiene and *meta*-quinonedimethane themselves have not been obtained. The hydrocarbon of Schlenk and Brauns and its analogues are probably dimers and the possible partial dissociation of such dimers at an elevated temperature does not present a special problem—it is fully included in the problem of the dissociation of dimers of monoradicals such as triphenylmethyl.

The third type of biradicals are molecules consisting of two parts each of which is an ordinary monoradical, but in which the overall molecule is constructed in such a way that the interaction between the unpaired electrons over a distance corresponding to a normal C–C π-bond is impossible because of the presence of an insulating group—for example, an oxygen atom, one or several $-CH_2$ groups, etc. This class includes substances which are formally derivatives of Chichibabin's hydrocarbon (I), but in which the two halves of the molecule are located in planes forming a considerable angle relative to one another due to the steric hindrance of the substituents, and this also prevents the interaction between the electrons of the two halves. With compounds of this type, the central problem is the question whether or not they consist of two completely independent halves, i.e. are in fact two radicals, or whether electron exchange takes place between the two components.

A review of information about biradicals which had accumulated towards the middle of the 1940's was published in 1947 by Dyatkina and Syrkin [2]. At that time the data on the biradical state were based mainly on measurements of static magnetic susceptibility. In some cases such data were confirmed by investigations of the ortho–para conversion of hydrogen.

However, the method of static magnetic susceptibility has considerable limitations. The magnetic susceptibility measured experimentally is the sum of two parts which have different signs: the diamagnetic and paramagnetic susceptibilities. In order to determine the paramagnetic susceptibility, it is necessary to subtract from the total susceptibility the diamagnetic component, which cannot be measured directly. Therefore the diamagnetic susceptibility is calculated from the increments corresponding to individual bonds or atoms. Such a procedure can involve considerable errors. When one deals with strongly paramagnetic substances, their paramagnetism obscures the diamagnetism to a large extent and experiment shows their behaviour to be paramagnetic. This is in fact the behaviour of organic substances when there is a large concentration of radical species, i.e. in the case of biradical molecules in the triplet state in which we are interested. The inaccuracy of the diamagnetic susceptibility may then lead to a small error in the numerical value of the paramagnetic susceptibility but does not prevent, in principle, the detection of radicals and biradicals. On the other hand, if the fraction of biradical species is small, the paramagnetic susceptibility corresponding to them may be extinguished due to the presence of a very large number of diamagnetic molecules. Then the substance behaves as a diamagnetic material, despite the presence of paramagnetic molecules. The fraction of such paramagnetic species, which are not taken into account, may reach 10%. This was in fact the reason for the prolonged controversy concerning the question of the presence of an appreciable fraction of biradical molecules in Chichibabin's hydrocarbon.

Furthermore, in the case of biradicals, apart from the equilibrium between the monomeric singlet and triplet molecules, there is a possibility of thermodynamic equilibrium between paramagnetic monomers on the one hand and diamagnetic dimers (or polymers) on the other. This is an additional complication, which makes it difficult to arrive at a conclusion concerning the concentration of biradicals on the basis of static magnetic susceptibility.

In biradicals there may be different degrees of interaction between the unpaired electrons—ranging from the case where the spins of the two electrons give a resultant spin equal to unity to those where the spins of both unpaired electrons are separated from one another and behave independently. These extreme cases correspond to different values of their magnetic susceptibility. (For $S = 1$, the magnetic moment $\mu = \sqrt{4S(S+1)}\mu_B = \sqrt{8}\mu_B$ and the magnetic susceptibility at 300°K is $N\mu^2/3kT = 3390 \times 10^{-6}$ e.s.u., while in the presence of two separated spins, each of the latter corresponds to a magnetic moment $\mu = \sqrt{3}\mu_B$ and the magnetic susceptibility is 1280×10^{-6} e.s.u., so that the overall susceptibility is 2560×10^{-6} e.s.u.). However, it is impossible to distinguish them on the basis of measurements of the static susceptibility, since systems in which all the molecules are in the biradical state are almost never investigated.

A new stage in the development of our knowledge about biradicals began when the method of electron spin resonance became available. Without changing significantly the basic postulates concerning biradicals, these investigations greatly extended the available information about this interesting class of substances. In the first place, the method makes it possible to establish the presence of biradicals in those cases where data on static magnetic susceptibility do not permit unambiguous conclusions. An even more significant factor is that, with the aid of this method, an approach is possible to the question of the interaction between the unpaired electrons in biradicals.

It is known from ESR theory that, when a conjugated organic system has only one unpaired electron, i.e. we are dealing with a monoradical, the spectrum of such a monoradical in solution can be described by a spin-Hamiltonian of the form

$$\hat{H} = g\beta \mathbf{H}_0 \mathbf{S} + \hat{A}\mathbf{S}\mathbf{I}, \qquad (1)$$

where the first term describes the interaction between the electron spin and the external magnetic field $\mathbf{H}_0$ and the second the hyperfine interaction of the electron spin with the magnetic moment of the nucleus (g is the factor and β a Bohr magneton). In this case the resonance condition can be written thus:

$$h\nu = g\beta H_0, \qquad (2)$$

which corresponds to the allowed transitions $\Delta m_S = +1$, where m_S is a projection of the electron spin. However, in a spin-Hamiltonian system consisting of two unpaired

electrons it is necessary to introduce an additional term describing the interaction between the electron spins:

$$JS_1S_2 ,$$

where J is an exchange integral of the type

$$J = \int \Phi_A(1)\Phi_B(2)\frac{e^2}{r_{12}}\Phi_A(2)\Phi_B(1)\,dv_1dv_2 , \qquad (3)$$

Φ_A the orbital of the unpaired electron in one half of the molecule and Φ_B the orbital in the second half, and r_{12} is the distance between the two electrons.

From the complete formulation of the spin-Hamiltonian in the form

$$\hat{H} = g\beta\mathbf{H}_0(\mathbf{S}_1 + \mathbf{S}_2) + A(\mathbf{S}_1\mathbf{I}_1 + \mathbf{S}_2\mathbf{I}_2) + J\mathbf{S}_1\mathbf{S}_2 \qquad (4)$$

it follows that the hyperfine structure in this case depends not only on the magnetic interaction between the electrons and nuclei but also on the extent of exchange J between the two electrons. If there is no interaction between the electron spins ($J = 0$), resonance will be observed under the same conditions as in a monoradical. If this interaction is sufficiently large and leads to an overall spin $S = 1$, then the transition $\Delta m_S = +2$ also becomes possible. The resonance condition can be written thus:

$$h\nu = 2g\beta H_0 , \qquad (5)$$

which in the presence of a field $0.5H_0$ corresponds to an ESR signal with a formal g-factor of 4.

The changes in the ESR spectra due to the presence of exchange can be best understood as follows. In the presence of exchange interactions between two electrons the energy levels can be described to a certain approximation by the magnetic quantum numbers M_1 and M_2 for the two nuclei, where M_1, $M_2 = -I, -I+1, \ldots, I-1, I$ are the projections of the spins of the nuclei on the z axis and m_1 and m_2 are the projections for the two electrons (m_1, $m_2 = -S, -S+1, \ldots, S$).

If it is assumed that each electron interacts only with its nucleus, the following expression is obtained for the energy:

$$E = g\beta H_0(m_1 + m_2) + A(m_1M_1 + m_2M_2) \qquad (6)$$

or

$$E = g\beta\left(H_0 + \frac{AM_1}{g\beta}\right)m_1 + g\beta\left(H_0 + \frac{AM_2}{g\beta}\right)m_2 . \qquad (7)$$

It is evident from the second equation that the hyperfine interaction for electron 1 is equivalent to a magnetic field $AM_1/g\beta$ set up by the nucleus with a spin I near this electron, while for electron 2 the field is $AM_2/g\beta$. Under the action of a high-frequency field ν applied at right angles to the direction of the permanent magnetic field H_0, resonance transition determined by the selection rules $\Delta m_1 = +1$, $\Delta m_2 = 0$, or $\Delta m_1 = 0$, $\Delta m_2 = 1$ will occur, i.e. the spin of each electron changes by unity. Since an electron transition does not involve changes in the orientation of the nuclear spin, the second selection rule can be written $\Delta M_1 = \Delta M_2 = 0$, i.e. the transitions will occur between states with the same projections of the nuclear spin. In Eqns. (2) and (7), it is possible to determine the resonance values of the magnetic field at which absorption takes place:

$$H_{1,2} = \frac{h\nu}{g\beta} \mp \frac{AM_1}{g\beta} . \qquad (8)-(9)$$

The difference between them is

$$\Delta H = \frac{2AM_1}{g\beta} . \qquad (10)$$

Such a system of equations can also be written for the second electron.

For two nuclei with the same spin values $I_1 = I_2 = I = 1/2$, we have $\Delta H = A/g\beta$, and the line splits into $(2I + 1)$ components, separated by a distance A.

When the exchange between the unpaired electrons is extensive, it can be assumed that the two electrons form a system described by the quantum numbers S and m, where $S = 0,1$ and $m = -S, \ldots, S-1, S$. As before, the nuclei are characterised by the magnetic numbers M_1 and M_2. Then the energy of the system can be expressed in the form[3]

$$E = g\beta H_0 m + \frac{A}{2}(M_1m + M_2m) + \frac{1}{2}J\left[S(S+1) - \frac{3}{2}\right] . \qquad (11)$$

If $g\beta H_0 \ll J$, $g\beta H_0 \gg A$, and $J \gg A$, then the levels of the triplet are of the form $\frac{1}{4}J$ and $\frac{1}{4}J \pm g\beta H_0 \pm \frac{1}{2}AM$, where $M = M_1 + M_2$. Taking into account the selection rules $\Delta m = +1$ and $\Delta M = 0$, we obtain an electron transition at $h\nu = g\beta H_0$ with $2M + 1$ hyperfine components. The distances between them are $A/2$ and not A as was the case for two independent electrons.

Apart from the $h\nu = g\beta H_0$ transition allowed by the selection rule $\Delta m = +1$, the interaction between the electrons also leads to partial absorption of the field energy on transitions between levels with spin projections $m_S = 1$ and $m_S = -1$ ($\Delta m = \pm 2$). It is evident from Eqn. (5) that this transition corresponds to a g-factor twice as large as for the free electron, i.e. here the g-factor should be approximately 4.

The derivation of expressions for the frequency of transitions and their probabilities in a general form on the basis of Eqn. (4) is a very complex problem, which has been solved only for certain special cases. Sakun et al.[4] describe the motion of unpaired electrons by an effective self-consistent potential, which for a biradical has the form of a well with two minima. Then calculation leads to an ESR spectrum consisting of three frequency groups:

$$\omega_{1,2} = A(M_1 + M_2) \pm 2\sqrt{J^2 + [(A/2)(M_1 - M_2)]^2} , \qquad (12)-(13)$$

$$\omega_3 = A(M_1 + M_2) . \qquad (14)$$

Taking into account the selection rules specified above, the intensities of the corresponding lines are

$$F_{\omega_{1,2}} = \frac{1}{1 + (J/A)^2\left(\frac{2}{M_1 - M_2}\right)^2} , \qquad (15)$$

$$F_{\omega_3} = \frac{2}{1 + (A/J)^2\left(\frac{M_1 - M_2}{2}\right)^2} . \qquad (16)$$

It follows from these formulae that, when $J = 0$, there are no ω_3 frequencies in the ESR spectrum, and there remain $(2I_{1,2} + 1)$ lines of equal intensity. In the case of rapid exchange ($J \gg A$) there are no lines corresponding to the frequencies ω_1 and ω_2 and there remain $4I + 1$ lines with the intensities $1:2:3:2I:2I+1\ldots 3:2:1$. In the intermediate cases there are only $(2I + 1)^2 + 2$ lines. Fig. 1 shows that, for two electrons located respectively at two nuclei with a spin $I = 1/2$, the number of lines ranges from 2 in the absence of exchange $[(2I + 1) = 2]$ to 3 $[(4I + 1) = 3]$ when the extent of exchange greatly exceeds the hyperfine interaction constant. With intermediate values of J, "satellite" lines, characteristic of biradicals, appear at the wings of the relevant absorption curve and between the principal lines.

Thus the value of the g-factor for those cases where there are $\Delta m = +2$ transitions, and also the number of hyperfine components and their intensities, which both

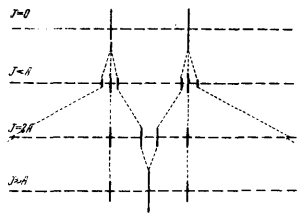


Figure 1. Theoretical spectrum for two electrons and two nuclei with a spin of 1/2.

depend on J, provide information about the degree of electron interaction in biradicals.

The aim of the present review is to examine the data on biradicals obtained with the aid of the ESR method. Furthermore, additional data on the chemical and physical properties of biradicals which have appeared in the literature since the 1947 review will be included. Molecules belonging to all three types of biradicals considered above will be discussed.

II. BIRADICALS WITH THE SINGLET GROUND STATE

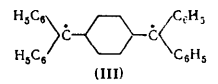
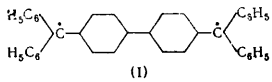
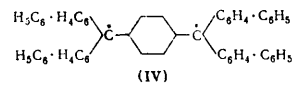
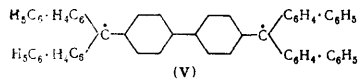
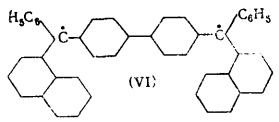
When the ESR method appeared, the biradical nature of compounds could be established, among substances of this type, for which earlier results did not lead to unambiguous conclusions. This applies in the first place to the forerunner of such substances, namely Chichibabin's hydrocarbon, for which both the static susceptibility and the ortho–para conversion of hydrogen methods failed to solve the problem of whether the substance passes to a biradical state under normal conditions. In his measurements of the static magnetic susceptibility, Müller[5] observed diamagnetism and on this basis rejected the possibility of the presence of molecules in the triplet state. However, the work of Schwab and coworkers[6], who investigated the ortho–para conversion of hydrogen in the presence of Chichibabin's hydrocarbon, indicates the presence of a considerable fraction (up to 10%) of biradical molecules.

Even the first investigations of this compound by the ESR method, carried out by Hutchinson et al.[7], showed that 0.005 M liquid solution contains 4% of paramagnetic molecules and that this fraction can increase with temperature.

It should be noted that fully reproducible results are not always achieved in the synthesis of substances of the Chichibabin's hydrocarbon type. Some workers obtained very brightly coloured solutions and assumed that the reaction products are biradicals in the monomeric state. Others obtained colourless substances consisting in all probability of dimers or polymers. It was not until 1957 that Sloan and Vaughan[8] developed the most complete modern method for complex syntheses of biradicals[8]. They obtained a number of derivatives of Chichibabin's hydrocarbon showing as distinct a resonance paramagnetic absorption as in hydrocarbon (I)—the parent of this type of compounds (Table 1).

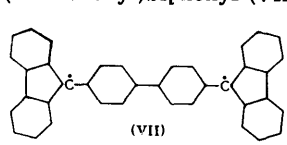
On the other hand Thiele's hydrocarbon(III) does not give rise to an ESR signal since the fraction of molecules in the triplet state is extremely low, but the tetra(biphenylyl) derivative (V) does exhibit resonance absorption. These data are in good agreement with the results of the calculations of the energies of the highest occupied and lowest free orbitals by the MOH method. In Thiele's hydrocarbon the energy of this transition (0.31β) is greater by a factor of 2 than in Chichibabin's hydrocarbon (0.15β). This explains why an appreciable fraction of biradical molecules is observed in the first compound, while in the second it is much smaller. The introduction into Thiele's hydrocarbon of biphenylyl groups [compound(IV)] instead of phenyl groups also reduces the energies of the highest occupied and lowest free orbitals (to 0.13β), which leads to a concentration of molecules in the triplet state susceptible to detection.

Table 1.

Compound	Presence of ESR signal	Colour of solution
 (III)	—	orange
 (I)	+	violet
 (IV)	+	brick red
 (V)	+	bright blue
 (VI)	+	dark purple

It is noteworthy that all these substances readily undergo changes in which the radical properties are probably lost. When air is admitted, only compound (III) and compound (IV) do not change colour, while compounds (I), (V), and (VI) are decolourised. This shows that conclusions concerning the biradical character of a substance can be arrived at only in those cases where special precautions have been taken to prevent dimerisation and polymerisation, oxidation, decomposition, etc.

A new compound of this class synthesised by Theilacker et al.[9] is 4,4'-bis(9-fluorenyl)biphenyl (VII):



(VII)

It proved to be a colourless sparingly soluble polymer. When a solution in α-methylnaphthane was heated from 80° to 165°C, its colour changed from brown to bright green. Depolymerisation with increase of temperature is accompanied by an appreciable increase in paramagnetism, possibly in consequence of dissociation into monomeric biradicals (Table 2).

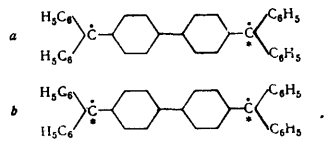
The first investigations of biradicals, where only the presence or absence of paramagnetism in the given molecules was established, were followed by the study of the intramolecular interactions between the two unpaired electrons. For substances of the type of Chichibabin's hydrocarbon, which have a singlet ground state, this problem has no physical significance. In the triplet state of these molecules, as in the triplet states of any other normal molecules, there are no separate components where unpaired electrons could be localised. The problem of whether or not there is interaction between two halves,

Table 2.

Temperature, °C	$\chi_{exp}-\chi_{calc}$	biradical content, %
20	—	—
105	+ 45	3
145	+141	8
165	+153	9

constituting in fact a single conjugated system, arose only due to the traditional approach whereby the structure of the triplet form of Chichibabin's hydrocarbon was represented as consisting of two triphenylmethyl radicals joined by a C–C bond in the *para*-position. However, it is possible to demonstrate by this example the errors which can arise in studies of ESR spectra without due attention being given to a reliable identification of the compounds to which the spectra refer. We shall consider the relevant studies because they demonstrate the danger of theorising about unusual properties of molecules in those cases where there is no certainty that they are in fact the properties of the molecules under consideration and not of some others (for example conversion products), for which they are reasonable and by no means surprising.

In an early investigation[10] it was found that the g-factors of Chichibabin's hydrocarbon and its diphenyl and phenylnaphthyl derivatives [compounds (V) and (VI)] are 2.0025 ± 0.0004, although transitions corresponding to $\Delta m = +2$ might also have been expected. The spectra were poorly resolved so it was difficult to draw inferences concerning the number of hyperfine structure lines. Later Reitz and Weissman[11] investigated the electron spin resonance of Chichibabin's hydrocarbon where the carbon atoms marked with an asterisk were labelled with carbon-13, the atomic nucleus of which itself has a magnetic moment. One atom was labelled in case a and both atoms in case b:



For system a ($^{12}C-^{13}C$), where there is only slow exchange compared with the frequency of hyperfine interaction, i.e. $A \gg J$, a triplet spectrum should have been obtained with a central line originating from the part of the molecule where the nuclear spin is zero, i.e. from the $(C_6H_5)_3{}^{12}C$ group, and two outer lines with intensities smaller by a factor of 2, which are due to splitting by carbon-13 in the $(C_6H_5)_3{}^{13}C$ group (Fig. 2).

The spectrum of system b ($^{13}C-^{13}C$) should consist of two lines in the presence of slow exchange (each electron located at its nucleus and $A \gg J$) or three lines with intensities 1 : 2 : 1 in the presence of rapid exchange, when the spins migrate from one half of the molecule to the other (Fig. 1).

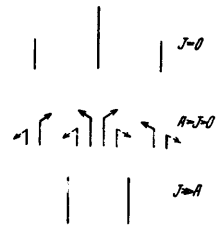


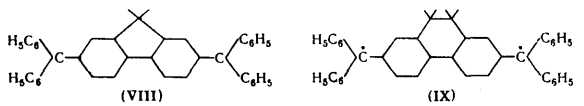
Figure 2. Theoretical spectrum of Chichibabin's hydrocarbon with a single ^{13}C tracer atom.

A surprising result of this investigation was the finding that the experimental data can be interpreted as demonstrating that the structure of the molecule of Chichibabin's hydrocarbon consists of two independent triphenylmethyl components with a frequency of exchange between the latter $< 7 \times 10^7$ s^{-1}, which was completely incomprehensible when the radical form of Chichibabin's hydrocarbon was treated as a triplet state of the molecule. However, instead of thoroughly testing the reliability of the experimental data and in the first place identifying the molecules which give rise to the spectra, a number of investigators undertook the development of a "theory" of these fantastic phenomena.

McConnell[12] estimated theoretically the frequency of hyperfine splitting on the basis of the singlet–triplet splitting Δ in the biradical, adopting for Δ the value found in the calculation by the simple MOH method, and obtained an exchange frequency of the order of 2.5×10^{13} s^{-1}. This discrepancy with the "experimental" value ($< 7 \times 10^7$ s^{-1}) led to the so called "biradical paradox", to the resolution of which a number of studies were devoted[12–14]. McConnell in fact started from the premise that Δ is determined only by the frequency of transmission of an electron from one half of the molecule to the other. Burshtein and Naberukhin[15] attempted to obtain a closer agreement between the theoretical estimate of the frequency of electron exchange and the "experimental" value by considering the mutual electrostatic repulsion of the electrons, i.e. by going over to the two-electron problem. When account is taken of the Coulombic interaction, singlet–triplet splitting is obtained corresponding to an exchange frequency of the order of 10^6 s^{-1}, i.e. a value close to or somewhat smaller than the frequency of hyperfine interaction. An impression was created that Chichibabin's hydrocarbon can indeed be regarded as consisting of two halves. However, the inconsistency of this conclusion with the general hypotheses concerning the origin of the biradical nature of substances of this type led to further studies in this field.

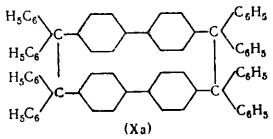
The latest results obtained by Waring and Sloan[16] provide a new interpretation of the observed independence of the unpaired electrons in Chichibabin's hydrocarbon: it is now attributed to a biradical dimer and not to the individual

monomeric molecule of the biradical. When, in experiments on Chichibabin's hydrocarbon and the biradicals (VIII) and (IX),



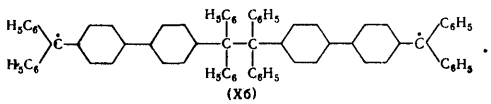
(VIII) (IX)

the specimen is cooled sufficiently rapidly, the intensity of the ESR spectrum observed at room temperature persists also at the low temperature. This can be regarded as proof that at sufficiently low temperatures the solution does not contain only monomeric biradicals but there is an equilibrium between paramagnetic and diamagnetic molecules. The most likely type of association is due to the formation of a weak C–C bond, as in hexaphenylethane. This may give rise to the formation of both diamagnetic cyclic dimers of the type



(Xa)

and linear dimers (or polymers) which retain a biradical character:



(X6)

The linear dependence of the intensity of the ESR signal on concentration in the range between 5.04×10^{-3} and 7.7×10^{-5} M at room temperature (Fig. 3) shows that the associated paramagnetic and diamagnetic molecules have the same molecular weight.

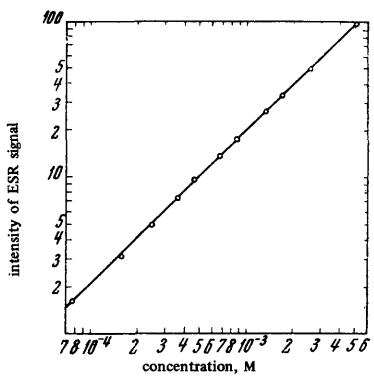


Figure 3. Variation of signal intensity with the concentration of Chichibabin's hydrocarbon in carbon disulphide.

The ESR spectrum of the biradical (VIII) at 25°C is shown in Fig. 4; the intensities of the lines in an individual section of the complete spectrum persist also on heating to 100°C, i.e. under these conditions there are no changes associated with the interaction between the electrons.

The presence of dimers or polymers of type (Xa) and (Xb) inevitably leads to observed independence of the unpaired electrons. These results provide a clear illustration of the danger of investigating exchange interactions on

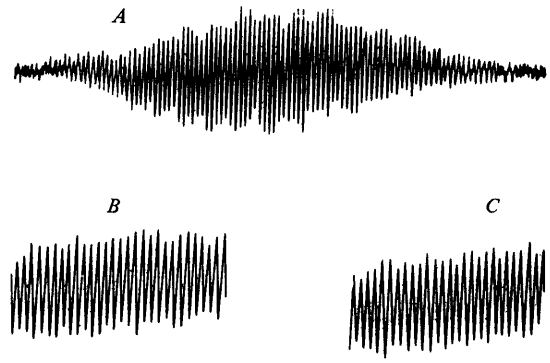
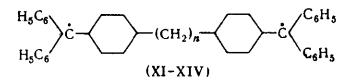


Figure 4. ESR spectrum of the biradical (VIII) in carbon disulphide: *A*) complete spectrum at 25°C; *B*) section of the spectrum at 25°C; *C*) section of the spectrum on heating to 100°C.

the basis of ESR spectra without a detailed identification of the molecules to which these spectra refer. Thus, the ESR data in no way contradicted the treatment of compounds of the type of Chichibabin's hydrocarbons as normal molecules with a low energy of excitation to the triplet state.

III. BIRADICALS WITH INSULATING GROUPS

Bridged biradicals [(IX)–(XII)], among which diphenylmethane and diphenylethane may be included, were obtained for the first time by Wittig and Leo[17,18].

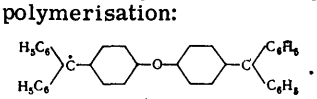


(XI-XIV)

(n = 1,2,3,4).

From the chemical point of view, they behave as free radicals; compound (XI) formed a bright red and compound (XII) a dark red solution exhibiting green dichroism in thin layers. However, in diphenylbutane derivatives (XIV) radical properties were completely absent according to the results of Wittig and Leo[18]. They attributed the weak colour, slow reaction with oxygen, and the constancy of the colour of this hydrocarbon to disproportionation. Nevertheless latest work[19] has shown that solutions of triarylmethyls frequently retain the initial colour although their paramagnetism falls to zero. All this weakens the arguments of Wittig and Leo.

Measurements of static magnetic susceptibility[20] led to the conclusion that hydrocarbon (XII) is diamagnetic; Müller failed to repeat the Wittig synthesis and his compound was completely colourless. Compound (XV), synthesised by Müller and Bunge[21], also proved to be diamagnetic (according to measurements of static magnetic susceptibility) and its diamagnetism was explained by dimerisation or polymerisation:



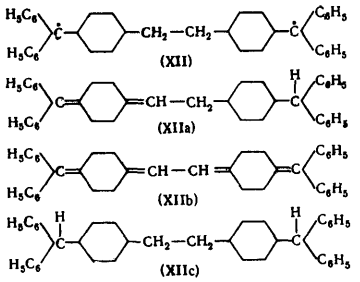
(XV)

The biradicals (XI)–(XV) have now been studied by the ESR method[10,11]. Table 3 shows that they exhibit intense paramagnetic absorption, but even in the absence of light and oxygen the paramagnetism vanishes after a time. This is evidently due to disproportionation. In his study of the

Table 3.

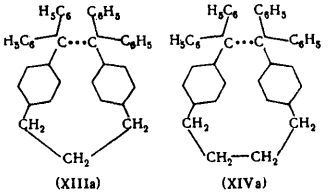
Compound	Initial colour	Presence of ESR signal	Colour of decomposed solution	Colour after access of air
(XI)	bright red	++	pale yellow	colourless
(XII)	wine red (green in thin layers)	++	pale blue	colourless
(XIII)	yellow	++	pale yellow	pale yellow
(XIV)	yellow	++	pale yellow	pale yellow
(XV)	yellow	++	pale yellow	pale yellow

biradical (XII), Müller obtained three decomposition products which he believed appeared as a result of subsequent inter- and intra-molecular disproportionation reactions.



It is interesting to note that, although compound (XIIb) is diamagnetic, it has a dark red colour and is sensitive to oxygen. Judging from Tables 1 and 3 compiled by Sloan and Vaughan[8], conversion into coloured diamagnetic compounds which retain their sensitivity to oxygen is a common property of biradicals.

Speaking of the disproportionation mechanism, it is difficult to explain why the colour of the decomposed solution of compound (XI) differs from that of the solution of compound (XII), if it is assumed that inter- and intramolecular disproportionation converts compound (XI) to the same product. Furthermore, it is not altogether clear why diphenylpropane and diphenylbutane differ so much from diphenylmethane and diphenylethane derivatives. Possibly the biradicals forms (XIII) and (XIV) are in equilibrium with monomeric diamagnetic compounds of the type (XIIIa) and (XIVa), since in compounds (XI) and (XII) intramolecular saturation of valence is impossible, because the bond between trivalent carbon atoms would have to extend over a very large distance. This difference in fact leads to different disproportionation mechanisms:



The central problem which arises in the examination of biradicals with insulating groups is the question whether the biradical in fact consists of two independent monomeric radicals or whether there is exchange interaction between the two halves, leading to a spin $S = 1$. The method of static magnetic susceptibility, which predicted a diamagnetic behaviour of the majority of these hydrocarbons, could not of course resolve this problem.

Analysis of the ESR spectra of bridged biradicals[10] (Fig. 5) favours the first hypothesis, namely that the two halves of the biradical are independent. The measured values of the g-factor proved to be similar to those of a free electron and the sharp resolution of the spectrum and the narrowness of the hyperfine components suggested the absence of appreciable dipole interaction between the unpaired electrons. The impairment of the resolution of the hyperfine structure on increasing the number of methylene groups favours the hypothesis that, with a longer molecular chain, anisotropic hyperfine interaction makes a contribution to line width. The line in the spectrum of compound (XV) again becomes sharp and the g-factor decreases somewhat (from 2.0025 to 2.0031), which is characteristic of free radicals with oxygen atoms[11,12] (Fig. 6).

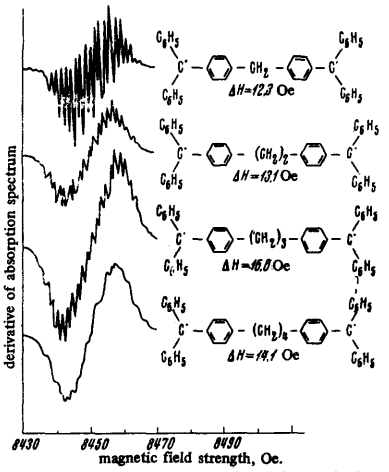


Figure 5. ESR spectra of biradicals with insulating groups.

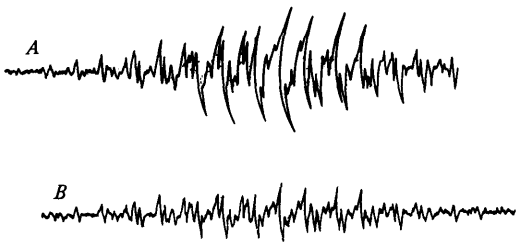
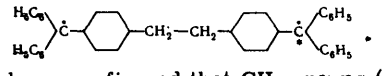


Figure 6. *A*) ESR spectrum of the biradical (XV) at 263°K; *B*) at 215°K.

Analysis of the hyperfine structure in the spectra of biradicals (XII) and (XV) labelled with the carbon-13 isotope, similar to that discussed above, confirmed the independence of the spins of the unpaired electrons[11]. Thus at 297°K the spectrum of compound (XII), in which one of the atoms (marked with an asterisk) was labelled with carbon-13, contains a central line which originates from the part of the molecule in which the nuclear spin is zero. The two outer lines are due to splitting by carbon-13 in the group $(C_6H_5)_3{}^{13}C$. Such a triplet spectrum corresponds to the condition $J = 0$ (see Figs. 2 and 7):



Thus it has been confirmed that CH_2 groups (even one such group) clearly insulate two conjugated systems. It

has been suggested that conjugation via such groups is possible in the radical-anions (monoradicals) of diphenylmethane and dibenzyl[23,24]. However, this has been disproved by the work of Kazokova, Syrkin, and Shapiro, who



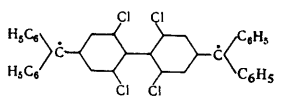
Figure 7. ESR spectrum of the biradical (XII) at 297°K (60% ^{13}C).

showed that the radical-anions are not in this case unchanged initial molecules to which an electron has been added, but undergo secondary reactions, which lead to a considerable rearrangement of the initial molecules[25-27].

IV. ATROPISOMERS

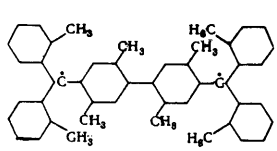
Numerous new data on static magnetic susceptibility were obtained in the 1950's for non-planar derivatives of diphenylquinonedimethane–atropisomers. The presence of bulky substituents in the *ortho*-position with respect to the central bond leads to the rotation of one part of the molecule relative to the other and both halves become just as independent as the bridged biradicals. Therefore, although formally these substances appear to be derivatives of compounds of type 1, in fact they belong to the third type.

The compound 2,6-2′,6′-tetrachloro-4,4′bis(diphenylmethyl)biphenyl (XVI), which in solution exhibits paramagnetism increasing with temperature and decreasing with concentration, was examined earlier by the method of static magnetic susceptibility[28]. Comparatively recently these data were confirmed by the study of the ortho–para conversion of hydrogen catalysed by compound (XVI).[29] It was found that this compound is a biradical to the extent of 100%:

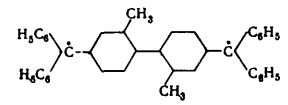


(XVI)

According to the results of Schwab and Baumel[30], compound (XVII) catalyses the ortho–para conversion of hydrogen with a conversion constant likewise corresponding to a 100% content of the biradical. Static magnetic measurements[9] fully confirm the data of Schwab and Baumel concerning the biradical nature of compound (XVII) (Table 4).



At one time Theilacker and Ozegowski[31] suggested that not four but two substituents are sufficient for the breakdown of coplanarity. They synthesised compound (XVIII), Theilacker's hydrocarbon, the solution of which is very sensitive to air and exhibits green-red dichroism. On this basis they suggested that the solution contained the biradical form (XVIII):



(XVIII)

It was not until much later that data on the percentage content of the biradical (XVIII) were obtained by measurements of the magnetic susceptibility of this hydrocarbon in α-methylnaphthalene[9] (Table 5).

Table 4. Magnetic susceptibility of 2,2′,5,5′-tetramethyl-4,4-bis(ditolylmethyl)biphenyl in α-methylnaphthalene (M) and benzene (B).

Concn.%	Temp., °C	$\chi_{exp}-\chi_{calc}$	biradical content, %	Concn., %	Temp., °C	$\chi_{exp}-\chi_{calc}$	biradical content, %
M, 1.5	20	+2493	97		80	+2142	100
	50	+1809	96		99	+1972	98
	80	+2141	100	B, 4.0	20	+2518	99
	105	+1948	98		51	+2329	100
M, 4.6	20	+2494	97		82	+2119	100

Table 5.

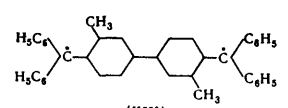
Concentration, %	Percentage of biradical form		
	20°	51°	82°
5.12	4	10	21
4.96	4	8	19
5.05	5	10	21
2.05	5	12	25
2.07	5	12	28

Table 6. 2,2′-Difluoro-4,4′-bis(diphenylmethyl)biphenyl in α-methylnaphthalene.

Concentration, %	Percentage content of biradical form				
	21°	53°	80°	105°	130°
5.00	1	—	8	11	2
5.33	3	—	12	13	11
5.11	2	—	9	13	11
2.62	3	4	9	—	—

The substitution of methyl groups by fluorine atoms leads to a smaller percentage content of the biradical and therefore the equilibrium quinonedimethane ⇌ biradical is more strongly displaced to the left (Table 6).[9]

However, the steric effect is evidently not the only factor in such cases, since substance (XIX), with methyl groups in *meta*-positions with respect to the central bond, is also paramagnetic and actually more so than Theilacker's hydrocarbon[9,32] (see data in Table 7):



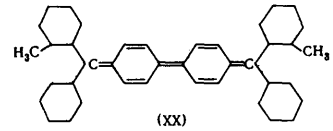
(XIX)

Apart from steric effects, the presence of substituents in the biphenyl system which reduce the energy of excitation to the triplet biradical state probably also plays a significant role in this case.

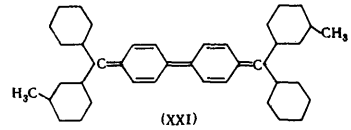
Table 7. 3,3′-Dimethyl-4,4′-bis(diphenylmethyl)biphenyl in α-methylnaphthalene.

Concentration, %	Percentage content of biradical form		
	21°	55°	84°
5.05	14	31	47
4.18	15	32	47
2.23	17	39	50
2.01	18	38	46

Compounds (XX) and (XXI) proved to be diamagnetic[32]:



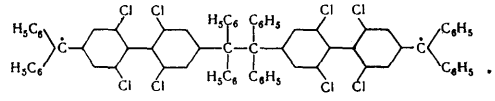
(XX)



(XXI)

It should be noted that data on the percentage content of the biradical forms in atropisomers listed in the tables were obtained on the assumption that both halves of the biradicals are completely independent ($\chi_p = 2560 \times 10^{-6}$ e.s.u.). However, in some cases the angles between the two halves of the biradical can assume intermediate values between 0° and 90°C, which should result in a weak π-bond. Therefore complete reliance cannot be placed on data obtained on the assumption that such a bond is altogether absent.

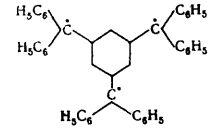
The extent of interaction between unpaired electrons might be inferred from ESR spectroscopic data, but unfortunately the only biradical [compound (XVI)] investigated by this method is appreciably associated in solution[16], forming open-chain biradical dimers (or polymers) of the type



Clearly such association prevents the correct interpretation of the ESR spectra.

V. POLYRADICALS

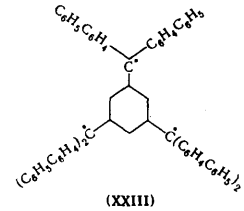
In 1965 there appeared a brief communication that German investigators[33] had succeeded in repeating Leo's attempt to obtain a hydrocarbon triradical of the type



(XXII)

However, the product did not have a definite melting point and, according to elemental analysis and molecular weight measurements, was a weakly associated polymer. On dissolution in benzene, an ESR spectrum with a resolved hyperfine structure appeared.

The replacement of phenyl groups by biphenylyl groups yields the triradical (XXIII)



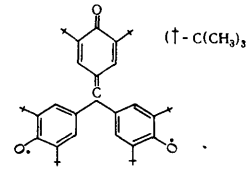
(XXIII)

which consists of red-violet crystals. It gives rise to an ESR signal but the hyperfine structure is not resolved in the spectra of either the solid radical or its solution in benzene. The solution also contains both monomeric and polymeric molecules.

VI. BIRADICALS WITH HETEROATOMS

Recently an intensive study of biradicals with heteroatoms by the ESR method was begun. With the exception of the previously known porphyrindine, most of the radicals constitute completely new classes of paramagnetic organic molecules. As with hydrocarbon biradicals, this method makes it possible to determine from the number of hyperfine components of the ESR spectrum and the g-factor the class of biradicals to which the given compound belongs, i.e. to elucidate whether it is simply a double monoradical or whether it is in the triplet state, like Chichibabin's hydrocarbon.

Jang and Castro[34] described the synthesis of a substance with the hypothetical structure (XXIV)



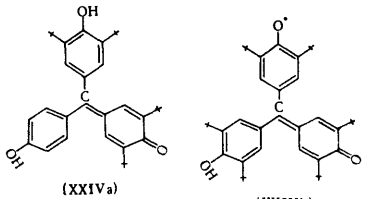
(XXIV)

Calculations were made on this molecule[35] by the MOH method on the assumption that the phenyl rings are displaced from a single plane and are rotated by 30°, as in triphenylmethyl. The calculation led to the conclusion that the last two electrons should occupy a degenerate nonbonding orbital when all the Coulombic integrals are equal, and a degenerate orbital with the energy 0.542β when the Coulombic integral for the oxygen atom is assumed to be $\alpha_O = \alpha_C + 1.5\beta$, so that in both cases there is a triplet ground state. The most significant results proved to be the theoretical prediction of a transition at very long wavelengths (20.000 Å) and its experimental observation in absorption spectra. This transition takes place from the bonding level with the energy 0.827β to the partially filled degenerate bonding levels (0.542β) where the unpaired electrons of the molecule are located.

Measurements of the static magnetic susceptibility gave 3.1×10^{-3} cm³ mole⁻¹ as the paramagnetic contribution. However, in the authors' view there is a possibility here of a large experimental error.

The ESR spectrum of Jang's biradical consists of seven overlapping lines (hyperfine constant $A_H = 0.86$ Oe), which indicates the interaction of the unpaired electrons with six equivalent protons[36]. Evidently the spin exchange is very rapid and each electron interacts with the six *meta*-protons

of the three aromatic rings. The addition to the biradical of the initial substance (XXIVa) in methyltetrahydrofuran leads to the formation of the monoradical (XXIVb):



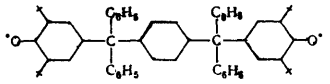
(XXIVa) (XXIVb)

Evidently a disproportionation reaction takes place:

$$\text{XXIV} + \text{XXIVa} \rightleftarrows \text{XXIVb}.$$

On cooling a solution containing the biradical, the lines in the ESR spectrum broaden and at −50°C the spectrum consists of a single broad line. In the spectrum of the frozen solution (glass at −160°C) dipole splitting is observed, and the lines originating from the monoradical and the biradical become superimposed (large doublet splitting). The extent of this splitting depends on the dipole interaction between the unpaired electrons, which is inversely proportional to the cube of the distance between the magnetic dipoles. Thus the distance between the intense lines of the doublet enables (see Pake[37]) the distance between the two unpaired spins to be found, in this case 9 Å.

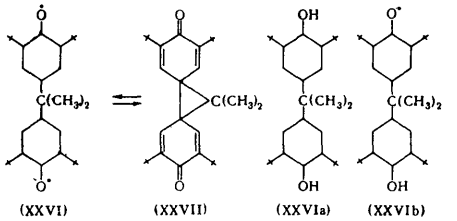
Another bisaroxyl biradical (XXV) was studied by Müller and coworkers[38]. Measurements of static magnetic susceptibility in benzene showed that the solution contained 88% of the biradical molecules. The ESR spectrum of this biradical consists of three lines, which can be attributed to two protons of the phenoxyl ring. Hence it follows that the unpaired electrons are localised only in the phenoxyl groups surrounding the molecule and do not interact with one another via the insulating $C(C_6H_5)_2$ groups, the biradical behaving simply as a double monoradical:



(XXV)

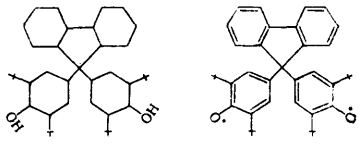
The attempt of Chandross and Kreilick[39] to detect by the ESR method the biradical (XXVI) obtained by the oxidation of compound (XXVIa) was unsuccessful, although the monoradical (XXVIb) gave rise to a distinct ESR spectrum consisting of a triplet (two equivalent *meta*-protons with a hyperfine structure constant of 1.67 Oe) split by the weaker interaction with the six equivalent protons of the isopropylidene group (hyperfine structure constant of 0.38 Oe).

The absence of an ESR signal due to the biradical (XXVI) can be attributed to the equilibrium between the biradical species and the diamagnetic spirodiene (XXVII):



(XXVI) (XXVII) (XXVIa) (XXVIb)

The replacement of the *gem*-dimethyl group in compound (XXVIa) by a 2,2-diphenylene group yields compound (XXVIIIa)[40]. The ESR spectrum obtaining during the oxidation of this substance was investigated. Initially three lines due to the monoradical appeared (hyperfine structure constant of 1.65 Oe). As the oxidation progressed, the intensity of the signal increased and then fell, but did not disappear altogether. At −180°C two groups of lines appeared in the spectrum, corresponding to the transition $|\Delta m| = 1$ with splittings of 126 and 30 Oe, and absorption corresponding to $|\Delta m| = 2$ occurred when the field strength was reduced to 50%. The larger splitting was attributed to the biradical (XXVIII) and the smaller to the dimer containing two molecules of compound (XXVIII), probably joined by a peroxide bond:

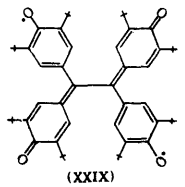


(XXVIIIa) (XXVIII)

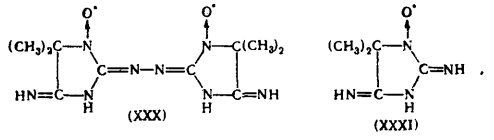
Although the formation of such a bond is fairly unusual in this case (due to the presence of bulky substituents in the phenyl ring), the concentration dependence of the extent of splitting in a zero field confirms the occurrence of dimerisation. On dissolution, the intensity of the smaller splitting decreases and vanishes much faster than that of the larger splitting, which persists for a fairly long time. The position of the lines indicates that the average distance between the unpaired electrons in compound (XXVIII) is 6 Å and in the dimer 9.8 Å.

Recently Chandross[41] obtained an interesting stable biradical (XXIX) which he called bisgalvinoxyl. It is a dark crystalline substance with a metallic lustre. In the solid state the biradical is very stable, but in inert solvents (10^{-3}–10^{-4} M) it is decolourised by air in several hours. The bisgalvinoxyl spectrum recorded in glasses at 77°K clearly shows that this substance is in the triplet state. In methyltetrahydrofuran a hyperfine line structure appears, transitions both from $|\Delta m| = 1$ and transitions at 1635 Oe, corresponding to $|\Delta m| = 2$, being observed. Using the model of 2 point dipoles, it can be shown that the splitting at $|\Delta m| = 1$ corresponds to an average interelectron distance of 6 Å.

In contrast to the biradicals (XXIV) and (XXIX), the ESR spectra of which indicate that these compounds have two unpaired electrons in different parts of the molecule interacting with one another, in the ESR spectrum of porphyrindine (XXX) there is no clear proof of the interaction between the two unpaired electrons[42].



(XXIX)



(XXX) (XXXI)

The spectrum of the dimethylsulphoxide solution of this substance consists of three groups of lines with a hyperfine structure constant of about 10 Oe. Each line is split further into four components with a hyperfine structure constant of the order of 3 Oe (Fig. 8). The main splitting is evidently due to the interaction of the unpaired electron with the nucleus of the nitrogen atom. In contrast to this,

the spectrum of compound (XXX) in ethanol at 300°K consists of only two lines, although porphyrexide (XXXI), which constitutes as it were one half of porphyrindine, gives rise under these conditions to an ESR spectrum consisting of three lines. Possibly in this case there are solvent and temperature effects on the exchange interaction.

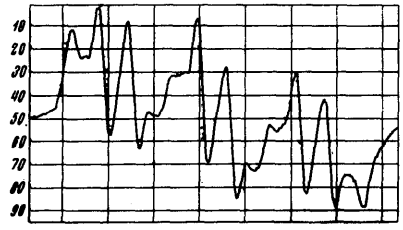
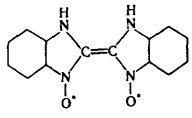


Figure 8. ESR spectrum of the biradical (XXX) in dimethylsulphoxide at 80°C.

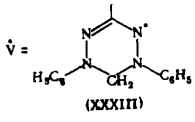
The decrease of the paramagnetism of porphyrindine on reducing the temperature previously, observed by the magnetic susceptibility method, is found to occur also for NO-indigo[43]:



(XXXII)

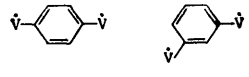
At room temperature the fraction of biradical molecules is high and the susceptibility of this compound is 10% higher than the value calculated for the double monoradical. However, at the temperature of liquid nitrogen it is diamagnetic. Evidently, in this case the diamagnetic form of NO-indigo, like the diamagnetism of porphyrindine at low temperatures, is associated with the displacement of the equilibrium between the diamagnetic and paramagnetic forms towards the former. The diamagnetic form may be either a polymer or, what is more likely, a diamagnetic monomer.

On the basis of the fragment



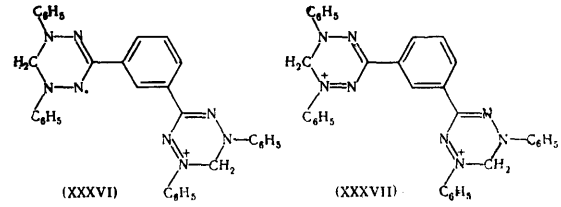
(XXXIII)

the green biradicals (XXXIV) and (XXXV) were obtained[44]:



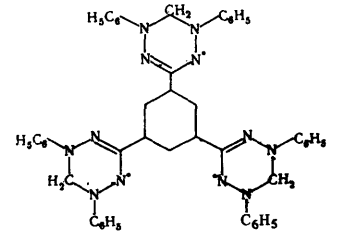
(XXXIV) (XXXV)

While the monomeric radical (XXXIII) gives rise to nine lines in the ESR spectrum, which can be accounted for by interaction with two nitrogen atoms, the spectra of biradicals (XXXIV) and (XXXV) contain a different number of lines, corresponding to exchange between two unpaired electrons. Reversible polarographic oxidation leads to the monocation (XXVI), violet in colour, the spectrum of which again shows the nine lines of the monoradical, and then the diamagnetic dication (XXXVII):



(XXXVI) (XXXVII)

The interesting triradical (XXXVIII) was also obtained on the basis of (XXXIII):[45]

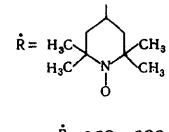


The resultant magnetic spin moment of the molecule for three independent unpaired electrons is $\mu = \sqrt{9}\mu_B$. Table 8 shows that, in contrast to porphyrindine and NO-indigo, the paramagnetism of the triradical does not continue to decrease down to the temperature of liquid nitrogen. This suggests that the three electrons of the triradical are indeed independent. The hyperfine structure of the ESR spectrum of the triradical is unresolved.

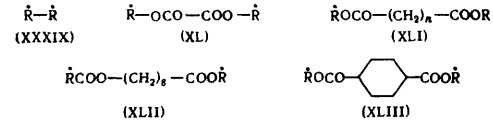
Table 8.

T°K	μ/μ_B
298	2.96+0.06
195	2.97
77	3.01

Because of the presence of an insulating grouping between the two halves of the molecules of the hydrocarbon biradicals examined above, there is no exchange between them, i.e. the σ-bond system of the bridge prevents interaction between the electrons. The insulating bridge in biradicals with heteroatoms plays the same role. However, it has been suggested that the exchange of unpaired electrons can occur also in the presence of insulating groupings, but by a different mechanism. Roxantsev, Buchachenko, and coworkers[46,49] and also Lemair and coworkers[50,51] obtained and investigated iminoxy-biradicals, which are exceptionally stable both in the solid state and in solutions. The iminoxy-biradicals contain the following residue with the unpaired electron:

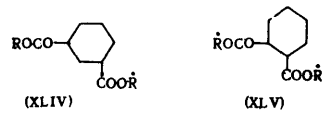


$n = 2, 4, 5$



(XXXIX) (XL) (XLI)

(XLII) (XLIII)



In the absence of exchange between the unpaired electrons in the two halves of the iminoxy-biradical, each electron interacts with the nucleus of the nitrogen atom of "its half" and the biradical behaves as a double monoradical. In this case the ESR spectrum consists of three lines with a hyperfine structure constant A. If there is strong exchange interaction between the two electrons, the spectrum consists of five lines with a hyperfine structure constant $A/2$ (see p. 378 and Fig. 9).

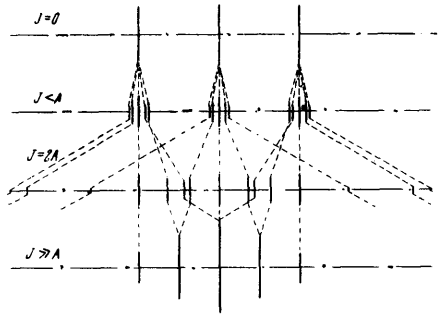
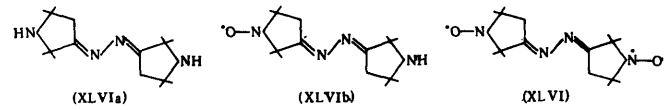


Figure 9. Theoretical spectrum as a function of the presence or absence of exchange interaction.

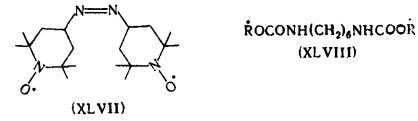
In contrast to the spectrum of the monoradical $\dot{R}$, the hyperfine structure of which consists of a triplet due to the ^{14}N nucleus (hyperfine structure constant $A_N = 15.6$ Oe) split by the β-protons ($A_H = 0.35$ Oe), in the spectra of the biradicals additional lines appear between the components of the triplet. Their number and intensity depend on the structure of the biradical. Thus the spectrum of the biradical (XXXIX), where the NO groups lie very close together, consists of five lines, which are regarded as due to the interaction of the two equivalent ^{14}N nuclei. In the spectrum of the biradical (XL), where there is an -OCO-OCO- group, additional lines do not appear and the spins behave independently. In the ESR spectrum of the biradicals (XLI) four additional lines appear, which Buchachenko et al. [48] believe to be due to the enhanced interaction between the unpaired electrons. The spectra of compounds (XLIII) and (XLIV) consist of triplets without additional lines, while in the spectrum of (XLV) there are again five lines, which are interpreted as indicating the occurrence of interaction between the two nitrogen atoms.

The monoradical (XLVIb) and the biradical (XLVI), which consists of large yellow crystals, were obtained by the oxidation of azine (XLVIa) [50]. The intensity of the ESR spectrum of the polycrystalline biradical is higher by a factor of 2.16 than the intensity of the polycrystalline monoradical containing the same number of molecules. In dimethylformamide the monoradical gives rise to the classical triplet with $A_N = 14.4$ Oe and $g = 2.0055$, while the biradical gives rise to a highly resolved triplet with $A_N = 7.2$ Oe. The authors explained these data by the occurrence of exchange interaction, the frequency of which is higher than that of the hyperfine interaction, i.e. $J \gg A$.



The width of the biradical line (2.4 Oe) does not differ much from the line width measured in the spectrum of the monoradical under the same conditions. (2.2 Oe). This means that the bond between the unpaired electrons is not strong enough to widen the ESR line due to dipole interaction.

The radical (XLVII) gives rise to a similar spectrum (Fig. 10a). [51] When the nitrogen atom in the iminoxy-groups is replaced by the ^{15}N isotope, three lines appear in the spectrum (Fig. 10b). This is accounted for by the interaction of the unpaired electron with the two nuclei of the ^{15}N atoms, which have a nuclear spin $I = \frac{1}{2}$ (case $J \gg A$, Fig. 1). The absence of splitting by the nitrogen atoms of the azine bridge shows that the electron exchange does not involve the system of σ-bonds. This is also indicated by the ESR spectrum of the biradical (XLVIII), in which there is no additional splitting by the ^{14}N nuclei of the heterochain bridge [48]:



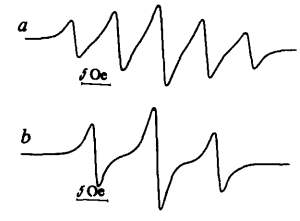


Figure 10. ESR spectra of the biradical (XLVII): a) unsubstituted biradical; b) biradical containing nitrogen-15.

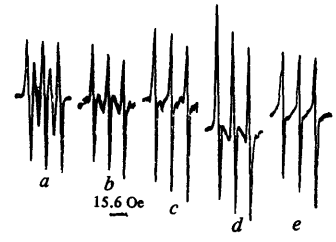
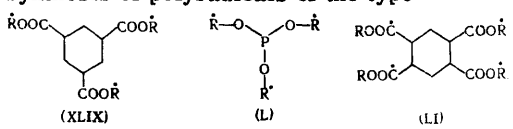


Figure 11. ESR spectra of the biradical (XLII) in different solvents: a) hexane; b) benzene; c) chloroform; d) carbon tetrachloride; e) acetic acid.

The ESR spectra of iminoxy-biradicals vary both with temperature and the nature of the solvent. Thus, when the temperature is raised, additional lines appear in the spectrum of compound (XL), the intensity of which increases with temperature. Fig. 11 presents the spectra of

the biradical (XLII)[47] in various solvents. Evidently here the shape of the spectrum is influenced not only by the viscosity of the solvent but also by the different solvation effects.

The synthesis of polyradicals of the type



(XLIX) (L) (LI)

on the basis of the monomeric biradical Ṙ has been described recently[52]. They have all been investigated by the ESR method.

It is interesting to note that the g-factors of iminoxy-biradicals are the same as those of the corresponding monoradicals and in none of the cases has it been possible to observe ESR signals with $g = 4$, which would correspond to $[\Delta m] = 2$ transitions.

Finally, the true mechanism of the exchange observed in the iminoxy-radicals has not yet been elucidated. Some workers[46-49] believe that the overlapping of the π-orbitals of the unpaired electrons and hence the exchange between the two halves of the biradical occur as a result of the bending of the molecules and the deformation of the chemical bonds and the angles between them, i.e. there is "conformational" exchange interaction when close mutual intramolecular approach of the paramagnetic fragments of the biradical takes place.

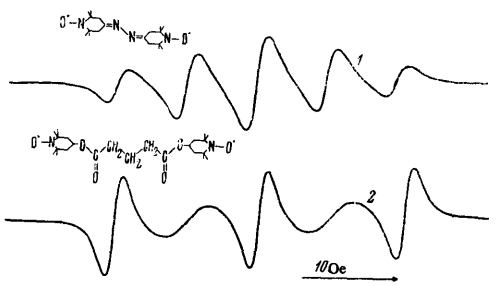
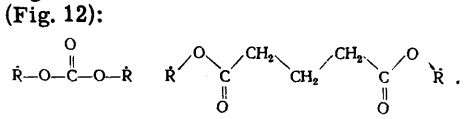


Figure 12. ESR spectra of the biradicals (XLVII) (curve *1*) and (LIII) (curve *2*).

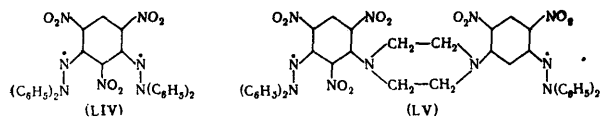
The influence of exchange interaction on line width has been investigated with the biradicals (LII) and (LIII) as examples[53] (Fig. 12):



(LII) (LIII)

When J varies in such a way that its average value $\overline{J}$ remains greater than A, the width of the central line and of the two outer lines remains constant, since their positions are independent of the changes in J. Other, intermediate lines become broader. This broadening is due to the modulation of the exchange integral J. When the exchange integral is expressed by formula (3), it is evident that its value depends on the extent of the overlapping $\Phi_A\Phi_B$ of the two wave functions $\Phi_A(1)$ and $\Phi_B(2)$, where $\Phi_A(1)$ is the orbital of the unpaired electron in one half of the molecule and $\Phi_B(2)$ is the orbital in the other half. When the extent of overlapping is low, the integral is large, and, correspondingly, a decrease in the extent of overlapping leads to a decrease of J. Since the biradical is not a rigid molecule, it can assume various configurations, each of which corresponds to a particular degree of overlapping $\Phi_A(1)\Phi_B(2)$ and different values of the integral J. This modulation of the integral J by intramolecular conformational changes does in fact constitute the relaxation mechanism which influences the biradical line width.

Biradicals of the hydrazine series (LIV) and (LV) have been synthesised recently and have been investigated by the ESR method[54,55]:



(LIV) (LV)

The theoretical spectrum of the biradical (LIV) is consistent with experiment (Fig. 13), provided that the unpaired electrons are localised in their halves and that each

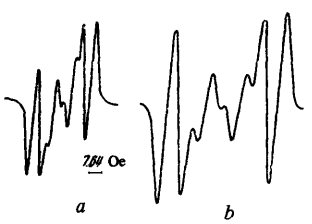
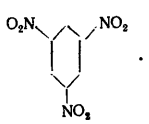
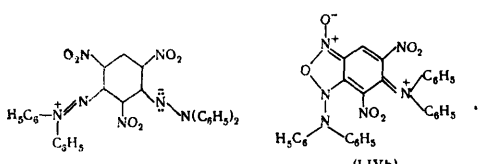


Figure 13. ESR spectra of the biradicals (LIVa) and (LIVb).

electron interacts only with the two non-equivalent nitrogen atoms and $A_{N_1}/A_{N_2} = 0.64$ and $A_{N_1} + A_{N_2} = 17.13$ Oe. This suggests that $J \ll A$ and there is thus no electron interaction via the bridge



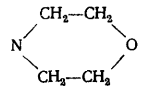
It is interesting to note that Heidberg and Weil[56] failed to observe the biradical form (LIV) in the oxidation of the bihydrazine monoradical and they attributed the singlet ground state of the resulting compound to the presence of ionic structures of the type



(LIVa) (LIVb)

The biradical (LV) gives rise to an ESR spectrum consisting of nine hyperfine structure components (Fig. 14). The theoretical spectrum containing nine components with intensity ratios 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1 corresponds to four equivalent nitrogen atoms. Evidently each unpaired electron is not linked to its hydrazyl group and migrates from one half of the molecule to the other, i.e. in this case

$J \gg A$ and the electrons do interact with one another. Since in this case the interaction via the σ-bonds of the bridge



is excluded, it can be supposed that here the exchange mechanism is probably the same as in iminoxy-biradicals.

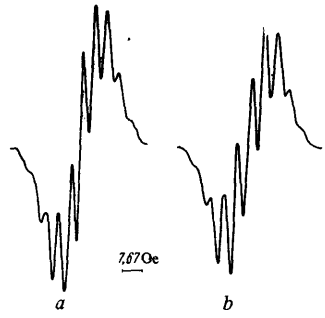
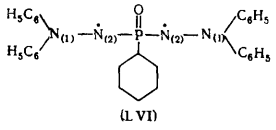


Figure 14. ESR spectra of the biradical (LV): *a*) experimental spectrum; *b*) theoretical spectrum.

A variation of the intensity of the spectrum of the biradical (LV) with temperature in the range between +60°C and −50°C could not be observed. Further reduction of temperature leads to a broadening of the ESR lines and the disappearance of the hyperfine structure. The spectrum of the supercooled solution shows one ESR line with a width of about 20 Oe between the points of inflexion and a g-factor of 2.0035. Other lines, characteristic of $S = 1$ as well as $|\Delta m| = 2$ transitions, were not observed. This may be due either to the low intensity of the $|\Delta m| = 2$ transition, which is weaker by 3 powers of 10 than the $|\Delta m| = 1$ transition, or to the breakdown of the intramolecular exchange bond between the two halves of the molecule on going to the supercooled state. In this case the anisotropic hyperfine structure is not resolved because of the dipole-induced broadening.

A biradical based on a phenylphosphonic dihydrazide has also been obtained[55]:

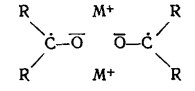


(LVI)

At the beginning of oxidation the ESR spectrum of the monoradical, consisting of seven hyperfine structure components, is observed. Comparison with the theoretical spectrum showed that the experimental spectrum results from the superposition of two quintets. The five lines in each quintet are due to the equally probable interactions of the unpaired electron with the two atoms of hydrazine. The isotropic hyperfine structure constant $A_N = 6$ Oe. The doublet with the constant $A_P = 10$ Oe must be assigned to the phosphorus nucleus. On further oxidation, the seven-component spectrum is converted into a quintet with the intensity ratios 1 : 2 : 3 : 2 : 1. The five lines of the hyperfine structure correspond to the delocalisation of each electron in its half of the molecule only, under conditions of interaction with the two nitrogen atoms of hydrazine. The form of the spectrum suggests that the nucleus of the phosphorus atom does not participate in splitting. There may be several reasons for the non-involvement of the phosphorus atom in hyperfine splitting and probably the main one is the breakdown of the p_π–d_π conjugation when the environment of the phosphorus changes on transition from the monoradical to the biradical. The constants A_{N_1} and A_{N_2} become larger by a factor of 1.5 than those of the monoradical, and the overall splitting $A_{N_1} + A_{N_2}$ increases from 12.2 to 17.6 Oe. An anisotropic hyperfine structure broadened by dipole interactions appears in the spectrum of the supercooled solution. No lines, additional to those with $g \simeq 2$, were observed.

VII. BIRADICALS OF METAL KETYLS

The study of the ESR spectra of the ketyls derived from hexamethyl- and pentamethyl-acetones showed that their hyperfine structure is due to splitting by protons in the ketone components, and furthermore that the unpaired electron is linked to the two equivalent nuclei of the alkali metal[59]. This finding can be accounted for on the basis of a dimeric structure of the ketyl molecule in which the two organic radicals are joined by two equivalent alkali metal ions:



The presence of dimers is also confirmed by optical spectra[57,59], which vary markedly with the concentration of the ketyls. Thus the spectrum of the fluorenonesodium ketyl in methyltetrahydrofuran at a high concentration shows a peak at 450 nm, while at lower concentrations this peak appears at 525 nm. Evidently there is a monomer–dimer equilibrium in the solution and since the spectra of the dimers and monomers are almost identical, it is evident that dimerisation does not involve any changes in the electronic structure. Thus the dimer molecules may be regarded as a kind of biradical system in which each electron spin belongs predominantly to one half of the dimer but is divided between the nuclei of the alkali metal. The ESR spectrum of solid ketyl solutions at 77°K shown in Fig. 15 is characteristic of triplet systems. The spectrum corresponding to the $|\Delta m| = 1$ transition results from the superposition of two spectra—a narrow central singlet and a broad doublet. With increase in the size of alkali metal ions, the doublet splitting increases from 118 Oe for the fluorenonelithium ketyl to 82 Oe for the fluorenonepotassium ketyl. The optical spectra at 77°K indicate the existence of both a monomeric and a dimeric form. The central singlet peak can be attributed to monomers (or dimers with a low degree of dipole interaction) and the doublet to dimers with a high degree of dipole interaction. Apart from the $|\Delta m| = 1$ transition, an absorption peak is observed when the field strength is reduced by one-half. This is due to the $|\Delta m| = 2$ transition (Fig. 15*f*). Its intensity is of the order of 10^{-3} of the intensity associated with the $|\Delta m| = 1$ transition.

The hyperfine structure of the spectra of liquid solutions of dimers with a high degree of dipole interaction is broadened by relaxation, while dimers with a low degree of dipole interaction give rise to a well resolved structure. Analysis of the Reitz–Weissman type of hyperfine splitting

in the spectra of ketyl dimers[11] shows that both the splitting by the ^{13}C nuclei and by protons in the ESR spectra of divalent- and trivalent-metal ketyls corresponds to the condition $A \gg J$. The rate of spin exchange between the two halves of the ion pair is thus much lower than the frequency of the hyperfine interaction and the spectrum of the dimer is similar to that of the monomer. The temperature variation of the absorption intensity is consistent with the low value of J.

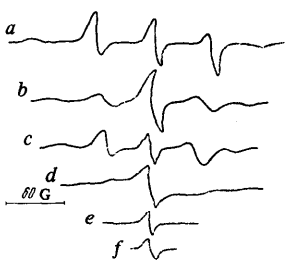


Figure 15. Spectra of paramagnetic ketyls in methyl tetrahydrofuran at 77°K; $|\Delta m| = 1$:
a) fluorenonelithium; *b*) fluorenonesodium; *c*) xanthonelithium; *d*) fluorenonebarium; *e*) fluorenonemagnesium; *f*) $|\Delta m| = 2$, fluorenonelithium.

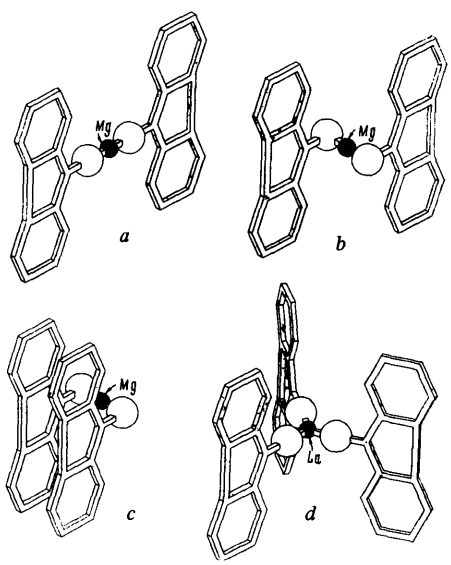


Figure 16. Possible structures of paramagnetic ketyls.

The possible structures of the dimeric ketyls can be inferred from the magnitude of the doublet splitting. Divalent-metal ketyls, apart from fluorenonebarium and fluorenonestrontium, give rise to spectra in which the half-width is about 10–15 Oe. Since divalent-metal ketyls do not dissociate, it can be assumed that the dipole interaction in them amounts to about 10 Oe. A possible structure of such a dimer is presented in Fig. 16*a*. The line half-width of 25 Oe observed in the spectra of trivalent-metal ketyls (Fig. 16*d*) indicates a high degree of dipole interaction. Structures of types *b* and *c* (Fig. 16) are possible in those cases where the line is broader and the dipole interaction more pronounced. In all probability there is an equilibrium between the dimeric forms and the most stable structure is determined by several factors: the structure of the initial ketone, the charge and the dimensions of the metal atom, and the nature of the solvent.

The data described above permit the following conclusions.

Electron spin resonance has proved most useful for the determination of the biradical nature of those compounds, the paramagnetism of which had not been demonstrated unambiguously by static magnetic susceptibility measurements and ortho–para conversion of hydrogen. For biradicals consisting of components separated by insulating groups, the ESR method permits certain inferences about their structure—the distribution of unpaired electrons. It follows from the hyperfine structure analysis of the spectra of biradicals of this type that each unpaired electron is localised in its own half and the biradical is a double monoradical.

However, there are as yet no convincing experimental data which would permit the analysis of the properties of systems of the type of Chichibabin's hydrocarbon in the triplet state (with "strong exchange interaction" between the two electrons). Possibly the absence of a hyperfine structure from the ESR spectra of certain biradicals of this type (and sometimes also the absence of an ESR signal at room temperature) is associated with the mechanism of the broadening, the main contribution to which comes from the spin–lattice relaxation. For this reason, the $|\Delta m| = 2$ transitions corresponding to the triplet state in these biradicals and also in the metal ketyl biradicals have been observed at very low temperatures only.

Atropisomers have not been investigated at all, although there is no doubt that the degree of coplanarity of the two halves of the biradical could be inferred from the hyperfine structure of the ESR spectra.

Further, more detailed study of the mechanism of the so called "conformational exchange" is essential.

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