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Electron spin resonance measurements in organic compounds

J.H. LUPINSKI

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PROEFSCHRIFT TER VERKRIJGING VAN DE GRAAD VAN
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Promotor: Prof. Dr. L.J. Oosterhoff

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INTRODUCTION

Shortly after its discovery electronspin resonance (ESR) has become a source of information in chemistry which is of still growing importance. It has opened up new possibilities for the investigation of a wide variety of chemical problems. The application of this method to a number of such problems in organic chemistry forms the subject of this thesis.
Actually ESR gives information of the interaction of unpaired electrons with magnetic fields originating from surrounding particles. To understand the terms in which this interaction is represented in the experimental results we will first describe briefly a few fundamentals of ESR.

In the presence of a constant magnetic field (H) the magnetic moment of an unpaired electron is either parallel or antiparallel with respect to the direction of the field. The two situations have different energies:

$$E_{-\frac{1}{2}} = + \tfrac{1}{2} g_e \mu_e H$$
$$E_{+\frac{1}{2}} = - \tfrac{1}{2} g_e \mu_e H \qquad (1)$$

g_e is usually called the spectroscopic splitting factor, while μ_e is the Bohr magneton. In ESR experiments transitions between the two levels are effected by irradiation. The frequency (γ) of the radiation must satisfy the Bohr condition

$$h\ \gamma = g_e \mu_e H \qquad (2)$$

in which h is Planck's constant.
In practice this is realized by keeping γ constant and bringing H in the proper range (of which H_o is the centre). The sample will then absorb energy from the radiation. Measurement of this absorption results in a curve which is a function of the applied external magnetic field (fig.1).
As for the intensity of the signal it should be mentioned that the surface under the curve is proportional to the number of unpaired electrons. Since quantities as small as about 10^{12} unpaired electrons can be detected the method belongs to the most sensitive techniques used in chemistry.
In general equation (2) does not apply to electrons in organic

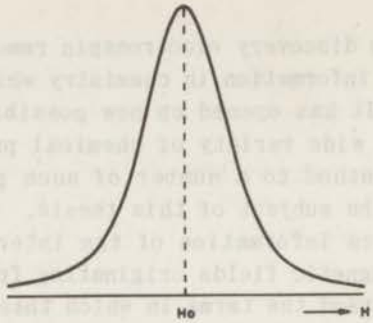

Fig. 1. Absorption versus magnetic field.

substances, since most electrons may be considered as occurring in pairs with opposite spins coupled by exchange forces. This coupling, being much stronger than the interaction with an external field, prevents the orientation of the electronic magnetic moment in such a field.

For this reason the applicability of the method may seem rather limited. Until recently only a very small part of the organic compounds were known to contain unpaired electrons, i.e. free radicals, biradicals and some metal-organic compounds. However, due to the high sensitivity of the ESR spectrometers it appears that unpaired electrons occur frequently and can be detected by the technique of ESR. Otherwise no direct proof of their presence could be given.

Equation (1), giving the energy levels of free electrons in an external field, has to be extended for electrons in chemical compounds in which they are subjected to interactions with surrounding particles and with crystalline fields. These interactions are manifested in the shape of the line and in the position of its centre.

For a discussion of the line shape we consider the energy operator of the system. Since a complete operator, accounting for all of the interactions, would be very complicated and difficult to handle it is a lucky circumstance that not all of the terms are of importance at the same time. As an example we consider the interaction of an unpaired electron spin with the magnetic moment of a nucleus in its vicinity. The Hamiltonian for such a system is:

$$\mathcal{H}_{op} = H\vec{\mu}_e + \frac{\vec{\mu}_e\vec{\mu}_n}{r^3} - \frac{3(\vec{r}\vec{\mu}_e)(\vec{r}\vec{\mu}_n)}{r^5} - \frac{8\pi}{3}\,\delta(r)\,\vec{\mu}_e\vec{\mu}_n \qquad (3)$$

in which $\vec{\mu}_e$ and $\vec{\mu}_n$ are the operators for the electron- and nuclear magnetic moments respectively, r is the distance between electron and nucleus and $\delta(r)$ is the Dirac delta function for that distance. The second and third terms of equation (3) pertain to dipole-dipole interaction between the magnetic dipoles of an unpaired electron and a nucleus at a distance r apart, this interaction being anisotropic. The last term represents the so called "Fermi interaction" which is an isotropic dipole-dipole interaction. It only becomes effective if both particles are at the same spot.

If the influence of neighbouring unpaired electrons has to be taken into account then three more terms have to be included. These are of the same form as the last three terms of equation (3), only the operator for the nuclear moment must be replaced by that for the electron. The third term, the equivalent of the Fermi interaction, in that case being of minor importance, is usually omitted. Further it should be noted that in calculations starting from equation (3) the electronic spin is in many cases supposed not to affect the nuclear wave function and therefore the operator for the nuclear moment can be replaced by its eigenvalue.

The shape of the absorption line may vary widely depending upon the importance of the different terms in the operator. For free electrons, to which only the first term of equation (3) applies, the energy levels (given by equation 1) between which transitions occur are sharp and consequently the line will be narrow. If dipole-dipole interaction is present the energy levels are split up in a number of components and one would expect to find a corresponding number of lines. Because of the anistropy the magnitude of the splitting depends upon the spatial orientation of the molecules. If in the sample all orientations are present this will result in bands of energy levels, the transitions between the levels of such bands forming a broad line. Therefore the splitting will only be observed in single crystals.

In a liquid solution of a radical however, the orientation of the molecules changes so rapidly that the dipole-dipole interaction is averaged out except for the Fermi term which is independent of the spatial orientation [1,2] and again a distinct number of lines can be observed. This is an example of motional narrowing of the absorption line.

In another type of motional narrowing the unpaired electron moves over the substance and does not belong to a particular molecule. The dipole-dipole interaction is cancelled out and a single narrow line remains.

A third mechanism that also diminishes the line width is exchange narrowing and this operates in situations where the molecules containing the unpaired electron are rather close, so that the electrons can exchange their spins mutually. If this occurs very frequently the dipole-dipole interactions are again averaged out and the spectrum consists of a single narrow line.

In liquid solutions, when only the Fermi term is of importance, hyperfine structure may appear in the absorption line. Such a spectrum shows that interaction with different nuclei takes place so that the electron is certainly not localized. The hyperfine structure offers a good possibility to study the behaviour of an unpaired electron within a radical molecule. The hyperfine structure spectra can be understood with the aid of the energy levels derived from equation (3). The second and third terms of this equation do not contribute to the final result in this case. If the Hamilton operator is averaged over the orbital part of the wave function and the operator for the nuclear spin is replaced by its eigenvalue (I) the last term reduces to aI, a being an interaction parameter. The energy levels are then given by an equation very similar to equation (1)

$$E = \pm \tfrac{1}{2} \{g_e \mu_e H + aI\} \qquad (4)$$

If interactions with more than one nucleus have to be considered the sum of aI must be taken ($\Sigma a_j I_j$). In cases where no calculated a_j's are available one may construct different spectra by choosing various sets of a_j's. Often a set of a_j's can be found that leads to a spectrum similar to the experimental one. This method however has an empirical character and sometimes it is possible to construct the same spectrum starting from different sets of a_j's. To check the theoretical ideas concerning the distribution of unpaired spin a calculated and an experimentally determined a_j are required. It should be noted that the study of the hyperfine structure of the ESR spectra is hitherto the only means by which the theoretical considerations regarding the distribution of spin density can be checked.

Contrary to the rather extended discussion of the line shape we will not pay much attention to the position of the line centre since in our problems this centre was practically always found at the same value of H_0.

In chapter II the ESR spectra of liquid solutions of triphenylmethyl and similar radicals are discussed. The complicated hyperfine structure is the most important feature of the line shape and attempts have been made to demonstrate the influence of substituent groups on the hyperfine structure pattern.
In the study of irradiated glassy solutions of aromatic hydrocarbons ESR was principally used as a means of detection. However it appeared, rather unexpectedly, that in some spectra of the radicals formed by irradiation, hyperfine structure could be observed so that also the line shape becomes of interest in such cases. The results are given in chapter III.
Organic molecular compounds are discussed in chapter IV. In a number of such compounds a small paramagnetic character could be detected and there are some indications that a line narrowing mechanism is present here. From the line shape and the circumstances under which ESR occurs one is inclined to conclude that the common idea concerning the structure of these charge transfer complexes has to be extended. That these complexes show semiconductor properties points in the same direction.
A typical example of an application of the method as a means for detecting radicals is demonstrated for the case of violanthrone. It will be shown in appendix I that the dye violanthrone is diamagnetic and that the paramagnetism mentioned in the literature is due to an impurity.
The technique has also been used to observe the line width of radicals in solid solutions. The experiment of Gordy and Van Roggen regarding a solid solution of diphenylpicrylhydrazyl (DPPH) in benzene has been extended to other solvents. The details of this work are given in appendix II.
The apparatus, used in these experiments, is briefly outlined in chapter I.

CHAPTER I

APPARATUS

For the measurement of ESR different kinds of spectrometers can be used. The design of the instruments is governed by the relation $\gamma = \frac{g_e \mu_e}{h} H$ which shows that γ is a linear function of H. Magnetic fields that can easily be realized lie in the range between 1000 and 10000 gauss. This puts the frequency into the microwave region where klystrons are necessary to provide for the proper frequency. Detailed descriptions of ESR spectrometers have been given in the literature and a recent survey is given by Ingram [3].

The instrument of which a block diagram is shown in fig. 2 is of the heterodyne type and thus contains two oscillators (klystrons). Its main oscillator is protected from unwanted reflections by a "uniline", while its frequency of about 9350 MHz is kept constant by a Pound stabilization system. Via a directional coupler the energy reflected by the cavity between the magnet poles is mixed with the signal of another klystron in such a way that the intermediate frequency (I.F.) is 35 MHz.

If the cavity containing the sample is tuned as well as possible to the main oscillator frequency, practically no microwave energy will be reflected. If the proper external magnetic field is then applied the sample will absorb energy from the high frequency radiation and consequently the cavity will no longer be tuned, reflecting a signal that is proportional to the absorption by the sample.

Since the external magnetic field is modulated at a low frequency the information from the sample entering the detection system is a low frequency amplitude modulated 35 MHz signal. In the amplifier/detector the 35 MHz signal is amplified and detected, but the low frequency part is only amplified.

By means of a large modulation amplitude of the magnetic field the output signal from the amplifier/detector can be fed into an oscilloscope to display the absorption curve. When the magnetic field is modulated with a small amplitude the amplifier/detector output can be further amplified in a phase sensitive amplifier and finally be put on a recording meter where the absorption line will be represented as its first derivative. For these experiments the power amplifier feeding the modulation coils is so constructed that it can provide the coils with the

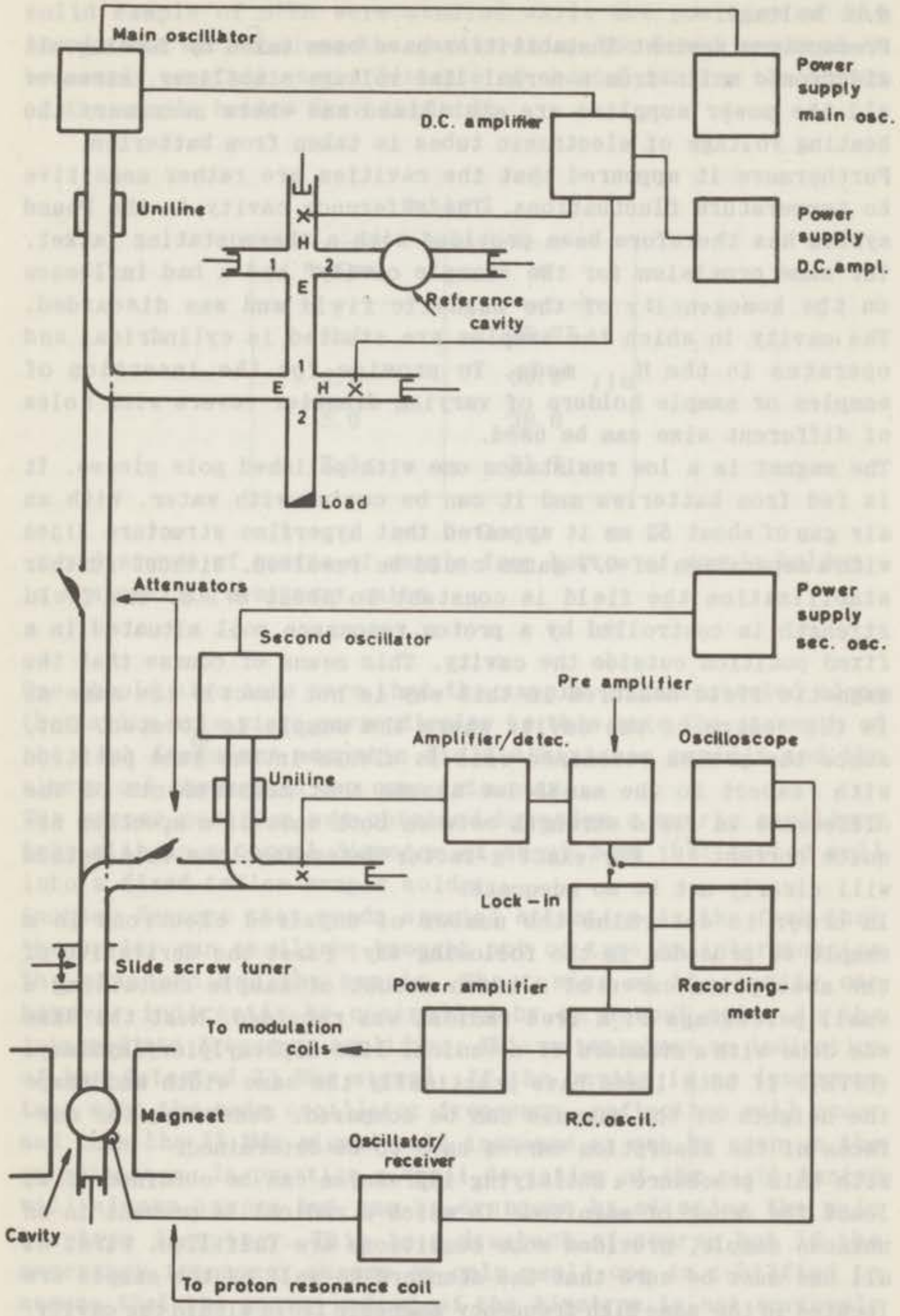
Main oscillator
Power supply main osc.
D.C. amplifier
Uniline
Power supply D.C.ampl.
X
H
1
2
E
Reference cavity
1
E
H
X
2
Load
Attenuators
Power supply sec. osc.
Second oscillator
Pre amplifier
Amplifier/detec.
Oscilloscope
Uniline
X
E
Lock – in
Slide screw tuner
Power amplifier
Recording-meter
To modulation coils
Magneet
R.C. oscil.
Oscillator/ receiver
Cavity
To proton resonance coil

Fig. 2. Block diagram

modulation frequency and in addition with a linearly increasing d.c. voltage.

Precautions against instabilities have been taken by feeding all electronic units from a normal line voltage stabilizer, moreover all the power supplies are stabilized and where necessary the heating voltage of electronic tubes is taken from batteries.

Furthermore it appeared that the cavities are rather sensitive to temperature fluctuations. The reference cavity in the Pound system has therefore been provided with a thermostating jacket. The same provision for the "sample cavity" had a bad influence on the homogeneity of the magnetic field and was discarded.

The cavity in which the samples are studied is cylindrical and operates in the H_{011} mode. To provide for the insertion of samples or sample holders of varying diameter covers with holes of different size can be used.

The magnet is a low resistance one with polished pole pieces. It is fed from batteries and it can be cooled with water. With an air gap of about 52 mm it appeared that hyperfine structure lines with a separation of 0.7 gauss could be resolved. Without further stabilization the field is constant to about 0.1 %. The field strength is controlled by a proton resonance coil situated in a fixed position outside the cavity. This means of course that the magnetic field measured in this way is not exactly the same as in the centre of the cavity where the sample is located. But, since the proton resonance coil is always in the same position with respect to the sample we assume that measurements of the difference in field strength between both ends of a spectrum are quite correct *). For exact g-factor determinations this method will clearly not be so adequate.

In order to determine the number of unpaired electrons in a sample we proceded in the following way. First the derivative of the absorption curve of a known amount of sample containing a small percentage of a free radical was recorded. Next the same was done with a standard of a radical like diphenylpicrylhydrazyl (DPPH). If both lines have practically the same width and shape the heights of the signals can be compared. Otherwise the surfaces of the absorption curves have to be determined.

With this procedure a satisfying impression can be obtained of at least the order of magnitude in which a radical is present in an unknown sample, provided some conditions are fulfilled. First of all one must be sure that the standard as well as the sample are located in the same high frequency magnetic field within the cavity.

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*) A similar assumption was also made by Venkateraman, Segal and Fraenkel 4).

To get an idea of the variation of this field the signals of a solid sample of DPPH were studied while the position of the sample was varied along the cavity-axis. The field appeared to be nearly constant over a distance of about 5 mm from the bottom of the sample holder (see table 1).

Table 1

r (mm)	s
1.2	39.75
2.5	39.9
5.0	39.0
7.5	31.7

r = distance of centre of sample from bottom of sample holder.
s = signal in arbitrary units.

One should also take care that the sample is concentrated along the cavity axis since perpendicular to this axis the strength of the high frequency magnetic field diminishes rapidly and the electrical absorption can come into play.
The proper position was obtained by using a quartz capillary tube with an external diameter of about 2 mm that fitted well into a fixed teflon sample holder.
Another feature that needs special attention is the fact that the cavity can easily be brought out of tune by interchanging the standard and the sample. The tuning of the cavity can however indirectly be controlled by an output meter in the intermediate frequency amplifier. This meter gives an indication of the detected 35 MHz signal. If the cavity is no longer on tune with the main oscillator frequency, reflection will occur and thus the 35 MHz signal will increase as can be seen on the output meter. In practice a small deviation of the right tuning will always happen but can be overcome by altering the main klystron frequency. This is a drawback of course but if the necessary frequency change is only small one is justified to assume that the energy output of the klystron is not seriously affected. Furthermore the variation must be small, otherwise the intermediate frequency will differ appreciably from 35 MHz and

since the I.F. amplifier has a band width of about 1 MHz, large deviations from 35 MHz are not allowed.

The sensitivity of ESR spectrometers is usually determined with the aid of DPPH. As accurate weighing is not possible for quantities in the order of one gamma the DPPH is diluted with an indifferent carrier, as for instance Hirshon and Fraenkel [5] have done. However it should be borne in mind that although DPPH is a fairly stable radical it nevertheless decomposes in the course of time, especially when mixed with "indifferent" carriers. We observed a rather rapid decomposition of DPPH when mixed with $BaSO_4$ or ZnO. DPPH combined with pure NaCl is more stable but after a longer period of time new samples have to be made to check the sensitivity of the apparatus.

In a later chapter the paramagnetism of some organic complexes will be described and it will turn out that some of them are to be preferred for sensitivity measurements.

In general we were able to observe on the oscilloscope a signal from 3.5×10^{-9} moles of a free radical, as long as the line width was not extremely large. When using the lock-in amplifier and recording meter a better signal to noise ratio could be obtained. Due to the small modulation amplitude, to be used in connection with the lock-in amplifier, much smaller signals were difficult to detect.

A further impression of the resolving power and sensitivity of the spectrometer might be obtained from those spectra of diluted solutions of free radicals which display a complicated hyperfine structure pattern. Such spectra are shown in chapter II.

CHAPTER II

FREE RADICALS IN LIQUID SOLUTION

In liquid solutions of free radicals the isotropic Fermi interaction of the unpaired electron with the nuclear moments can be observed since the anisotropic dipole-dipole interaction is cancelled out by the motions of the molecules.

The fact that interactions with different nuclei can be observed is a direct experimental indication that the unpaired electron is not localized. Actually the unpaired electron is more delocalized than was formerly thought, for it appears that Fermi interaction occurs between unpaired electrons and hydrogen nuclei. The magnitude of this interaction is conveniently expressed in terms of spin density *) which is the product of the electron density and the average spin moment in the field direction at the same spot. McConnell 7) pointed out that the spin density can be negative. The electron density, formerly used to describe the system, is always positive and the sum of the local densities must be one in the case of one unpaired electron. The sum of the integrated spin densities must also be one, but now the local densities may be negative.

In the common stable organic free radicals the unpaired electron is thought of as belonging to the π-electron system of the molecule. The π-electrons are distributed in clouds on both sides of a nodal plane so that at first sight it seems impossible for π-electrons to have a Fermi interaction with nuclei (protons) situated within that nodal plane. Nevertheless experiments clearly indicate that this happens (for instance in semiquinones and in aromatic hydrocarbon mononegative ions).

The explanation now generally accepted is that there is "resonance" between the σ- and π-electrons of a molecule 8-11).

This means that there is a reasonable chance to find the electrons forming the σ-bond in a non-bonding state, so that one of the σ-electrons and a π-electron are coupled. The remaining σ-electron now has an unpaired magnetic moment that may interact with a nucleus within the nodal plane.

By quantum mechanical calculations one can also understand that the electron spin density on a hydrogen nucleus is proportional to the integrated spin density on the adjacent carbon atom 7).

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*) The spin density is described in more detail by Adam and Weissman 6).

On this basis De Boer [12)] was able, for the mononegative ions of biphenyl, naphtalene, anthracene, e.g. to correlate spin densities, calculated according to simple molecular orbital theory, with the hyperfine structure spectra.
These radicals consist of an even number of carbon atoms and all are ions. When however the experimental hyperfine structure spectra of neutral free radicals like triphenylmethyl are compared with the theoretical ones, calculated with the aid of molecular orbital theory, there appears to be a serious discrepancy. Brovetto and Ferroni [13)] demonstrated that valence bond calculations led to a quite different result, in better agreement with experiment. Adam and Weissman [6)] extended the valence bond calculations of Brovetto and Ferroni for triphenylmethyl and pointed out that spin densities on the carbon atoms linked to the central one and on carbon atoms in the meta position are negative. Generally in odd alternating neutral free radicals the spin densities have alternating signs.

On this basis it becomes interesting to observe hyperfine structure of free radicals in order to see if the patterns can be understood along the lines described above, thus gaining more insight in the electronic structure of the molecules.
We studied a number of substituted triphenylmethyl radicals to see if the substituents have a marked influence on the hyperfine structure spectra. There are examples in which a slight change in the structure of a radical results in a divergent hyperfine structure pattern. DPPH and N-picryl-9-aminocarbazyl [14)] are such examples. The difference between these two compounds consists only in the presence of an extra carbon-carbon bond between the two phenyl groups. The hyperfine structure spectra are quite different however. Similar changes in hyperfine structure are observed when in DPPH one of the nitro groups is replaced by a sulfonate group [14)]. It is known that only the two nitrogen atoms in the centre of the molecule are responsible for the hyperfine structure. Although those atoms are not directly involved in the changes, the effect of the different situations in other regions of the molecule on the spectrum is remarkable. Similar phenomena have been observed by a number of authors [15-17)], while on the other hand experiments have shown that introduction of small changes in the structure of radicals not always leads to different ESR absorption spectra [18)].
In the case of triphenylmethyl, the complicated spectrum of which was first reported by Jarrett and Sloan [19)], there are many

variations possible because the substituted positions may vary as well as the substituent groups. Since it is known that in triphenylmethyl even the ortho hydrogen atoms give rise to a slight steric hindrance, substituents in the ortho position will strongly influence the steric orientation of the phenyl groups.

To a lesser extent the same is true for the meta positions. Here, only bulky groups will force the phenyl groups out of their most favourable orientation. If however the substituent groups are placed in the para position no steric hindrance will occur and the only difference with unsubstituted triphenylmethyl is a different number of ring hydrogen atoms and probably a changed distribution of spin density.

Most of the observed compounds carry a substituent on one or more para positions while occasionally we studied a meta- and an ortho-derivative of triphenylmethyl.

The following known radicals and their hyperfine structure spectra, as far as they could be resolved, will be discussed:

1. Triphenylmethyl
2. Diphenyl (p-tolyl)methyl
3. Tri(p-tolyl)methyl
4. Tri(p-chlorophenyl)methyl
5. Diphenyl(p-anisyl)methyl
6. Diphenyl(m-tolyl)methyl
7. Diphenyl(o-chlorophenyl)methyl

In the discussion no mention will be made concerning the concentration of the solutions because we actually did not know them. The solutions of the radicals were made by shaking solutions of the corresponding chloromethanes in benzene with zinc dust. To complete the reaction the contact between the reactants should be extended over a period ranging from one to several hours. Such long reaction times often result in mixtures of different compounds, for instance in the case of the halogen substituted triphenylmethyl radicals [20]. In certain cases there is another reason that makes it impossible to determine the accurate concentration because some radicals can disproportionate rather rapidly. Tri(p-tolyl)methyl is an example of such a radical [21,22].

To minimize the above mentioned complications the spectra*) of freshly prepared solutions were recorded as quickly as possible.

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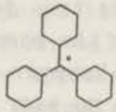
*) All spectra are represented as the first derivative of the ESR absorption.

Of course this procedure had to be repeated a few times to see if the results could be reproduced.



Triphenylmethyl

Diluted solutions of this radical have first been described in detail by Jarrett and Sloan [19]. They found 21 lines in the spectrum with a strong indication of further splitting of the individual lines. Originally we found 19 lines but improvement of our apparatus enabled us to observe 21 lines, the further splitting mentioned by Jarrett however could not be realized (fig. 3).

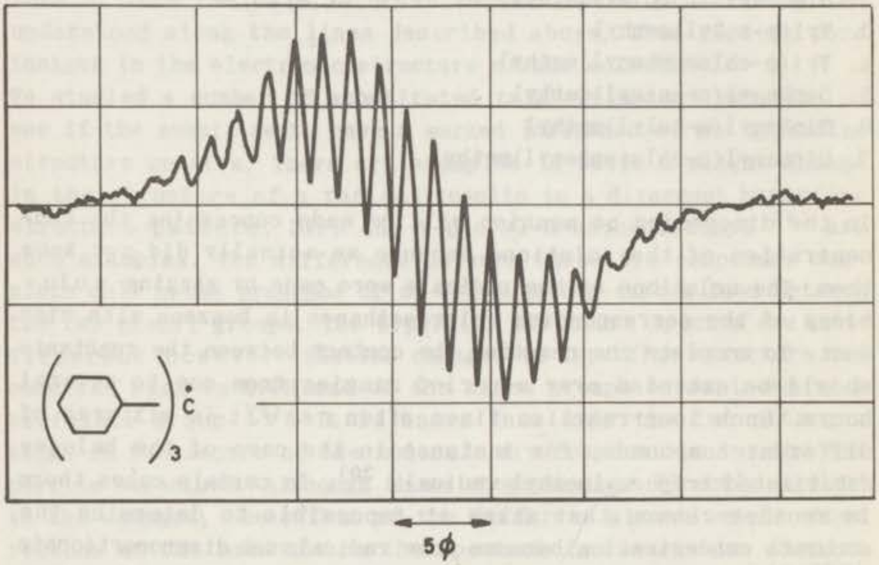


Fig. 3. Triphenylmethyl in benzene.

A typical feature of the spectrum is that the central line is of lower intensity than its nearest neighbours. This is not expressed by the spectrum in fig. 3, but it is seen in more diluted solutions where the resolution is somewhat better (fig. 4). In that case the number of still detectable lines has decreased and the signals on the edges of the absorption curve are too small to be recorded.

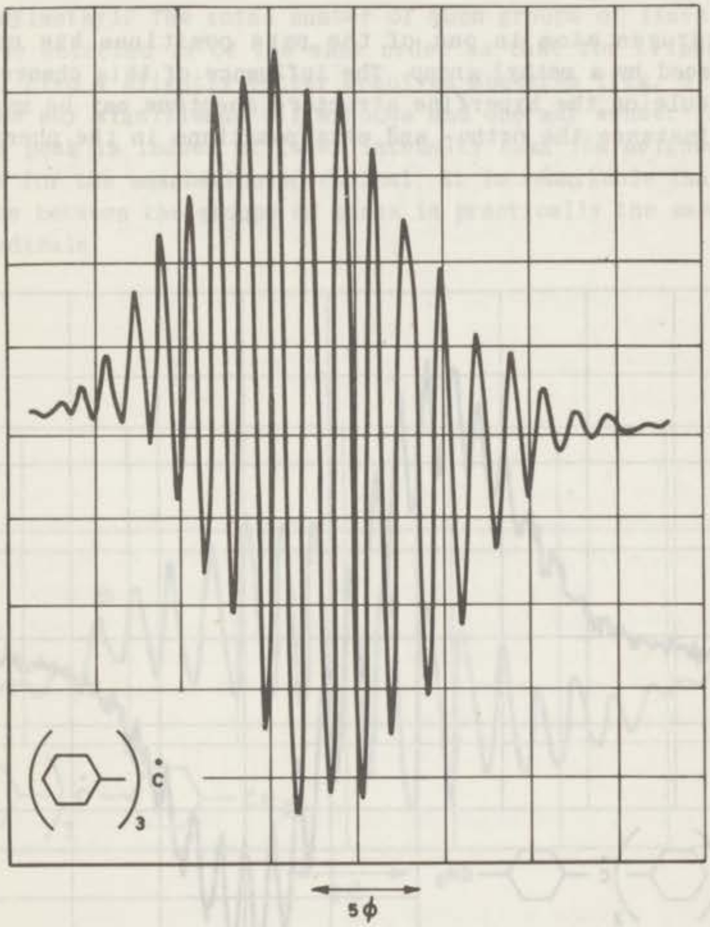
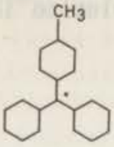


Fig. 4. Triphenylmethyl in benzene: more diluted solution.

Diphenyl(p-tolyl)methyl



A hydrogen atom in one of the para positions has now been replaced by a methyl group. The influence of this change in the molecule on the hyperfine structure spectrum may be manifold. For instance the ortho- and meta positions in the phenyl ring

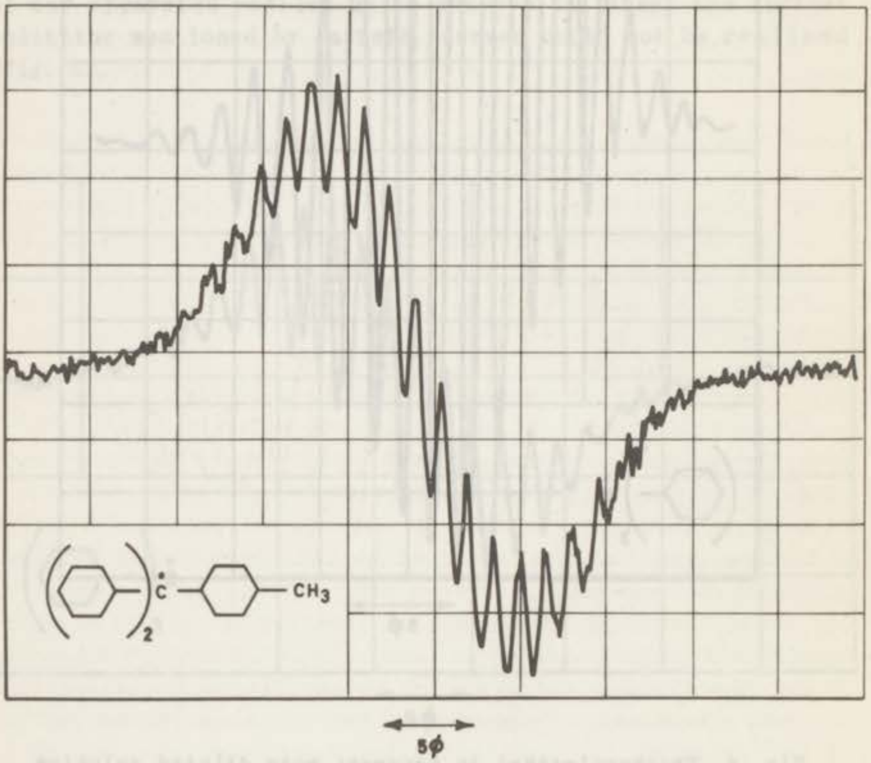


Fig. 5. Diphenyl(p-tolyl)methyl in benzene.

carrying the methyl group are probably no longer equivalent to those in the unsubstituted rings. Furthermore the protons in the methyl group may contribute to the final result. The different hyperfine structure splitting constants of the protons in the various positions of the molecule may give rise to a maximum number of 2700 hyperfine structure lines. From the spectrum (fig. 5) it appears that these lines occur in groups just as in triphenylmethyl. The total number of such groups of lines that could be detected is of the same order as that for triphenylmethyl. Also a slightly better resolved spectrum (fig. 6) does not show any significant differences and one may wonder if the central peak is indeed of lower intensity than its neighbours, just as for the unsubstituted radical. It is remarkable that the distance between the groups of lines is practically the same for both radicals.

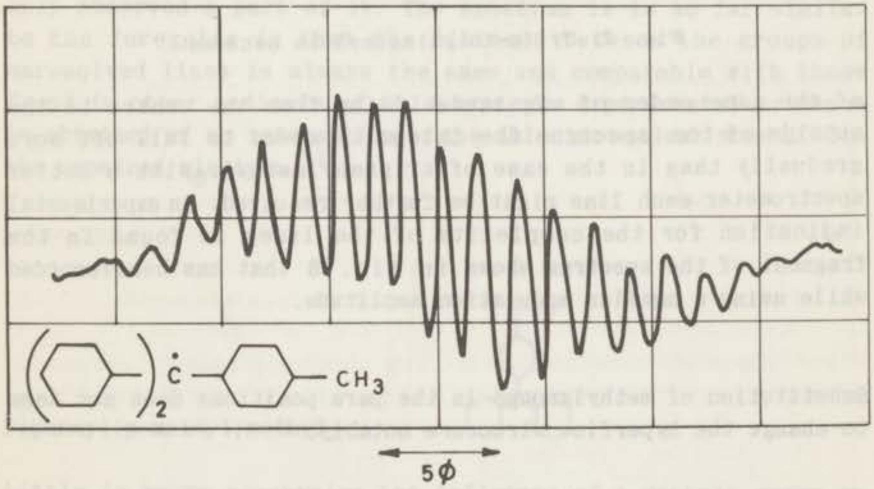
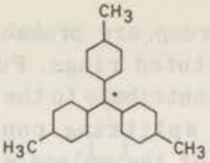


Fig. 6. More diluted solution of diphenyl(p-tolyl)methyl in benzene.

Tri(p-tolyl)methyl



Replacement of all the para hydrogen atoms by methyl groups neither changes the hyperfine structure pattern drastically (fig. 7). The total number of lines and their spacing is again

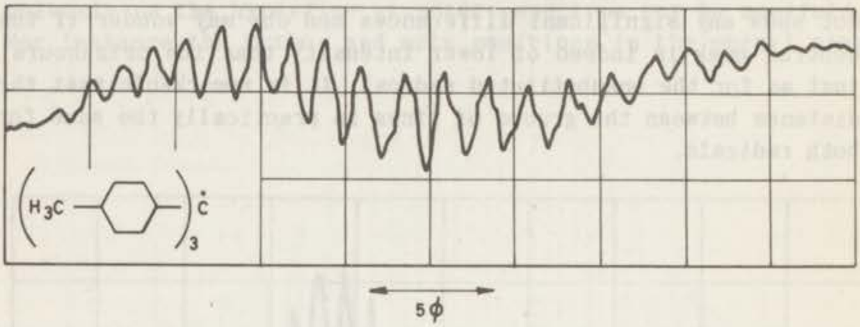
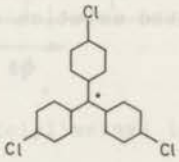


Fig. 7. Tri(p-tolyl)methyl in benzene.

of the same order of magnitude. Going from the centre to the outside of the spectrum the intensity seems to fall off more gradually than in the case of triphenylmethyl. With a better spectrometer each line might be further resolved. An experimental indication for the complexity of the lines is found in the fragment of the spectrum shown in fig. 8 that has been recorded while using a smaller modulation amplitude.

Substitution of methylgroups in the para positions does not seem to change the hyperfine structure notably.

Tri(p-chlorophenyl)methyl



In the foregoing spectra the number of hyperfine structure

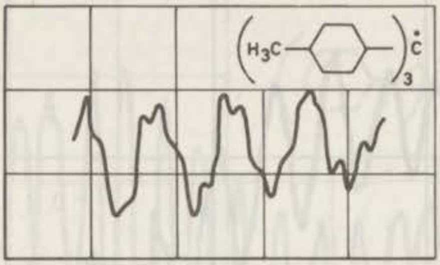
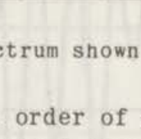


Fig. 8. Part of the spectrum shown in fig. 7.

components is always of the same order of magnitude. This was not found for tri(p-chlorophenyl)methyl (fig. 9). It is not sure whether this spectrum is really composed of a smaller number of lines than those of the above mentioned radicals or that we have only observed a part of it. The spectrum is in so far similar to the foregoing in that the distance between the groups of unresolved lines is always the same and comparable with those found in other radicals of this type. No experimental evidence is obtained of an interaction of the chlorine nuclear moment with the unpaired electron *).

Diphenyl(p-anisyl)methyl



Little is known concerning the influence of a methoxy group on the hyperfine structure spectrum of a free radical. It is not yet sure whether there is an observable interaction of the unpaired electron with the protons of the methoxy group. At any rate the spectrum (fig. 10) of diphenyl(p-anisyl)methyl closely resembles that of diphenyl(p-tolyl)methyl, so that the difference between the substituents is not clearly expressed in the

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*) A similar observation was made by Venkateraman, Segal and Fraenkel 4).

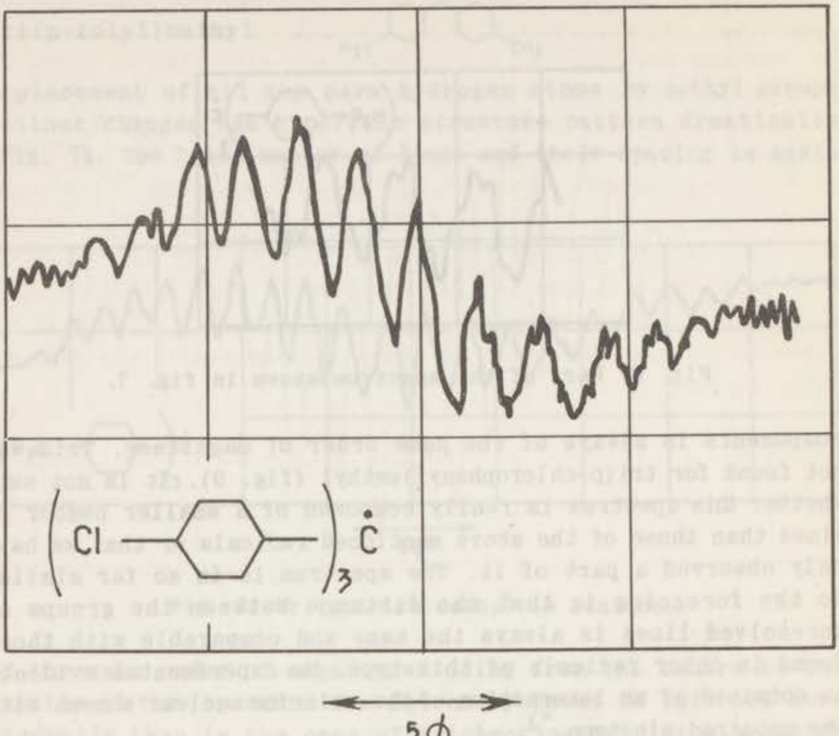
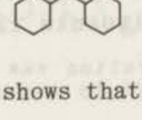


Fig. 9. Tri(p-chlorophenyl)methyl in benzene.

hyperfine structure spectrum. The interval between adjacent groups of lines is about 1.5 ϕ, just as was observed for the other radicals.



Diphenyl(m-tolyl)methyl

A "catalin" model of the radical shows that a substituent with

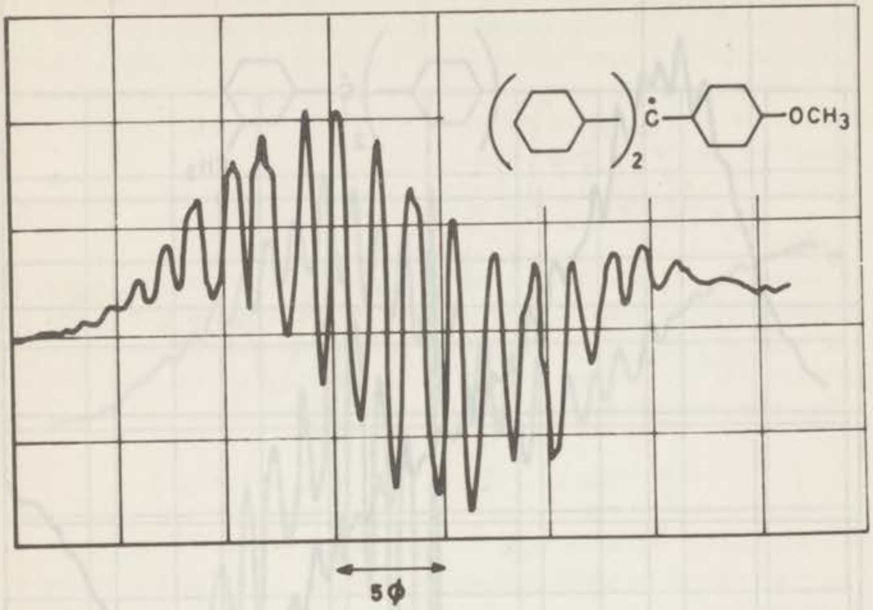
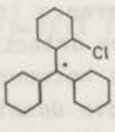


Fig. 10. Diphenyl(p-anisyl)methyl in benzene.

the dimensions of a methyl group does not interfere seriously with the spatial positions of the phenyl groups. The three rings may form a propellor of the same shape as triphenylmethyl itself or its para substituted derivatives. Nevertheless the spectrum (fig. 11) is different from that of the radical with the methyl group in the para position. As the steric influences are negligible we think that in this case the difference in the distribution of the spin densities is more pronounced.

Diphenyl(o-chlorophenyl)methyl



It is clear that in this radical the steric effects of the

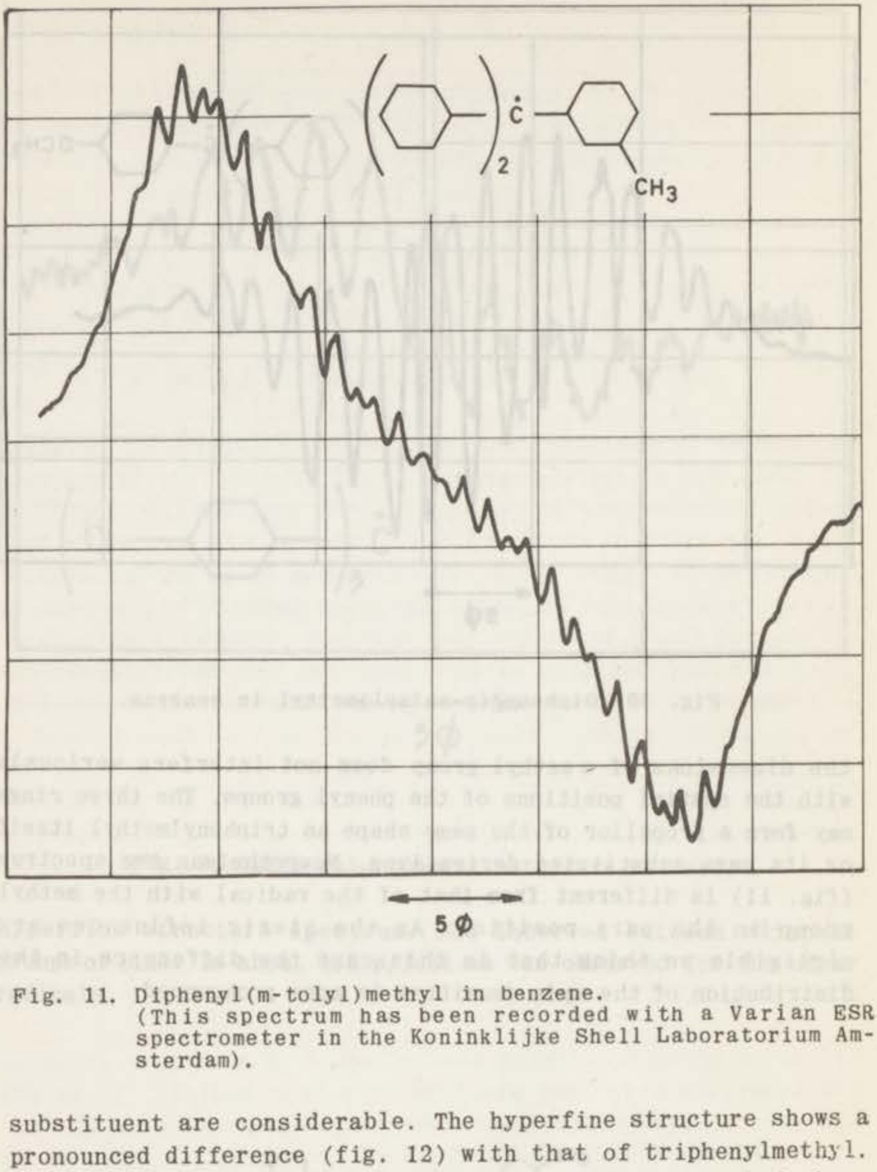


Fig. 11. Diphenyl(m-tolyl)methyl in benzene.
(This spectrum has been recorded with a Varian ESR spectrometer in the Koninklijke Shell Laboratorium Amsterdam).

substituent are considerable. The hyperfine structure shows a pronounced difference (fig. 12) with that of triphenylmethyl. More lines can be detected than in the spectra described above and the distance between the lines is smaller. This indicates that here the spin densities have values quite different from those found in other triphenylmethyl radicals. Remarkable is that the central peak has a definitely higher intensity.

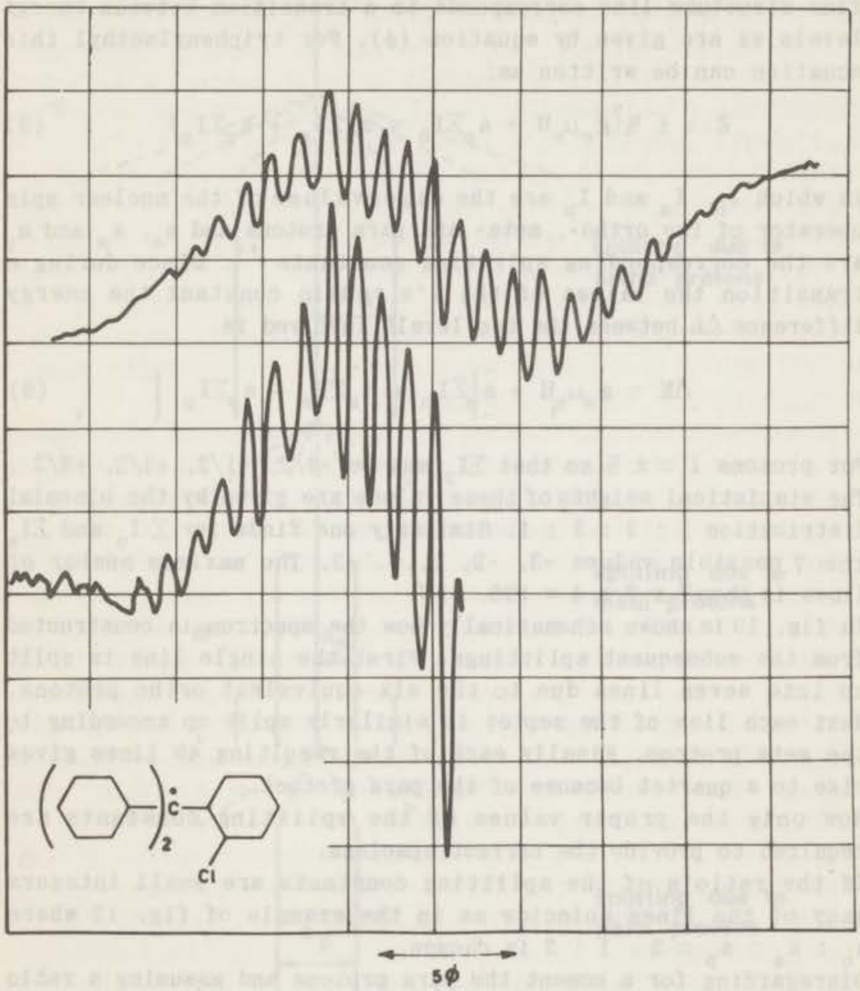


Fig. 12. Diphenyl(o-chlorophenyl)methyl in benzene.

Discussion

To understand the hyperfine structure in the spectra of triphenylmethyl derivatives the theoretical construction of the triphenylmethyl spectrum will be considered first. Each hyperfine structure line corresponds to a transition between energy levels as are given by equation (4). For triphenylmethyl this equation can be written as:

$$E = \pm \tfrac{1}{2}\{g_e\mu_e H + a_o\Sigma I_o + a_m\Sigma I_m + a_p\Sigma I_p\} \qquad (5)$$

in which I_o, I_m and I_p are the eigenvalues of the nuclear spin operator of the ortho-, meta- and para protons and a_o, a_m and a_p are the corresponding splitting constants *). Since during a transition the values of the I's remain constant the energy difference ΔE between the two levels involved is

$$\Delta E = g_e\mu_e H + a_o\Sigma I_o + a_m\Sigma I_m + a_p\Sigma I_p \qquad (6)$$

For protons $I = \pm \tfrac{1}{2}$ so that ΣI_p may be -3/2, -1/2, +1/2, +3/2 . The statistical weights of these values are given by the binomial distribution 1 : 3 : 3 : 1. Similarly one finds for ΣI_o and ΣI_m the 7 possible values -3, -2, ... +3. The maximum number of lines is then 7 x 7 x 4 = 196.

In fig. 13 is shown schematically how the spectrum is constructed from the subsequent splittings. First the single line is split up into seven lines due to the six equivalent ortho protons. Next each line of the septet is similarly split up according to the meta protons. Finally each of the resulting 49 lines gives rise to a quartet because of the para protons.

Now only the proper values of the splitting constants are required to provide the correct spacings.

If the ratio's of the splitting constants are small integers many of the lines coincide as in the example of fig. 13 where $a_o : a_m : a_p = 2 : 1 : 2$ is chosen.

Disregarding for a moment the para protons and assuming a ratio $a_o/a_m \approx 2$ one obtains already a spectrum that shows a part of the characteristic features, but not all that are found under conditions of high resolution. $a_o/a_m \approx 2$ leads to a spectrum of 19 lines. Further splitting of each line into four components

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*) The splitting constants (a) are connected with the spin density by the relation $a = Q\rho$. Q is a constant and ρ is the spin density $^{7)}$.

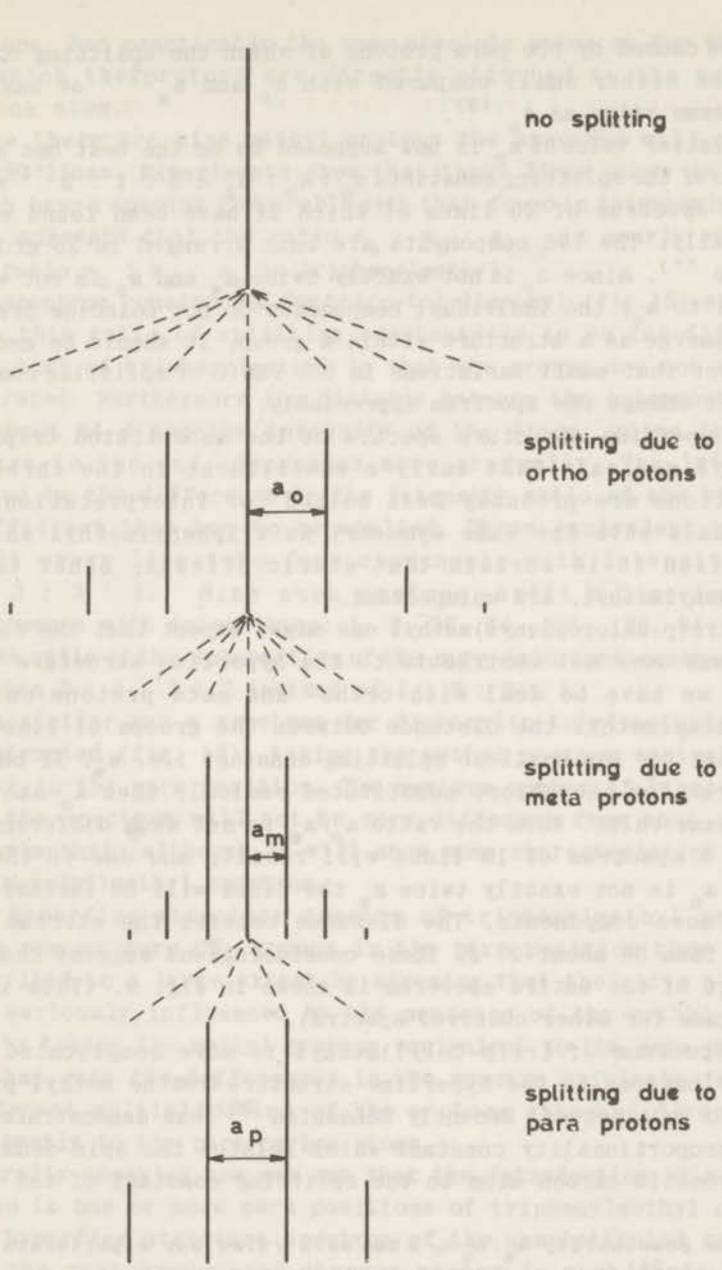
no splitting
splitting due to ortho protons
a o
splitting due to meta protons
a m
splitting due to para protons
a p

Fig. 13. Splitting of a single resonance line by non-equivalent protons.

can be caused by the para protons of which the splitting constant may be either small compared with a_o and a_m 23) or has about the same value as a_o 13).

The latter value of a_p is now supposed to be the best one and the ratio of the splitting constants $a_o : a_m : a_p \approx 2 : 1 : 2$ *) results in a spectrum of 25 lines of which 21 have been found experimentally. The 196 components are thus arranged in 25 groups of lines **). Since a_o is not exactly twice a_m and a_p is not exactly equal to a_o, the individual components do not coincide precisely and emerge as a structure within a group. It should be mentioned however that small variations in the ratio of splitting constants do not change the spectrum appreciably.

The hyperfine structure spectra of the substituted triphenylmethyl radicals that carry a substituent in the three para positions are probably best suited for interpretation. Such radicals have the same symmetry as triphenylmethyl while in addition it is certain that steric effects, other than in triphenylmethyl, are unimportant.

For tri(p-chlorophenyl)methyl one might expect that the chlorine nucleus does not contribute to the hyperfine structure 4), so that we have to deal with ortho- and meta protons only. In triphenylmethyl the distance between the groups of lines is a measure for the smallest splitting constant i.e. a_m. If the same is true for the chloro substituted radical, then a_m has about the same value. When the ratio a_o/a_m is not much different from two, a spectrum of 19 lines will result, and due to the fact that a_o is not exactly twice a_m the lines will be further split into more components. The distance between the extreme lines will then be about 27 ø. These considerations suggest that only a part of the entire spectrum is shown in fig. 9. (This is also the case for other observed spectra).

The spectrum of tri(p-tolyl)methyl is more complicated since contributions to the hyperfine structure from the methyl protons are to be expected. Recently McLachlan 25) has demonstrated that the proportionality constant which relates the spin density on an aromatic carbon atom to the splitting constant of the methyl protons, has practically the same absolute value as for the case in which the protons are directly attached to the aromatic carbon atom.

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*) The possibility $a_m/a_o \approx 2$ has been ruled out experimentally by Reitz 24) who studied deuterated triphenylmethyl radicals.

**) If the spin densities for triphenylmethyl, given by Adam and Weissman 6), are correct then the proportionality constant Q must be 15.5 ø in order to calculate a spectrum of the same length as is found experimentally. Another possibility is that the ratio of the spin densities at the o-, m- and p-positions is correct but that their numerical values must be changed.

Since there are nine methyl protons the spectrum will consist of 490 lines. Experiments show that these lines occur in groups which have a spacing comparable with that found in triphenylmethyl. This suggests that the ratio $a_o : a_m : a_{CH_3}$ is nearly equal to the ratio $a_o : a_m : a_p$ in triphenylmethyl.

The spectrum constructed for tri(p-tolyl)methyl (fig.15) starting from this ratio of splitting constants is in so far different from that of triphenylmethyl in that the groups are not so well separated. Furthermore the distance between the outermost lines is about 54 ø and the intensity of the lines, going from the centre to the end, decreases more gradually. The latter is caused by the difference in the intensity ratio of the binomial coefficient that has to be applied. Three equivalent protons split every line into four components with intensities of 1 : 3 : 3 : 1. Nine such protons split a line into ten components with intensities: 1, 9, 36, 84, 126, 126, 84, 36, 9, 1. The ratio of the intensities of the more important central lines is then 2 : 3 : 3 : 2 instead of 1 : 3 : 3 : 1.

In a similar way a spectrum for diphenyl(p-tolyl)methyl can be constructed (fig. 16), taking the methyl protons equivalent to those in the para position. The maximum number of lines is 294 and the spectrum will not be very different from that of triphenylmethyl, although it will show some characteristics of the tri(p-tolyl)methyl spectrum.

The hyperfine structure spectra of triphenylmethyl radicals with one or more CH_3 groups in the para position thus can be described to a large extent by assuming that the ratio a_o/a_m is not seriously influenced by the presence of the methyl groups and by taking the methyl protons equivalent to the para protons. In that case the differences in the spectra originate from the different multiplicities of the protons attached directly or indirectly to the para carbon atoms.

Generally speaking one may say that the introduction of a methyl group in one or more para positions of triphenylmethyl changes the hyperfine structure spectrum of the unsubstituted radical, but the most pronounced changes appear in such parts of the spectrum that are very difficult to observe.

It is not sure whether these conclusions apply also to diphenyl-(p-anisyl)methyl. The distance between the groups of lines seems to be of the same magnitude and if the methoxy group does not contribute to the hyperfine structure then the construction of a

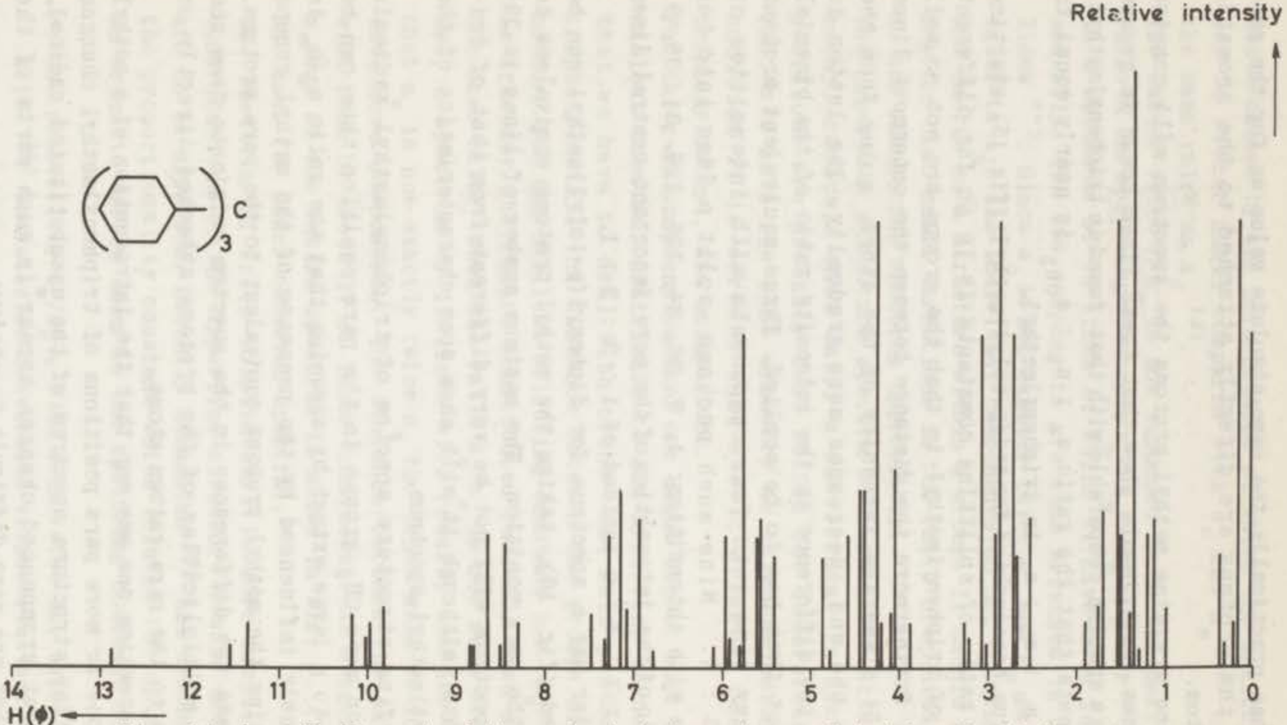

Fig. 14. Low field part of the calculated spectrum of triphenylmethyl. The calculation is based on the ratio of the spin densities at the ortho-, meta- and para positions given by Adam and Weissman [6) but the numerical values of the splitting are derived from experiment. (For simplicity all components being smaller than 2% of the most intense line have been omitted in figures 14-17).

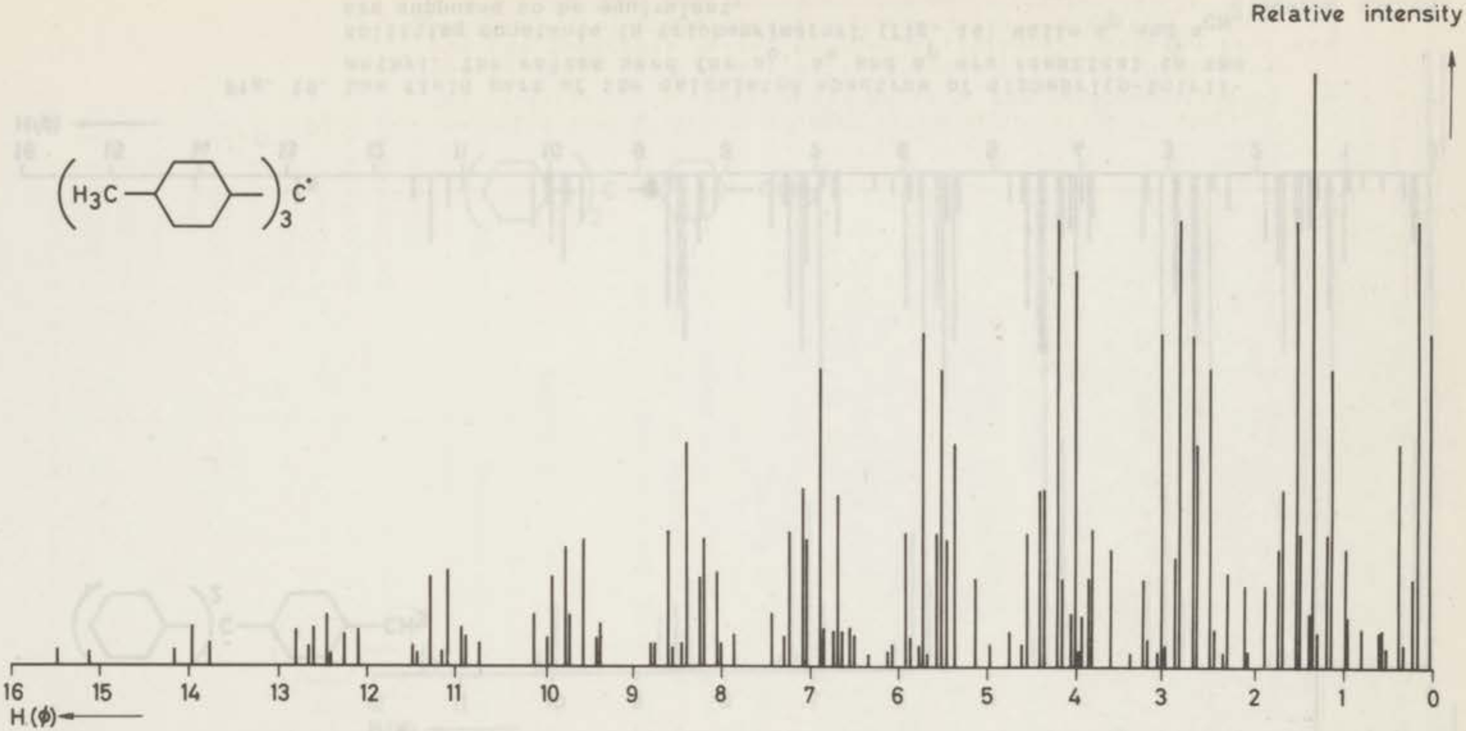

Fig. 15. Low field part of the calculated spectrum of tri(p-tolyl)methyl. a_o, a_m and a_{CH_3} have been taken equal to a_o, a_m and a_p for triphenylmethyl (see fig. 14).

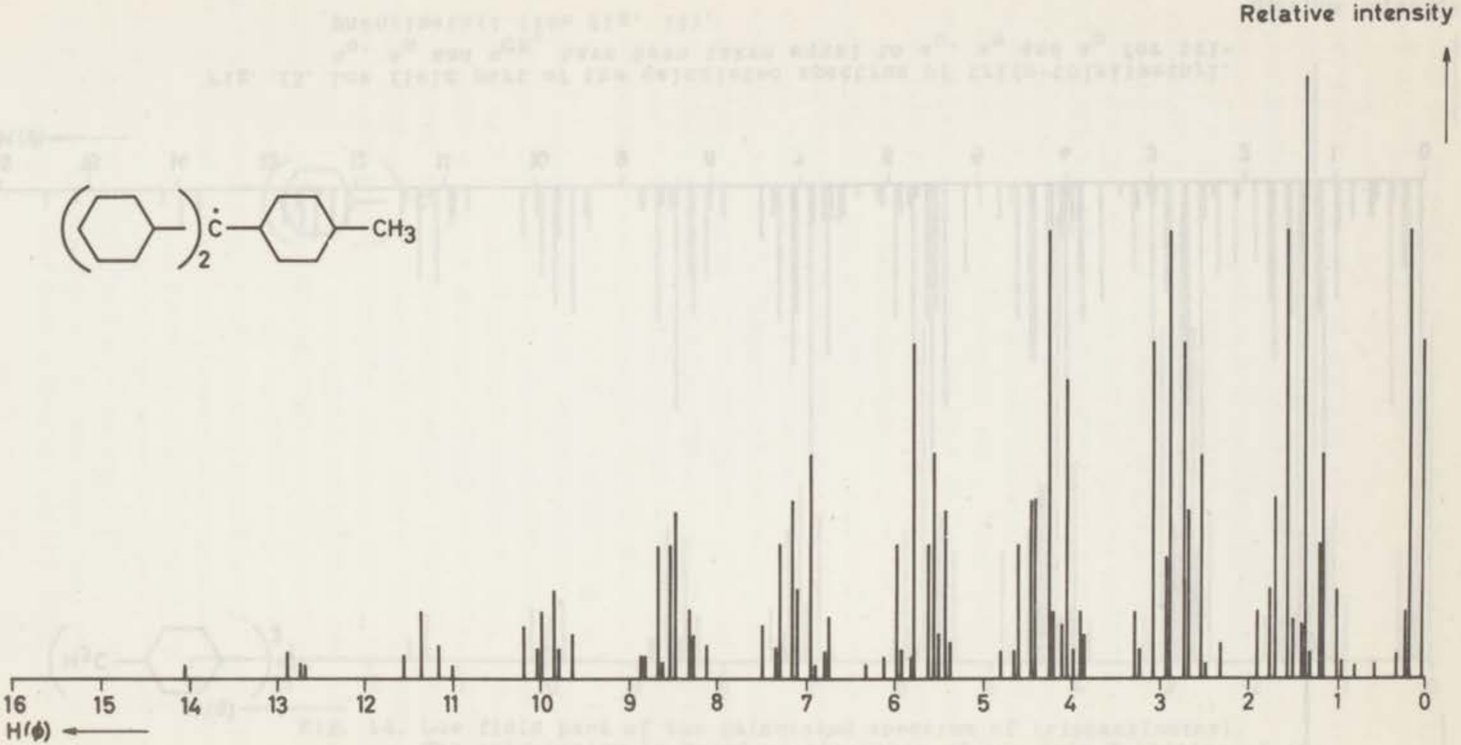

Fig. 16. Low field part of the calculated spectrum of diphenyl(p-tolyl)-methyl. The values used for a_o, a_m and a_p are identical to the splitting constants in triphenylmethyl (fig. 14) while a_p and a_{CH_3} are supposed to be equivalent.

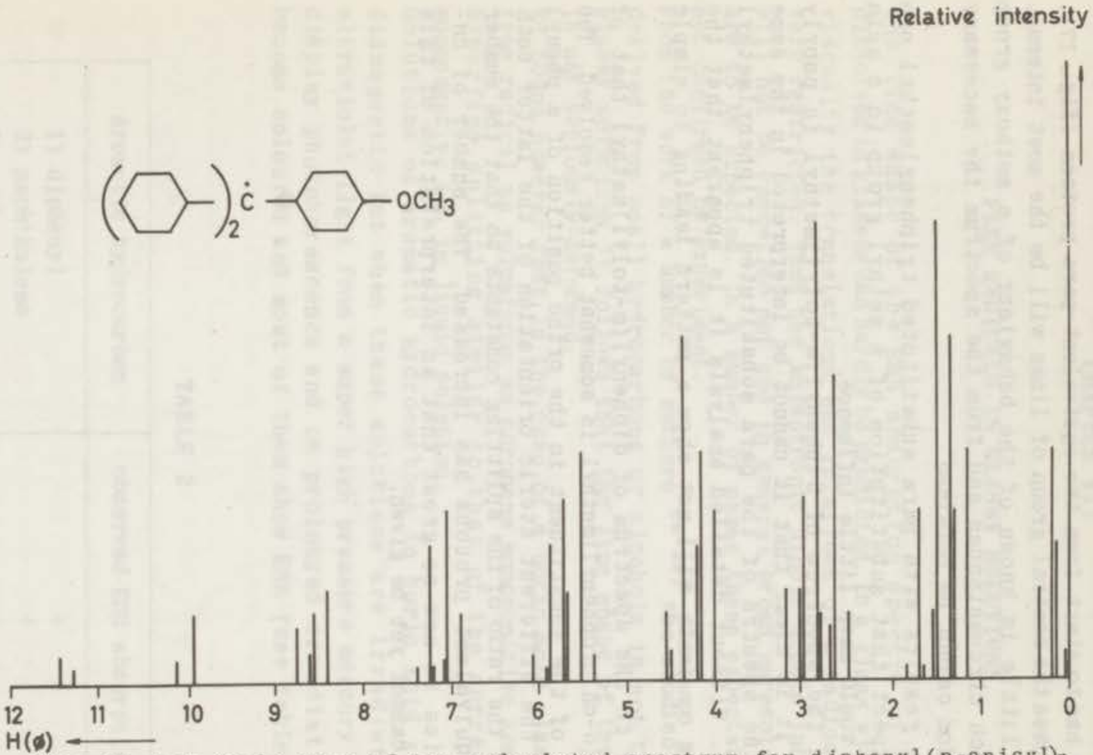

Fig. 17. Low field part of the calculated spectrum for diphenyl(p-anisyl)-methyl. a_o, a_m and a_p have been given the same value as in triphenylmethyl (fig. 14). The interaction of the unpaired electron with the protons of the methoxy group has been neglected.

spectrum has to start from two equivalent para protons (fig. 17). In that case the central group of lines will be the most intense. However little is known of the behaviour of a methoxy group under such circumstances and from the spectrum the necessary information cannot be obtained

From the results with para substituted triphenylmethyl one would expect that substitution of a methyl group in a meta position would have little influence.

Although the spectrum of diphenyl(m-tolyl)methyl is poorly resolved it is clear that it cannot be interpreted in the same way as the spectra of the para substituted triphenylmethyl radicals. Without detailed analysis it is apparent that the splitting constants will not show a pattern leading to simple ratio's.

Contrary to the spectrum of diphenyl(m-tolyl)methyl that of diphenyl(o-chlorophenyl)methyl is somewhat better resolved. The presence of the substituent in the ortho position of a phenyl ring and the different steric orientation of the latter both influence the ratio of the splitting constants so that the number of non-equivalent protons has increased. The number of uncertainties is now so great that an interpretation of this spectrum cannot yet be given.

CHAPTER III

FREE RADICALS IN GLASSY SOLUTIONS

The line shape of the ESR absorption spectra of radicals dissolved in glasses can hardly be predicted. In a glass with a high viscosity the translations and rotations of a radical may be very restricted. Thus the anisotropic dipole-dipole interaction will not be cancelled out and in general broad unresolved lines are to be expected. In a number of cases these expectations are not confirmed by experiment.

From the work of a number of authors 26-29) who studied radicals derived from small hydrocarbons or alcohols in not too rigid glassy solutions it follows that the line shape of the spectra is not seriously deformed.

We found however that in the case of a boric acid glass even a free radical as voluminous as coronene monopositive ion shows a hyperfine splitting similar to that of the corresponding mononegative ion in liquid solution.

Solutions of aromatic hydrocarbons in boric acid glass are diamagnetic but when these solutions are irradiated with ultraviolet light from a super high pressure mercury arc they display phosphorescence and on prolonged irradiation they become coloured and most of them show ESR (see table 2). The

TABLE 2

Aromatic hydrocarbon	observed ESR absorption
1) diphenyl	+
2) naphthalene	+
3) anthracene	+
4) phenanthrene	+
5) quaterphenyl	-
6) tetracene	+
7) triphenylene	+
8) pyrene	+
9) perylene	+
10) benzpyrene	-
11) coronene	+

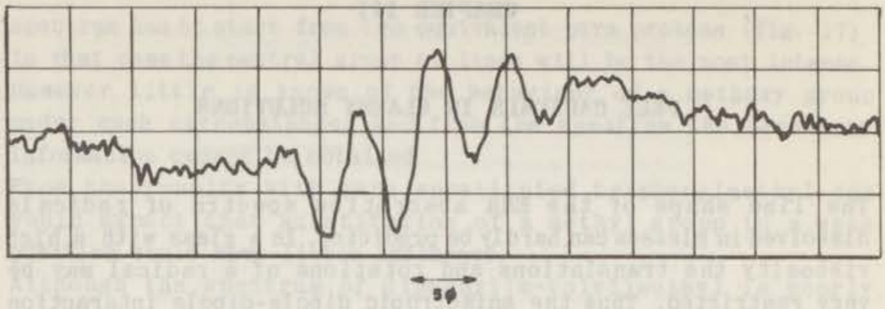

Fig. 18. Diphenyl monopositive ion in boric acid glass.

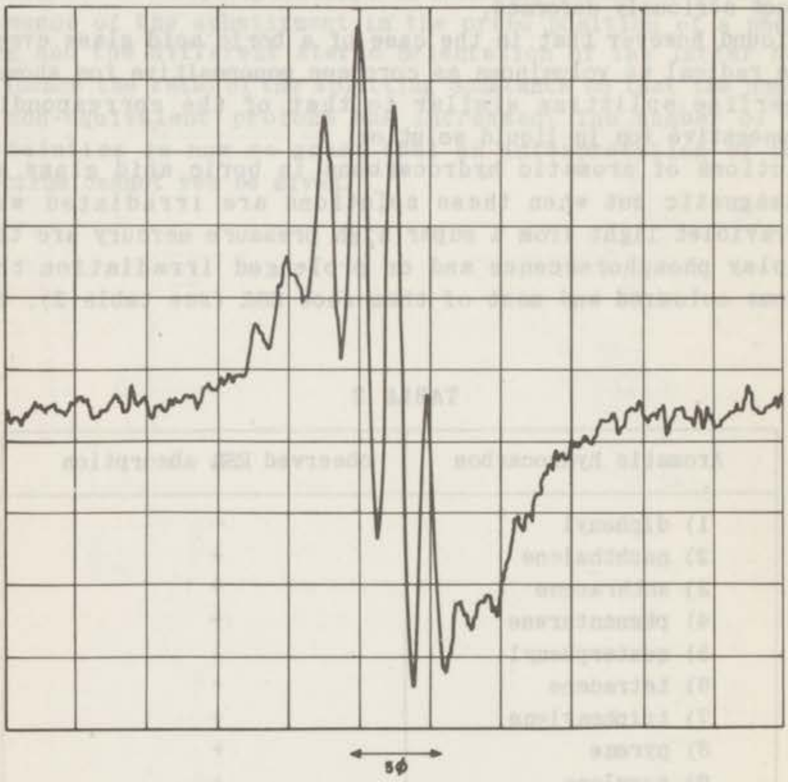

Fig. 19. Coronene monopositive ion in boric acid glass. (This spectrum has been recorded with the Varian ESR Spectrometer in the Koninklijke Shell Laboratorium in Amsterdam).

colour depends upon the hydrocarbon that has been dissolved. For instance diphenyl under these conditions becomes green, phenanthrene yellow and triphenylene blue. This colouring was first reported by Evans [30)] for the case of triphenylene and Evans assumed that free radicals were formed.

Since the solutions were made at normal pressure only such hydrocarbons could be dissolved that were not volatile. For this reason it was impossible to prepare solutions of benzene in boric acid glass.

To identify the radicals, spectra *) of the coloured glasses in the visible- and ultraviolet regions were studied. It appeared that the spectra of these solutions are nearly identical to those of the mononegative ions of the corresponding hydrocarbons in liquid solutions.

The formation of negative ions under these conditions cannot be understood very well. But since Hoijtink [31)] pointed out that for this kind of compounds the spectra of the mononegative- and monopositive ions are very similar, it seems that in this case positive ions have been formed by electron ejection from the hydrocarbon. It is supposed that the electron is captured by the glass and that the electron sextet of boron plays an important role in this process.

After increasing irradiation periods the intensity of the spectrum of the neutral hydrocarbon decreases, while the intensity of the peaks due to the monopositive ion becomes more pronounced. By comparing the spectra of the irradiated glass with the original one, it is possible to estimate the amount of radical that has been formed.

The fact that in some irradiated solutions no ESR could be detected does not necessarily mean that no radicals are formed, but there may be circumstances that hamper the detection of ESR.

In the ESR absorption lines of irradiated glassy solutions of diphenyl, naphthalene, perylene and coronene indications for hyperfine structure can be found. The ESR spectra of two of these compounds are shown in fig. 18 and fig. 19.

Since the g-factor was always about 2 there is no appreciable spin-orbit coupling.

Discussion

De Boer [12)] who observed the ESR absorption of coronene mononegative ion in liquid solution found a single line with indications for hyperfine structure. If the ESR spectra of the monopositive- and mononegative ions are compared it is remarkable that the hyperfine splitting, as far as it can be recognized, is practically the same. This is also true for the liquid solutions of the mononegative- and monopositive ions of perylene [32].

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*) The optical spectra were recorded by P. Bennema, Free University Amsterdam. Some of the spectra will be published in Molecular Physics.

De Boer's explanation for the poor resolution of the spectrum of coronene mononegative ion in liquid solution is that the lowest energy level, associated with the unpaired electron, is degenerate so that the behaviour of the electron cannot be defined by a single wave function. In the monopositive ion however, the same situation is to be expected [31], but here a better resolution of the hyperfine splitting can be observed. A similar result was obtained by Weissman [33] who found hyperfine structure in the ESR spectrum of benzene mononegative ion where the energy level in question is also degenerate. These experimental data suggest that degeneracy of a level associated with the unpaired electron does not always prohibit the resolution of a spectrum.

Although hyperfine structure could sometimes be observed in boric acid glasses, clearly not all the details were detected. Coronene monopositive ion for instance should show a spectrum of 13 lines due to 12 equivalent protons, but fig. 19 shows not more than 8 or 9 lines.

It is also to be expected that diphenyl monopositive ion has a hyperfine structure spectrum that is identical to that of the mononegative ion. The latter consists of 9 lines so that also in this case only a part of the hyperfine structure was found. A striking feature in the spectrum of diphenyl monopositive ion in boric acid glass (fig. 18) is that the hyperfine splitting is much greater than is observed for the mononegative ion in liquid solution. Similar observations were made in the case of naphthalene monopositive ion.

In solutions of aromatic monopositive ions in boric acid glass two effects may tend to broaden the absorption line i.e. a weak spin-lattice interaction and the anisotropic dipole-dipole interaction. Since it appeared that in the case of diphenyl monopositive ion saturation effects are considerable *) there must be a weak spin-lattice interaction and consequently a long spin-lattice relaxation time. Such a long spin-lattice relaxation

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*) The intensity of the microwave energy striking the sample had to be reduced to about 5-10% of the most usual value in order to avoid saturation effects.

time itself does not contribute to the line width but saturation effects may give rise to a broadening of the line. In extreme cases saturation can completely obscure the observation of ESR. It is our opinion that this situation occured in the samples where no ESR was found. For instance the optical spectrum of an irradiated solution of anthracene in boric acid glass unambiguously shows the presence of anthracene monopositive ion, while ESR could scarcely be detected.

The other line broadening process, the anisotropic dipole-dipole interaction, cannot be cancelled out (not even partially) by Brownian motions since it can be shown that for instance coronene mononegative ion in a rigid glass does neither change its position nor its orientation [34].

A thorough discussion of some of the mechanisms that determine the line width has recently been given by Hausser [2] who showed that a number of experiments on hyperfine structure can be understood in terms of relaxation times. A situation mentioned by Hausser that approaches the condition in boric acid glasses is that of viscous liquids. In such liquids the spin-lattice relaxation time is very long while the spin-spin relaxation time is short. The latter is then responsible for a broad unresolved spectrum. In boric acid glass, of which the viscosity is estimated to be at least 10^{12} times larger than that of common liquid solvents, the spin-spin relaxation time should be extremely short, resulting in a very wide line. This is not confirmed by experiment.

If these highly viscous solutions can be described in a similar way as the non-viscous solutions then there must be a mechanism that increases the spin-spin relaxation time so that a narrow absorption line will result. It may be that in spite of the high viscosity of the boric acid glasses the spin-spin relaxation time is relatively long due to the structure of the solution. The importance of structure is demonstrated in the experiments by Kozyrev [35] who studied ESR in solutions of manganous ions. It appeared that increase of the viscosity of the solvent changes the width of the absorption line. The changes were however strongly dependent on the way in which the increase of the viscosity was effected.

Although a long spin-spin relaxation time may lead to a narrow absorption line that may occasionally show hyperfine structure, the fact that the anisotropic part of the electron spin- nuclear spin interaction does not broaden the hyperfine splitting in the spectrum of coronene monopositive ion is still unexplained.

CHAPTER IV

ESR and semiconductivity in organic molecular complexes.*)

Molecular complexes can be formed from two components of which one has electron donor properties, while the other may act as an electron acceptor. A great variety of complexes are described in the literature and nowadays they are usually considered as charge transfer complexes.
Wizinger [37)] developed this idea from the colour and the chemical properties of these compounds. The quantum mechanical formulation was given by Brackman [38)] and elaborated in great detail by Mulliken [39)].
The stability and other properties of a charge transfer complex are ascribed to a resonance between a no-bond structure D,A (D = electron donor, A = electron acceptor) and a "dative" state D^+-A^-. Accordingly the wave function of the ground state is written as

$$\psi = a\phi(D,A) + b\phi(D^+\text{-}A^-) \qquad (7)$$

where a^2 and b^2 are a measure of the relative importance of the structures. In many cases $b^2 \ll a^2$ and the complex is expected to be diamagnetic as are the components from which the complex is formed. If however $b^2 \gg a^2$ the ionic structure dominates. This may even lead to dissociation into rather free ions, each having an odd number of electrons. Such a situation is to be expected in cases where the ions are known to be rather stable.
Thus Kainer, Byl and Rose-Innes [40)] showed that complexes between p-phenylenediamines and benzoquinones have a paramagnetic character. However the paramagnetism corresponds to a magnetic moment much smaller than a Bohr magneton per ion or per molecule. These authors suggested that the paramagnetism is due to a biradical which is in thermal equilibrium with a diamagnetic state [41)]. Later [42,43)] it was found that such a behaviour is not restricted to the compounds studied by Kainer and coworkers and complexes in which aromatic hydrocarbons, or various substituted aromatic hydrocarbons are the donor components appeared to have similar properties.

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*) The investigation of these complexes by means of ESR was suggested by H.M. Buck who extensively studied molecular compounds. (H.M. Buck, Acid-Base and Electron Transfer Complexes of Aromatic Molecules. Thesis Leiden 1959). Many of the ideas discussed in this chapter originated from a close cooperation.

In this chapter we shall mainly be concerned with the discussion of complexes made from substituted diphenyls, in particular 4,4'-diaminodiphenyl (benzidine) and 4,4'-dimethylaminodiphenyl (tetramethylbenzidine), and various acceptors. These substituted diphenyls may be compared with the donor p-phenylenediamine used by Kainer and coworkers. The acceptors iodine, bromine and tetranitromethane however which are the partners in our complexes, differ from the benzoquinones in that at room temperature no negative ion-radicals are known that are as stable as the semiquinones *).

Most of these complexes show a number of peculiar properties.

The intensity of the ESR signals is such that only a few molecules have an unpaired electron. In different samples we found percentages of 0.4 to 1.4. In general one may say that in the complexes derived from these substituted diphenyls about one unpaired electron is found per 100 molecules.

The g-factor is very close to that of DPPH and thus there is no indication of an appreciable contribution from the orbital moment.

Another feature that needs attention is the width of the ESR absorption line. Usually ΔH_{ms} (full width between points of maximum slope) is only a few gauss. Much broader lines are mentioned by other investigators [40,42], although a precise comparison is difficult since they give the line width at half power ($\Delta H_{\frac{1}{2}}$).

Equally important is the shape of the absorption line. In one case (benzidine-iodine complex) a determination of the line shape has been performed at 30 MHz **) and the line was found to have exactly a Lorentzian shape, indicating that there is motional narrowing.

Semiconductivity has also been observed in these complexes. For that purpose the powders were pressed into tablets, taking care to remove the air between the particles. The electrical conductivity (σ) of the tablets was measured in a rather simple manner and the results are not to be considered as accurate values, but as illustrations of the order of magnitude (about $10^{-6}\Omega^{-1}cm^{-1}$ at room temperature and about $10^{-11}\Omega^{-1}cm^{-1}$ at 90^oK). Benzidine itself turned out to be an insulator at room temperature.

Finally there is the temperature dependence of both paramagnetism and conductivity. We have not yet studied the temperature dependence of ESR and conductivity extensively, but from the few available data we have the impression that the intensity of the ESR signal as well as the conductivity change considerably with temperature.

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*) Experiments are in progress to treat a tetranitromethane solution with alkali-metal.

**) This work is carried out by Mr.R. Roest in the Kamerlingh Onnes Laboratory.

Some of the chemical aspects of these complexes will be discussed later, but it should be mentioned here that the complexes appeared to have a non-stochiometric composition. If D and A are the complex forming components and D.nA represents the complex, then n has not always the same value.

A striking example is furnished by the complex of iodine and 1,1-bis(dimethylaminophenyl)ethylene. The stochiometric compound consists of a carbonium ion and a I_3^- ion and shows extremely weak ESR absorption. Addition of a small amount of the ethylene gives rise to a pronounced paramagnetism and at the same time a change in the ultraviolet spectrum [36].

The results we have obtained are summarized in table 3.

TABLE 3

Complex	n	ΔH_{ms} (ø)	$\sigma(\Omega^{-1}cm^{-1}, 300^oK)$
Benzidine.nI_2	1.35	1.7	3×10^{-6}
Benzidine.nI_2	1.17	1.7	3×10^{-6}
Benzidine.nI_2 a)	1.50	6.5	5×10^{-3}
Benzidine.nI_2 b)	1.50	1.7	4×10^{-5}
Benzidine.nBr_2	0.96	4.4	4×10^{-10}
Benzidine.n$C(NO_2)_4$	0.38	<1 c)	5×10^{-6}
Tetramethylbenzidine.nI_2	1.35	3.7	6×10^{-10}
Tetramethylbenzidine.nBr_2	0.57	3.5	....
Tetramethylbenzidine.nBr_2	0.48	2.1	1×10^{-6}
Tetramethylbenzidine.nBr_2	0.51	2.1	3×10^{-6}
Tetramethylbenzidine.n$C(NO_2)_4$	0.55	1.1	....

a) Prepared in CCl_4.

b) Prepared in benzene which had been saturated with air.

c) Estimated for main peak (see fig. 23).

Experimental

The complexes were made by mixing solutions of the components and although the preparation of these complexes is very simple indeed [44,45] it appeared that the results of the syntheses sometimes are very divergent. A few details will now be given concerning our experiences in this field.

Benzidine.nI$_2$ complex

This complex may show an asymmetric ESR absorption curve (fig.20). The asymmetry is caused by the fact that there are two very closely spaced absorptions*). Usually the peak on the low field

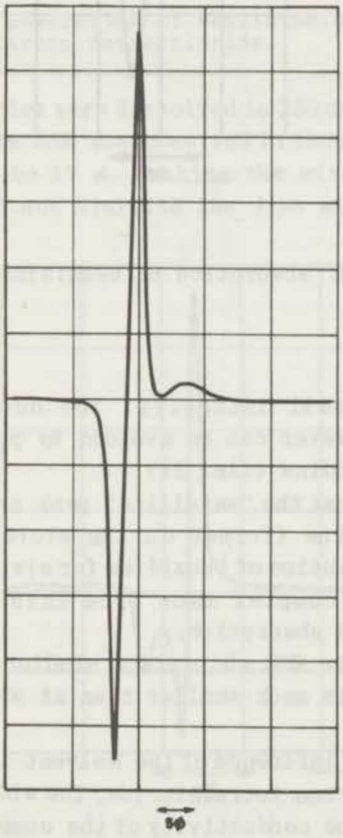

Fig. 20. ESR absorption of benzidine.nI$_2$ complex showing the satellite peak.

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*) A similar observation was made by Byl, Kainer and Rose-Innes [41].

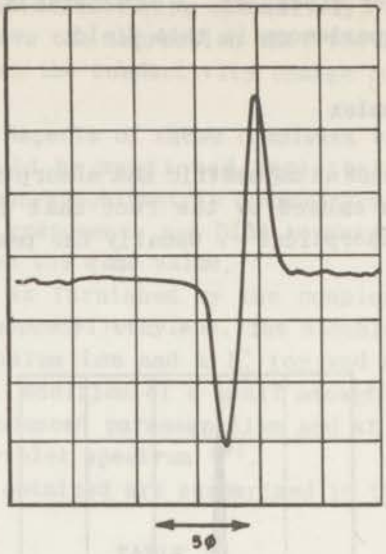


Fig. 21. ESR absorption of benzidine.nI_2 complex.

side has only a small intensity. The occurrence of such a "satellite" peak however can be avoided by preparing the complex from very pure benzidine (fig. 21).

To check the idea that the "satellite" peak arises from oxidation products of benzidine (formed during storage) air was sucked through a benzene solution of benzidine for six hours. Nevertheless the benzidine.nI_2 complex made from this solution showed a single symmetric ESR absorption.

The line width of the ESR absorption studied at 30 MHz appeared to be 0.25 ø. This is much smaller than at 9350 MHz where ΔH_{ms} = 1.7 ø is found.

A rather pronounced influence of the solvent is observed when the complex is made in carbon tetrachloride. The width of the absorption line (fig.22) and the conductivity of the complex are much larger than in complexes made in benzene (see table 3).

In general the benzidine.nI_2 complex seems to be fairly stable. Prolonged heating at 150° C does not alter the complex and it does not melt at that temperature either. Clearly a compound has been formed in which the iodine is firmly bonded.

The same is true when there is an excess of benzidine. 200 mg of

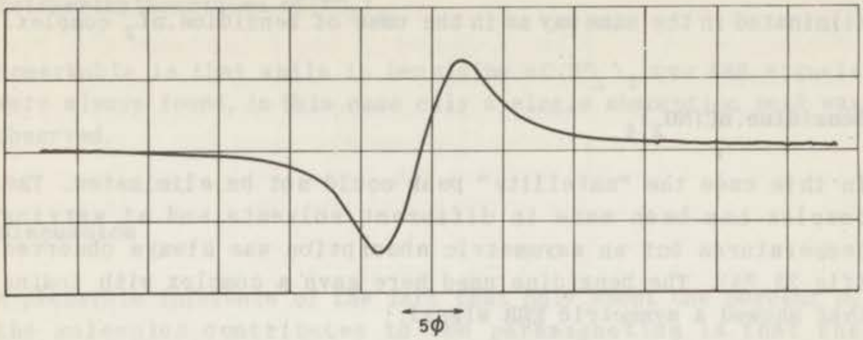


Fig. 22. ESR absorption of benzidine.nI_2 complex made in carbon tetrachloride.

benzidine.nI_2 complex were dissolved in 250 mg of molten benzidine. At room temperature ESR was observed in this mixture and the line width appeared to be 17 ø. Washing the mixture with hot alcohol or hot benzene did not diminish the line width.

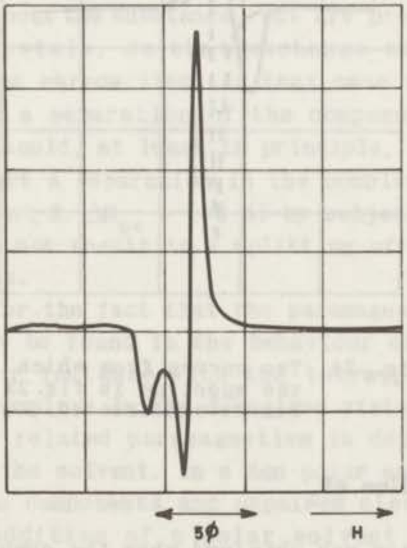


Fig. 23. ESR absorption of benzidine.nC$(NO_2)_4$ complex.

Benzidine.nBr_2 complex

Here also a "satellite" peak could be observed but it could be eliminated in the same way as in the case of benzidine.nI_2 complex.

Benzidine.nC(NO_2)$_4$

In this case the "satellite" peak could not be eliminated. The complex has been made in different solvents and at varying temperatures but an asymmetric absorption was always observed (fig.23,24). The benzidine used here gave a complex with iodine that showed a symmetric ESR signal.

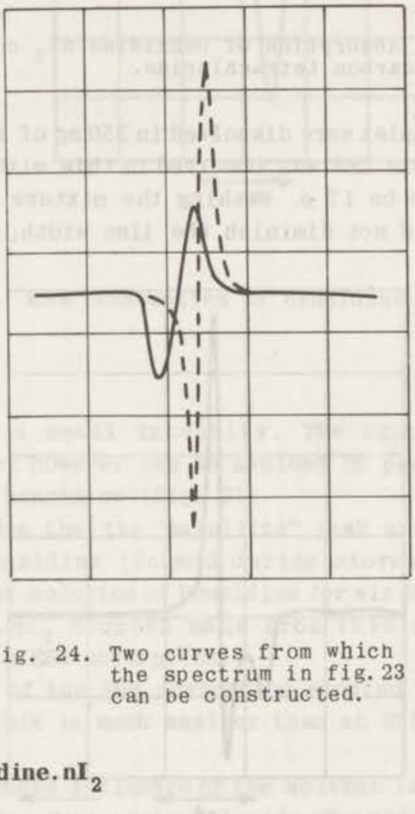


Fig. 24. Two curves from which the spectrum in fig. 23 can be constructed.

Tetramethylbenzidine.nI_2

A single absorption was obtained when the complex was made from very pure benzidine. Benzene was used as the solvent.

Tetramethylbenzidine.nBr_2

If the solution of bromine in benzene is added too rapidly to the tetramethylbenzidine solution the complex is not formed.

Tetramethylbenzidine.nC$(NO_2)_4$

Remarkable is that while in benzidine.nC$(NO_2)_4$ two ESR signals were always found, in this case only a single absorption peak was observed.

Discussion

A plausible inference of the fact that only about one percent of the molecules contributes to the paramagnetism is that the substance is contaminated with a paramagnetic impurity to the extent of one percent as has been found for violanthrone (Appendix I). Although the idea of impurities has to be kept in mind, there are indications that the paramagnetism originates from another source. For instance there is the ever growing number of complexes of which a similar behaviour is reported. Most of them have rather narrow ESR lines while solid solutions of free radicals usually have a broad ESR signal. It may be possible however that the radical molecules are not evenly distributed throughout the substance, but are present in clusters or very small crystals, so that exchange narrowing can be responsible for the narrow line. In that case the substance is inhomogeneous and a separation of the components by means of chemical methods should, at least in principle, be possible.
An attempt to effect a separation in the complex 4,4'-dimethoxydiphenyl .n HNO_3 ($n \gtrsim 2$, $\Delta H_{ms} = 1.6$ ø) by subjecting it to paper chromatography did not result in a splitting of the complex into different fractions.
Further evidence for the fact that the paramagnetism is inherent to the complex may be found in the behaviour of some complexes in solution as for instance with the tetra(p-methoxyphenyl)-ethylene-bromine complex. In the dissolved state the presence of a complex and the related paramagnetism is dependent upon the polar character of the solvent. In a non-polar solvent no complex is formed from the components and unpaired electrons cannot be detected. Upon addition of a polar solvent the complex is formed as is evidenced by the change in colour from brown to dark blue and unpaired electrons appear to be present. Both complex and unpaired electrons disappear when more non-polar solvent is added and finally they reappear when the solvent is again given a more polar character. From the ultraviolet absorption spectrum it follows that the blue colour is due to the double positive ion of the substituted ethylene [36]. A

change of colour in a solution of a charge transfer complex upon a variation of the polar character of the solvent has also been observed by Kainer et al [40].

A consideration of table 3 clearly demonstrates that there is no simple correlation between the composition of the complex, the line width of its ESR spectrum and the electrical conductivity. The same applies to the intensity of the ESR signal. This means that these results do not provide the key to frame a model that may be used to understand the experimental facts.

In order to get an idea of the situation in a complex in the solid state we first consider several processes that may partake in its formation.

In the following reactions a halogen molecule will be represented by X_2.

I) Formation of a carbonium ion.

$$D + X_2 \longrightarrow (DX)^+ + X^-$$

with the possible additional reaction

$$X_2 + X^- \longrightarrow X_3^-$$

II) Formation of a charge-transfer complex.

$$D + X_2 \longrightarrow D^+ \;....\; X_2^-$$

Dissociation of $D^+.....X_2^-$ into ions may take place. At room temperature free ions of the type X_2^- however are unknown for halogens [51] but the X_2^- ion may disproportionate.

$$X_2^- + X_2^- \longrightarrow X^- + X_3^-$$

or
$$X_2^- \longrightarrow X^- + X\cdot$$

The X· radical may react further, e.g. $D^+ + X\cdot \longrightarrow D^{++} + X^-$

III) $$D + X_2 \longrightarrow D^{++} + 2X^-$$

Reaction I will not be considered in detail since its products are diamagnetic. It should be realized that unreacted D or X_2 can also be present in the precipitate. With this in mind it is not so amazing that the samples showed a non-stochiometric composition. An excess of halogen may be due to the formation of X_3^- ions. An excess of donor molecules may be found when mixed crystals or solid solutions are formed between the complex and unreacted donor molecules (see experimental part of this chapter). This scheme does not apply to cases in which tetranitromethane is the acceptor. If the tetranitromethane negative ion appears to be stable the complexes are similar to a certain extent, to the compounds studied by Kainer and coworkers. An unstable moncnegative ion will however disproportionate.

One may expect that the paramagnetic properties of these complexes are connected with the occurrence of D^+ ions. For an explanation of the observed phenomena it has to be assumed that

1) the number of D^+ ions is of the order of 1%.

2) the positive charge is not localized on one molecule.

Several models are consistent with these assumptions. For example the lattice may consist of $D....X_2$ molecules of which a few may be dissociated into rather free ions. A process represented in reaction .

IV $$D....X_2 + D^+ \longrightarrow D^+ + X_2....D$$

enables the positive charge to move through the substance.

A similar process may apply to cases in which the negative ions have a greater stability.

Another model in which D^{++} ions are present may also lead to a situation in which a small amount of D^+ ions are formed because of the reaction $D^{++} + D \longrightarrow 2D^+$

A third possibility may apply to the combination of 1,1-bis-(dimethylaminophenyl)ethylene carbonium ion and the neutral ethylene molecules. Electron exchange between the two species gives rise to odd electrons which in this case can also be visualized as non-localized.

Such mechanisms will also influence the line width of the ESR absorption signal. I.e. the movements of an unpaired electron are no longer restricted to the regions of a certain molecule, but, due to these mechanisms, the unpaired electron can be found anywhere in the sample. If these migrations are of sufficiently frequent occurrence, the effect will be that the interaction of the unpaired electron with the magnetic moments of the surrounding particles is averaged out.

This picture is to a certain extent similar to that of the well known alkali-metal ammonia solutions. Here the electron is supposed to be situated in a hole surrounded by rapidly rotating ammonia molecules. Due to the high rotation frequency the influences of the proton magnetic moments are averaged out. In the case of the complexes, the surroundings of the electron can be presumed to be fixed (or nearly so) while the electron itself has a great mobility.

Models like those mentioned explain the small amount of paramagnetism, the ESR line width and its shape and the occurrence of semiconductivity.

A temperature dependence of the ESR signal and the conductivity may either be caused by a change in the number of D^+ ions (and consequently in the number of unpaired electrons) or by a change in the mobility of the unpaired electron. Of course both effects may act simultaneously.

A restricted mobility of the unpaired electron means that reactions like IV do not proceed with an appreciable rate at lower temperatures. In that case the conductivity will be less than at room temperature, while the diminished mobility of the unpaired electrons leads to a broadening of the ESR absorption line.

An estimate of the frequency with which the electron exchange takes place can be obtained from a determination of the line width at different resonance frequencies. Since ΔH_{ms} of benzidine-nI_2 complex at room temperature measured at 30 MHz and at 9350 MHz is 0.25 ø and 1.7 ø respectively the electron exchange frequency is supposed to have a value between 30 MHz and 9350 MHz.

An equation giving the conductivity as a function of the temperature cannot yet be given, but it is to be expected that the conductivity will be dependent on the number of D^+ ions (which may change with temperature) and on the rate of migration.

If the benzidine.nI_2 complex is considered as a mixture of diamagnetic- and paramagnetic particles being in thermal equilibrium the equation $\frac{N}{N_o} = e^{\frac{-\Delta E}{kT}}$ gives for ΔE about 3 kcal/mol (N_o and N represent the number of diamagnetic- and paramagnetic particles respectively, ΔE is the energy difference between the two states and kT has its usual meaning).

If for a moment the complex is considered as a normal semiconductor one finds from the equation $\sigma = Ae^{\frac{-\Delta E}{kT}}$ (in which σ = specific conductivity, A = proportionality constant, ΔE = energy required to bring an electron from the valence band into the conduction band) ΔE to be about 3 kcal/mol.

It should be emphasized that the equality of the values found for ΔE is fortuitous because there is no evidence of a direct relation between the two quantities.

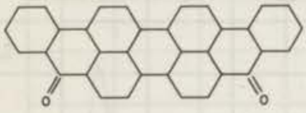
In the models mentioned above the conductivity is associated with the unpaired electrons. The possibility that there is a conduction band and that electrons within this band are quite distinct from the unpaired electrons that are responsible for the ESR absorption cannot be excluded.

APPENDIX I

THE PARAMAGNETISM OF VIOLANTHRONE

Yokozawa and Tatsuzaki [46)] reported that about one percent of the violanthrone molecules is in a paramagnetic state. In a later paper [47)] they describe the temperature independent paramagnetism of purified violanthrone and they assume that this paramagnetism might be due to an impurity.

On considering the structural formula of violanthrone one is certainly not inclined to relate it to a free radical or to a biradical. If the latter were true, then a great number of other aromatic ketones should show the same behaviour. Since this was never observed we checked the idea that violanthrone itself is diamagnetic and that the paramagnetism is caused by impurities [*)].



A fact that supports this suggestion is that the most common synthesis of this dye occurs under drastic conditions.

Indeed the violanthrone prepared from benzanthrone by heating it with potassium hydroxide for four hours at 150° C in aniline showed, after two recrystallizations from nitrobenzene, the paramagnetic character mentioned by Yokozawa and Tatsuzaki. However if a solution of the dye in nitrobenzene is chromatographed over a column of magnesium carbonate it is possible to collect two different fractions, a blue one (fraction I), first leaving the column on elution with the same solvent and a red one (fraction II) which is far more difficult to remove from the absorbent.

Since the quantity of the compound that can be treated in this way is very small (due to easy saturation of the column) the procedure was repeated several times and the different fractions were then concentrated under reduced pressure and were finally set to crystallize. After the first portions were crystallized (I^a and II^a) the mother liquors were further concentrated and a small quantity of solid was collected from either solution (I^b and II^b, the latter being practically nil).

[*)] Independently Jarrett started a search from the same point of view and arrived at identical conclusions (H.S.Jarrett, Private communication)

The different portions showed the following properties:

First band: I^a diamagnetic
I^b paramagnetic
Second band: II^a diamagnetic
II^b diamagnetic

Portions I^a and II^a, when dissolved in xylene, displayed identical spectra (fig. 25) in the visible region and are supposed to

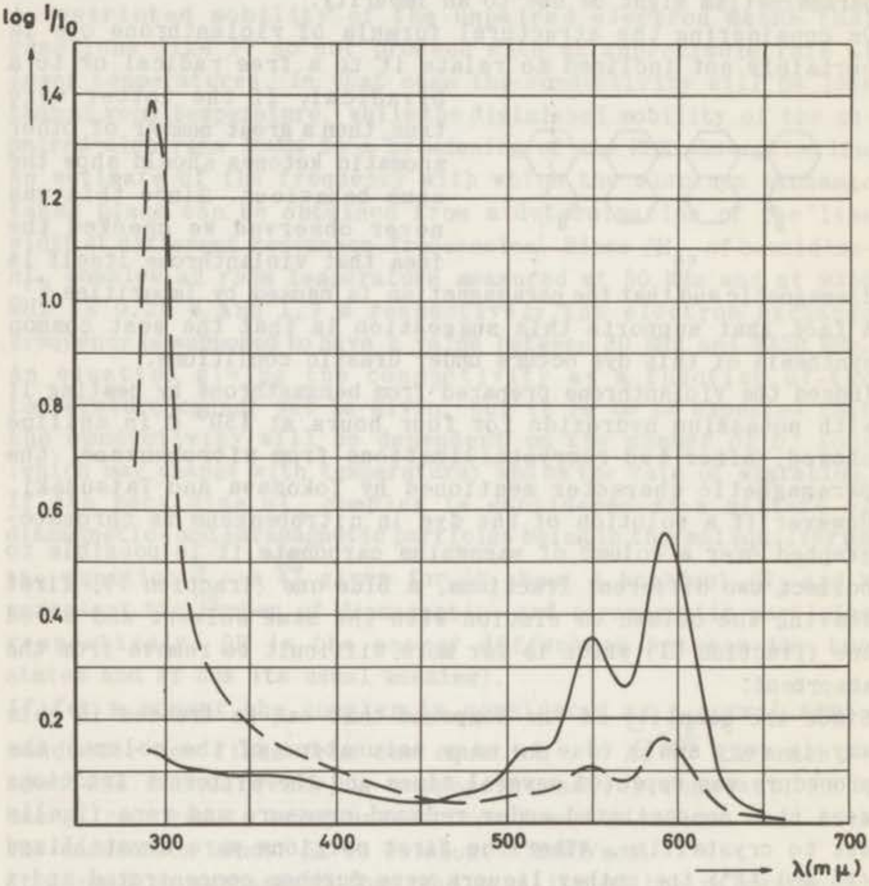


Fig. 25. ——— Absorption spectrum of diamagnetic violanthrone
- - - - - Absorption spectrum of violanthrone-aniline complex.

be pure violanthrone although the absorption maxima occur at a wavelength a little different from those given in literature. It is remarkable that from the first band two magnetically different fractions were obtained. This suggests that the first band contains more than one component. It is also possible that during the isolation a part of the paramagnetic material decomposed. We have no idea what kind of radical is responsible for the paramagnetism since the total weight of fraction I^b was about 1 milligram. Moreover we could show that portion I^b consists of at least two components, a paramagnetic- and a diamagnetic one. In fig. 26 the spectra are given of portion I^b.

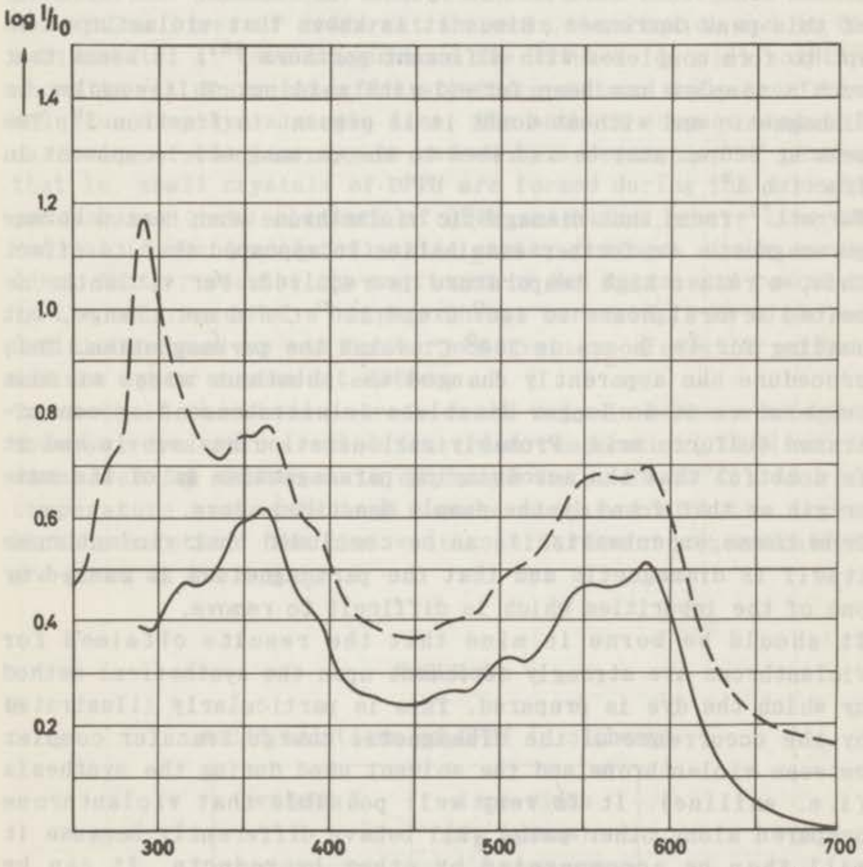


Fig. 26. - - - - Absorption spectrum of fraction I^b.
—— Same after one month.

In the course of one month the absorption maximum at 290 mμ has completely disappeared while the rest of the spectrum, apart from the intensity, has not changed. The peak at 290 mμ could be related to a diamagnetic substance which is formed when diamagnetic violanthrone is heated with aniline for four hours at 150° C. These conditions are the same as those used for the synthesis only the KOH has been omitted. The aniline was then evaporated at room temperature in a desiccator over concentrated sulfuric acid and the residue was washed thoroughly with ether until the latter was no longer coloured. The violanthrone treated in this manner gave an intense absorption at 290 mμ (fig. 25 dotted line) when dissolved in xylene. On standing the intensity of this peak decreases. Since it is known that violanthrone is apt to form complexes with different partners 48), it seems that such a complex has been formed with aniline. This complex is diamagnetic and without doubt it is present in fraction I^b. The peak at 360 mμ must be ascribed to the paramagnetic component in fraction I^b.

Jarrett*) found that diamagnetic violanthrone when heated became paramagnetic. On further examination it appeared that to effect this, a rather high temperature is required. For violanthrone heated several hours to 140° C and 180° C did not change, but heating for two hours on 300° C evoked the paramagnetism. This procedure has apparently changed the substance since at room temperature it no longer dissolves in nitrobenzene or concentrated sulfuric acid. Probably carbonization has set in and it is doubtful that the accompanying paramagnetism is of the same origin as that found in the sample described above.

From these experiments it can be concluded that violanthrone itself is diamagnetic and that the paramagnetism is caused by one of the impurities which is difficult to remove.

It should be borne in mind that the results obtained for violanthrone are strongly dependent upon the synthetical method by which the dye is prepared. This is particularly illustrated by the occurrence of the diamagnetic charge transfer complex between violanthrone and the solvent used during the synthesis (i.e. aniline). It is very well possible that violanthrone prepared along other paths will behave differently because it will then be accompagnied by other byproducts. It can be concluded however, that violanthrone as represented by its chemical formula is diamagnetic.

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*) H.S. Jarrett, Private communication.

APPENDIX II

SOLID SOLUTIONS OF DPPH

Solutions of DPPH in different solvents were made to observe the line width as a function of the concentration. Van Roggen and coworkers [49)] found that a solution of DPPH in benzene showed absorption lines of different shape in the liquid- and in the solid state. At room temperature the diluted (liquid) solution shows the well known hyperfine structure pattern while the frozen solution displays a single line. The authors suggest that this narrowing of the line may be caused by a separation of phases, that is, small crystals of DPPH are formed during the freezing process and these clusters of DPPH molecules behave like the radical in the (undiluted) solid state, giving a single narrow line. Another possibility mentioned by Van Roggen and coworkers is the occurrence of a superexchange narrowing . No clear cut definition is given and further observations of similar effects did not appear in the literature.
To check if this behaviour is found only in benzene we tried some solvents that are solid at room temperature. DPPH can be dissolved for instance in diphenyl (m.p. 69-71^{o}C). At room temperature such solutions can be compared with the frozen benzene solution. The line widths at different concentrations are given in table 4.

TABLE 4

solid solutions of DPPH in diphenyl

weight %	line width $\Delta H_{1/2}$ (gauss)
4.73	5.1
0.473	5.3
0.095	5.7
0.019	7.1

It is remarkable that the line width (at halfpower, $\Delta H_{1/2}$) in a solid sample at a certain concentration is only a fraction of that in the liquid state (0.1 weight % for diphenyl corresponds to about 2.5×10^{-3} mol/L and for benzene this is about 2.2×10^{-3} mol/L). In liquid solution the five hyperfine structure peaks are already visible at a concentration of 2×10^{-3} mol/L.

Clearly the broadening effected by dilution is much less pronounced than in the liquid state.

To ascertain if other solid solvents showed a similar behaviour DPPH was dissolved in naphthalene, diphenylamine, diphenylmethane and benzophenone. Only the first mentioned solvent showed the same feature as diphenyl. Solutions of concentrations ranging between 4 and 0.2 weight % gave line widths of 5-7 gauss. In diphenylamine and diphenylmethane DPPH decomposed while in benzophenone a concentration of about 0.1 weight % displayed a line width of about 35 gauss.

The observed line widths of DPPH in diphenyl are not as small as that of undiluted DPPH (2.7 gauss at half power). It should be noted that DPPH when rigorously dried to eliminate any adhering solvent molecules has a smaller line width than DPPH recrystallized from benzene or chloroform. Such samples contain crystal benzene or crystal chloroform. Therefore it is to be expected that the line width of solid solutions is at least equal to that of DPPH crystals.

Generally in solid solutions no hyperfine structure is observed, but only a broad absorption line. The solution of DPPH in benzophenone seems to be in accordance with these facts. Clearly no clusters or radical molecules are formed here. If the same is true for solutions of DPPH in diphenyl and in naphthalene it is amazing that the line width is so small.

If in these solutions the unpaired electron can move freely, this should tend to narrow the absorption line just as in cases where motional narrowing occurs.

It is our impression that in the solid solutions of DPPH in diphenyl and naphthalene where small line widths are found, no separation of phases needs to occur, but that some narrowing mechanism might be responsible for the line shape. However it is rather difficult to prove this unambiguously.

In a private communication Dr Bersohn suggested that the Overhauser effect of such solutions should be measured. This experiment has however not yet been done. From the experiments of Beljers, Van der Kint and Van Wieringen 50) it is already known that undiluted DPPH shows a small Overhauser effect. This interaction of the unpaired electrons with the protons of the DPPH molecules may obscure a possible interaction between the unpaired electrons and the protons of the solvent molecules.

It would be better if the solvent molecules contained an atomic species that is not present in DPPH itself. This can be realized by using deuterated diphenyl (or benzene at temperatures below 0^{o} C). So if the unpaired electron should spend a part of the time in the solvent molecules, an enhanced deuterium magnetic resonance signal must be observed when the electron spin resonance absorption is saturated.

In order to check if the unpaired electrons have an exceptional mobility in these solutions the conductivity of a solution of 1 weight percent of DPPH in diphenyl was measured. It appeared that this solution has a conductivity comparable with that of pure diphenyl.

SUMMARY

Using the technique of electron spin resonance (ESR) a number of problems of organic chemical character were studied.

a) The delocalization of the unpaired electron as evidenced by the hyperfine structure of the ESR spectra appeared to be in qualitative agreement with theory for a number of para substituted triphenylmethyl radicals. The ESR spectra of an ortho- and a meta substituted triphenylmethyl could not be interpreted.

b) The products responsible for the colour of the irradiated solutions of aromatic hydrocarbons in boric acid glass could be identified as the hydrocarbon monopositive ions. In the ESR spectra of these solutions the isotropic- as well as the anisotropic dipole-dipole interaction is observed in some cases. This interaction caused a broadening of the hyperfine structure lines as was to be expected for solutions of extremely high viscosity. Apart from this broadening a hyperfine splitting was observed that was much larger than in the corresponding mononegative ions in liquid solution. In the solution of coronene monopositive ion in boric acid glass the anisotropic part of the dipole-dipole interaction seems to be completely cancelled out and the hyperfine splitting is identical to that of coronene mononegative ion in liquid solution.

c) A number of organic molecular compounds appeared to contain unpaired electrons and showed properties of semiconductivity. It is demonstrated that these compounds have a non-stochiometric composition and that slightly different circumstances during the preparation may sometimes lead to compounds with quite different electric and magnetic behaviour. It is suggested that the unpaired electrons are not necessarily the only contributors to the semiconductivity.

d) The presumption that the paramagnetism of the dye violanthrone is due to an impurity has been verified. By subjecting the dye to chromatography diamagnetic violanthrone could be isolated. The paramagnetism appeared to be inherent to one of the additional products with which the dye is contaminated.

d) A preliminary investigation concerning the line width of ESR spectra of solid radical solutions showed that such solutions sometimes exhibit a narrow ESR absorption line.

SAMENVATTING

Met behulp van electronen spin resonantie (ESR) werden een aantal problemen van organisch chemisch karakter onderzocht.

a) De hyperfijn structuur in de ESR spectra die de delocalisatie van het ongepaarde electron in radicalen weer kan geven werd bestudeerd voor een aantal gesubstitueerde triphenylmethyl radicalen. Qualitatieve overeenstemming tussen theorie en experiment werd gevonden bij die radicalen die op de para plaatsen een of meer substituenten dragen. Van de ESR spectra van een ortho- en een meta gesubstitueerd triphenylmethyl kon geen interpretatie worden gegeven.

b) De producten die de kleur veroorzaken van bestraalde oplossingen van aromatische koolwaterstoffen in boorzuur glazen bleken de monopositieve ionen van deze koolwaterstoffen te zijn. In de ESR spectra van deze oplossingen werd behalve de isotrope ook de anisotrope dipool-dipool wisselwerking waargenomen. Deze laatste wisselwerking veroorzaakte een verbreding van de hyperfijn structuur lijnen zoals te verwachten is in oplossingen van zeer hoge viscositeit. Niet verklaard is het feit dat de splitsingsconstanten schijnbaar een grotere waarde hebben. Dit werd evenwel niet waargenomen voor een oplossing van coroneen monopositief ion waar een zelfde splitsing werd gevonden als bij het mononegatieve ion in vloeibare oplossing. De anisotrope dipool-dipool wisselwerking schijnt hier geheel zonder effect te zijn.

c) In een aantal organische molekuul verbindingen werden ongepaarde electronen aangetoond en kon elektrische halfgeleiding worden waargenomen. De onderzochte verbindingen hadden een niet-stoechiometrische samenstelling en verder bleek dat in sommige gevallen een kleine wijziging in de omstandigheden tijdens de bereiding aanleiding gaf tot produkten met duidelijk verschillende elektrische en magnetische eigenschappen. Het is nog niet zeker dat het elektrische geleidingsvermogen uitsluitend door de ongepaarde electronen wordt veroorzaakt.

1) Het vermoeden dat het paramagnetisme van violanthron veroorzaakt wordt door een verontreiniging is experimenteel bevestigd. Door de kleurstof te chromatograferen kon diamagnetisch violanthron worden afgezonderd. Het paramagnetisme bleek samen te hangen met een van de bijprodukten die ook tijdens de synthese gevormd worden.

d) Een voorlopig onderzoek naar de lijnbreedte van vaste radikaal oplossingen toonde aan dat de lijnbreedte van het ESR spectrum niet altijd breed behoeft te zijn.

Op verzoek van de Faculteit der Wis- en Natuurkunde volgen hier enige details over mijn academische studie. Na het einddiploma H.B.S. B in 1945 te hebben verkregen aan de Dalton H.B.S. te Den Haag werd in dat jaar de studie aan de Rijksuniversiteit te Leiden aangevangen. Na een onderbreking van 1 september 1948 tot 1 augustus 1949 in verband met werkzaamheden voor het Kunststoffen-Instituut T.N.O. werd het candidaatsexamen Wis- en Natuurkunde letter F in december 1949 afgelegd.

De voorbereiding tot het doctoraalexamen dat in oktober 1953 werd afgelegd geschiedde onder leiding van de hoogleraren Dr. E.Havinga, Dr.C.J.F.Böttcher, Dr.L.J.Oosterhoff en Dr.A.E.van Arkel. Van 1 oktober 1949 tot 1 september 1951 was ik als assistent verbonden aan het Laboratorium voor Anorganische Chemie. Van 1 september 1951 tot 1 oktober 1953 was ik in dienst van het Nederlands Instituut voor Documentatie en Registratuur te Den Haag.

Tijdens het bewerken van het promotieonderwerp onder leiding van Prof.Dr.L.J.Oosterhoff was ik aanvankelijk als assistent, later als hoofdassistent en tenslotte als wetenschappelijk ambtenaar 1e klasse verbonden aan de afdeling voor Theoretische Organische Chemie.

Bij het verrichten van het onderzoek dat in dit proefschrift beschreven wordt, heb ik zeer veel steun mogen ondervinden van personen en instellingen buiten de Afdeling voor Theoretische Organische Chemie, in het bijzonder van het personeel van de chemische laboratoria.

De gebruikte electromagneet werd geconstrueerd in het Kamerlingh Onnes laboratorium onder supervisie van Prof.Dr.K.W.Taconis, de electronische- en microgolven apparatuur in het Natuurkundig laboratorium van de N.V. Philips.

In het beginstadium en bij de verdere uitbreiding van de apparatuur heb ik meerdere malen de medewerking kunnen verkrijgen van een aantal deskundigen. In het bijzonder van enige heren verbonden aan het Natuurkundig laboratorium van de N.V. Philips, namelijk Ir.H.G.Beljers, Dr.J.S.van Wieringen en de Heer L.van der Kint en verder van een aantal oud-medewerkers van het laboratorium voor Physische Chemie: Dr.F.F. Bos, Dr.F.C.de Vos, Dr.A.van Roggen en Ir.J.Arends. Prof.Dr.H.Wijnberg was mij behulpzaam bij het op juiste wijze formuleren van gedachten in de Engelse taal. Voor de aangename wijze waarop kon worden samengewerkt wil ik gaarne mijn dank uitspreken.

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