# ELECTRON SPIN RESONANCE STUDIES OF THE FREE RADICALS DERIVED FROM TETRAPHENYLHYDRAZINE

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AND

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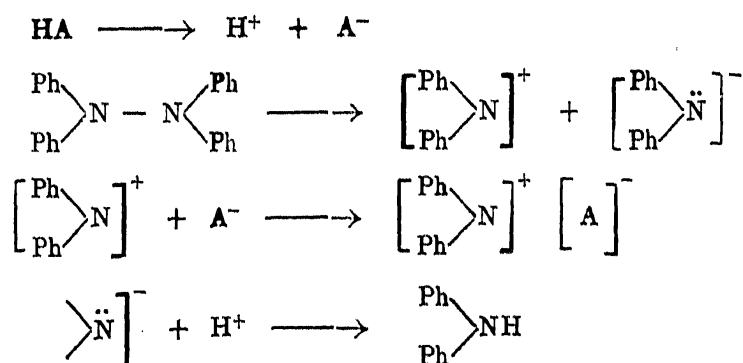
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## INTRODUCTION

WIELAND prepared tetraphenylhydrazine for the first time and proposed that: (1) when heated in a non-polar solvent like xylene or toluene to about 90° C., tetraphenylhydrazine dissociates into diphenylamino-radicals, and (2) the coloured compounds formed by the action of acids on tetra-phenylhydrazine have a quinonoid structure.[1] Weitz and Schwecten observed that tetraphenylhydrazine does not form salts with acids unless oxidizing agents are present and hence suggested that the action of acids on tetra-phenylhydrazine produces free radicals instead of quinonoid compounds.[2] Lewis and Bigeleison held the view that in solution tetraphenylhydrazine is in dynamic equilibrium with the positive and negative ions of diphenyl-nitrogen and, when an acid is added, the negative ions are first removed by protonation; the positive ions which accumulate combine with the anion of the acid[3]:

$$HA \longrightarrow H^+ + A^-$$

$$\frac{Ph}{Ph}N - N\frac{Ph}{Ph} \longrightarrow \left[\frac{Ph}{Ph}N\right]^+ + \left[\frac{Ph}{Ph}\ddot{N}\right]^-$$

$$\left[\frac{Ph}{Ph}N\right]^+ + A^- \longrightarrow \left[\frac{Ph}{Ph}N\right]^+ \left[A\right]^-$$

$$\left[>\ddot{N}\right]^- + H^+ \longrightarrow \frac{Ph}{Ph}NH$$

The action of ultra-violet rays on tetraphenylhydrazine held in a rigid medium was studied by Lewis and Lipkin and the following reactions were

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postulated: (1) photodissociation forming two molecules of diphenylamino radicals, (2) photoionization resulting in the formation of positive and negative diphenylamino ions, and (3) photo-oxidation resulting in the formation of the tetraphenylhydrazyl radical,[4]

$$Ph \diagdown \ddot{N} - \dot{N} \diagup Ph$$
$$Ph \diagup \qquad \diagdown Ph$$
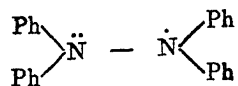
The technique of electron spin resonance spectroscopy was employed by Hoskins to investigate this problem. He attempted to observe the paramagnetic resonance of diphenylamino radical, which is presumably obtained by heating to 90° C. a solution of tetraphenylhydrazine in toluene.[5] A five-line spectrum contrary to an expected three-line spectrum was obtained; it will be seen later that an impure sample of tetraphenylhydrazine gives a five-line spectrum in the solid state and in xylene.

The present investigations on free radicals obtained from tetraphenylhydrazine under different conditions extend Hoskins' attempts to identify the diphenylamino radical. Electron spin resonance has proved very useful in the study of many organic free radicals, and the rich hyperfine structure found in the resonance spectra of many organic free radicals has been the subject of considerable theoretical and experimental studies.[6] This work was undertaken with the expectation that the several radicals obtained from tetraphenylhydrazine could be distinguished from one another with the help of the hyperfine structure in their resonance spectra and their g-values.

## Techniques and Materials

*The Spectrometer.*—The electron paramagnetic resonance studies were carried out in an x-band reflection cavity spectrometer consisting of a Varian V-4500-40 x-band microwave bridge, the Varian klystron power supply (V-4500-20) and their klystron control unit (V-4500-10); the low frequency magnetic field modulation for derivative recording was provided by a 37 cps. oscillator and power amplifier; the output of a twin-tee narrow band amplifier was detected with a phase-sensitive detector and recorded on a Honeywell-Brown strip chart recorder to obtain the derivative spectrum. The frequency of the klystron was stabilized with the sample cavity as reference; the klystron was frequency modulated by impressing a 10 kcs. modulation on its reflector voltage and the 10 kcs. component of the output of the microwave crystal diode, 1N23B, was detected with a phase-sensitive detector and used for the frequency stabilization of the klystron.

A Varian V-4012-A 12″-electromagnet with its associated V-2100-A power supply and a voltage regulator (V-2101-C) provided the magnetic

field for the resonance studies. The magnetic field was scanned linearly at a constant microwave frequency for obtaining the resonance spectra.

*Measurement of magnetic field strength.*—The magnetic fields were measured in terms of the proton magnetic resonance frequencies using a circuit of the type described by Knoebel and Hahn,[7] with mineral oil as the sample; the probe containing the mineral oil was placed as close to the paramagnetic sample as possible. The proton resonance frequency was measured with the aid of a loosely coupled antenna placed inside the proton oscillator box, followed by a tunable radio frequency amplifier. The output of the amplifier was fed into a Hewlett Packward frequency converter (hp-525-A) and counter (hp-524-B) combination. The error in the proton resonance frequency due to dispersion effects was measured by following, on the frequency counter, the changes in the oscillator frequency as the magnetic field passed slowly through resonance; it was found to be less than $\pm 40$ cps. in 14 mcs. (*i.e.*, about 3 parts in $10^6$). In order to minimise the errors due to dispersion, care was taken that the magnetic field did not drift during the period of measurement of the proton resonance frequency; the measurements were made only after allowing an initial warm up period of about 2 hours for the magnet and magnet power supply to stabilize. After making a series of measurements, the corrections to be applied for the difference between the magnetic field strengths at the proton probe position and the position of the paramagnetic sample were determined by removing the microwave cavity from the magnetic field and shifting the proton probe to the position originally occupied by the paramagnetic sample. The proton probe was easily reset at these two positions with the help of markings on an aluminium plate on which the proton oscillator box rested. This procedure could be followed very easily because of the high stability of magnetic fields attainable with the Varian 12″ magnet and its power supply.

*Measurement of microwave frequencies.*—The microwave frequencies were measured by coupling a portion of the microwave power and beating it with the harmonics of a transfer oscillator.[8] This method is capable of measuring the microwave frequency to 1 part in $10^6$, which is the accuracy of the counter.

*g-Value of DPPH.*—The $g$-value of $\alpha, \alpha'$-diphenyl-$\beta$-picryl hydrazyl (DPPH) was measured over several days to verify the accuracy of the method described above. When a speck of DPPH was used it was observed that though the ratio $(\nu_E/\nu_P)$ of the electron spin resonance frequency for DPPH $(\nu_E)$ and the proton resonance frequency $(\nu_P)$ at the same magnetic field could be measured to a precision of 3 parts in $10^6$ on

a single day, the values measured over several days varied about 2·5 parts in $10^4$ (corresponding to a g-variation from 2·0033 to 2·0038). This variation was later found to be due to anisotropy effects derived from the sample not being truly polycrystalline. Over a whole day the orientation of the sample with respect to the magnetic field was left unchanged and hence the constancy of the results over a day. When the sample tube was rotated with respect to the field between successive measurements on a single day, the g-values were found to show variations of the same order as reported above.

The g-value of a 0·002 M solution of DPPH in xylene, which is not expected to show anisotropy effects, was measured over several days and the extreme variations of the ratio, $(\nu_E/\nu_P)$, were within 2 parts in $10^5$; the ratio was found to be 658·6290±0·0030. The ratio of the proton magnetic moment in mineral oil to the proton magnetic moment in water is reported as 1·0000041±0·0000015.[9] Combining this with the most recent value of the gyromagnetic rotio for protons in water, $\gamma_P= 2.67513 \pm 0.00002) \times 10^4$ gauss$^{-1}$sec.$^{-1}$,[10] the gyromagnetic ratio of protons in mineral oil is (2·67513 ± 0·00002)×$10^4$gauss$^{-1}$ sec.$^{-1}$  The g-value for DPPH is given by

$$ g = \frac{\dfrac{\nu_E}{\nu_P}}{\dfrac{e}{2mc\gamma_P \text{ (mineral oil)}}} $$

and with $(e/mc) = (1.75887 \pm 0.00003) \times 10^7$ e.m.u./gm.[11]

$g$ (0·002 M DPPH in xylene) = 2·00347 ± 0·00004.

The g-value for DPPH has been previously reported to be 2·0036±0·0003.[12]

*Measurement of g-values,* hfs *spacings and line-widths of radicals other than DPPH.*—The g-values of the free radicals reported in this paper were measured by the method outlined for measurements on DPPH. The values obtained differ in their precision (as seen from Table I), depending on the line-width of the spectrum and the intensity of the paramagnetic resonance absorption that could be obtained. In all cases the derivative of the spectrum as seen on an oscilloscope was used to determine the centre of the absorption signal; whenever the sample gave a feeble absorption signal, the amplitude of field modulation was enhanced to several times the line-width in order to increase the ease of detection of the centre of the line. The amplitude of field modulation is known not to affect the position of the centre of the signal,

TABLE 1

*Electron spin resonance data on free radicals derived from and related to tetraphenylhydrazine*

| No. | Sample | Number of components | g-Values | Line-widths (gauss)[a] | HFS separations[b] | | Total spread of the spectrum (gauss) | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | Uncorrected (gauss) | Corrected (gauss)[c] | | |
| **I.** | **TETRAPHENYLHYDRAZINE (TPH)** | | | | | | | |
| 1. | TPH in xylene heated and cooled (Fig. 1) | 3 | 2·00549 ± 0·00011 | 5·5 | 9·1 | 10 | 43 | .. |
| 2. | TPH in xylene, kept for a week | 3 | 2·00537 ± 0·00014 | 4·0 (approximate) | 13 | .. | 39 | .. |
| 3. | TPH in acetic acid, heated and cooled (Fig. 2) | 5 | 2·00284 ± 0·00010 | 3·4 | 6·1 | 6·8 | 41 | .. |
| 4. | (a) TPH in acetic acid, shaken for ten minutes | .. | 2·00211 ± 0·00010 | .. | .. | .. | 50 | Very weak and poorly resolved |
| | (b) TPH in acetic acid, kept for a week | 5 | 2·00285 ± 0·00005 | 4·2 (approximate) | 7·6 | .. | 43 | .. |
| 5. | TPH in acetic acid — PbO$_2$ (Fig. 3) | 5 | 2·00289 ± 0·00009 | .. | 9·1 | .. | 54 | .. |
| 6. | TPH in concentrated sulphuric acid | 5 | 1·9972 ± 0·0007 | .. | .. | .. | 39 | The radical is very unstable |
| 7. | (a) TPH in acetic acid — sulphuric acid (green) Fig. 4 (a) | 6(?) | 2·00184 ± 0·00011 | .. | 5·7 | .. | 51 | .. |
| | (b) TPH in CH$_3$COOH — sulphuric acid (green) Fig. 4 (b) | .. | 2·00169 ± 0·00007 | .. | .. | .. | 43 | Very poor resolution |

TABLE I (*Contd.*)

| No. | Sample | Number of components | g-Values | Line-widths (gauss)[a] | HFS separations[b] Uncorrected (gauss) | Corrected (gauss)[c] | Total spread of the spectrum (gauss) | Remarks |
|---|---|---|---|---|---|---|---|---|
| II. | DIPHENYLAMINE (DPA) | | | | | | | |
| 1. | DPA in acetic acid + $PbO_2$ (Fig. 5) | 5 | 2.00289 ± 0.00010 | 2.9 | 7 | .. | 37 | .. |
| 2. | DPA oxidised with potassium permanganate and extracted with xylene (Fig. 6) | 3 | 2.00416 ± 0.00010 | .. | .. | .. | 45 | .. |
| III. | DIPHENYLBENZIDINE (DPB) | | | | | | | |
| 1. | DPB in acetic acid + $PbO_2$ (Fig. 7) | 5 | 2.00285 ± 0.00010 | 2.9 | 6.8 | .. | 39 | .. |
| 2. | DPB in xylene + AgO or $PbO_2$ (Fig. 8) | .. | .. | .. | .. | .. | 39 | The spectrum is asymmetric and consists mainly of 3 lines |

[a] The line-widths refer to distances between points of maximum and minimum slopes and are not correctedd for overlap.

[b] All the spectra [except III (2)] contained hyperfine components which were equally spaced, if overlap was taken into account.

[c] The corrections are made to take into account the overlap between the different hyperfine components; they are approximate and assume a Lorentzian shape for the individual hyperfine components.

The hyperfine structure separations were measured by observations on the oscilloscopes whenever possible. In most of the free radicals the line-widths were so large that the hyperfine structure separations could be obtained only from magnetic field marks put on the record of the spectra obtained with the strip chart recorder; and in certain cases only the overall spread of the spectrum could be estimated. Table I presents the data obtained on all the free radicals reported in this paper. The overlap corrections, whenever applied, are approximate and assume a Lorentzian shape for the individual hyperfine components. When making line-width and *hfs* separation measurements, the modulation amplitudes used were at least four times less than the estimated line-widths, so that the contribution to line-width from field modulation was negligible.

## MATERIALS

*Tetraphenylhydrazine.*—In the first few experiments a sample of tetraphenylhydrazine kindly sent to us by Dr. M. Vecera[13] was used. This sample, however, had turned green and gave an electron paramagnetic resonance spectrum by itself in the solid state and when dissolved in xylene. The sample was subjected to repeated crystallisations from a mixture of benzene and alcohol but failed to yield a colourless product.

A fresh sample of the material was prepared from diphenylamine by oxidation with powdered potassium permanganate.[14] On repeated crystalrsations from a mixture of benzene and alcohol, shining colourless crystals of tetraphenylhydrazine were obtained; these were dried under vacuum (M.P. 142° C. decomp.).

*Diphenylbenzidine.*—Diphenylbenzidine was prepared by the method described by Wieland.[15]

*Deuterated acetic acid* ($CH_3COOD$).—Deuterated acetic acid ($CH_3 COOD$) was prepared from acetic anhydride and 98% $D_2O$.[16]

*Silver oxide.*—Silver oxide was prepared by the oxidation of a solution of silver nitrate with potassium persulphate.[17]

The other chemicals were obtained commercially and were of ANALAR' grade.

## RESULTS AND DISCUSSION

*I. Studies on tetraphenylhydrazine.*—1. On heating a solution of freshly prepared, pure tetraphenylhydrazine in a non-polar solvent like xylene or toluene to about 90° C. the solution acquired a brownish green colour, which it retained on cooling to room temperature. The cooled

solution exhibited an electron spin resonance spectrum consisting of three lines with intensities in the ratio $1:1:1$ (Fig. 1). A sample of tetraphenylhydrazine, which had turned green on keeping, gave, however, a resonance line even in the powder-form. The line from the powder exhibited fine structure, which was not very well resolved, and seemed to consist of at least five components. A solution of the sample in xylene gave a weak, five-line spectrum, which changed to a strong, three-line spectrum on heating. It must be pointed out, however, that not all samples of tetraphenylhydrazine showed visible decomposition on keeping; the samples obtained as colourless crystals after repeated crystallizations were not prone to decomposition on keeping.
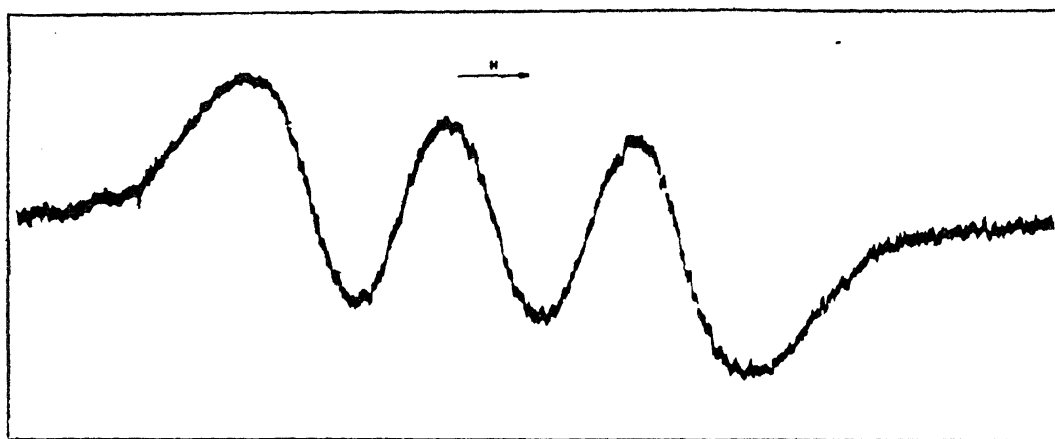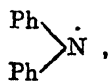


FIG. 1. Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in xylene heated to 90° C. and cooled. The radical is the diphenylamino radical, Ph-Ṅ-Ph.

The three-line spectrum obtained on heating a solution of tetraphenylhydrazine in a non-polar solvent is attributed to the diphenylamino radical,

$$\begin{array}{c} Ph \\ \diagdown \\ \diagup N \\ Ph \end{array} \;,$$

(sometimes called diphenylnitrogen), whose formation was predicted by Wieland.[1] The hyperfine structure is believed to be due to the hyperfine interaction between the odd-electron and the spin of the $N^{14}$ nucleus ($I = 1$), resulting in three equally spaced components with the same intensity.

2. If a solution of tetraphenylhydrazine in xylene was not heated, but allowed to remain for about a week, (or if oxygen was bubbled through the cold solution), the sample changed its colour slightly to a faint brownish hue and gave a weak resonance spectrum similar to Fig. 1. The $g$-value

also agreed with that of the diphenylamino radical within the limits of experimental error. The role of bubbled oxygen or atmospheric oxygen in this reaction is not well understood; it is possible that the first step in this reaction is oxidation, leading further to the cleavage of the molecule resulting in the formation of diphenylamino radicals.

3. A solution of tetraphenylhydrazine in acetic acid, however, showed an entirely different behaviour on heating or on keeping. On heating it turned violet and the cooled sample showed a very strong paramagnetic resonance absorption consisting of five lines (Fig. 2). The 5-line spectrum,
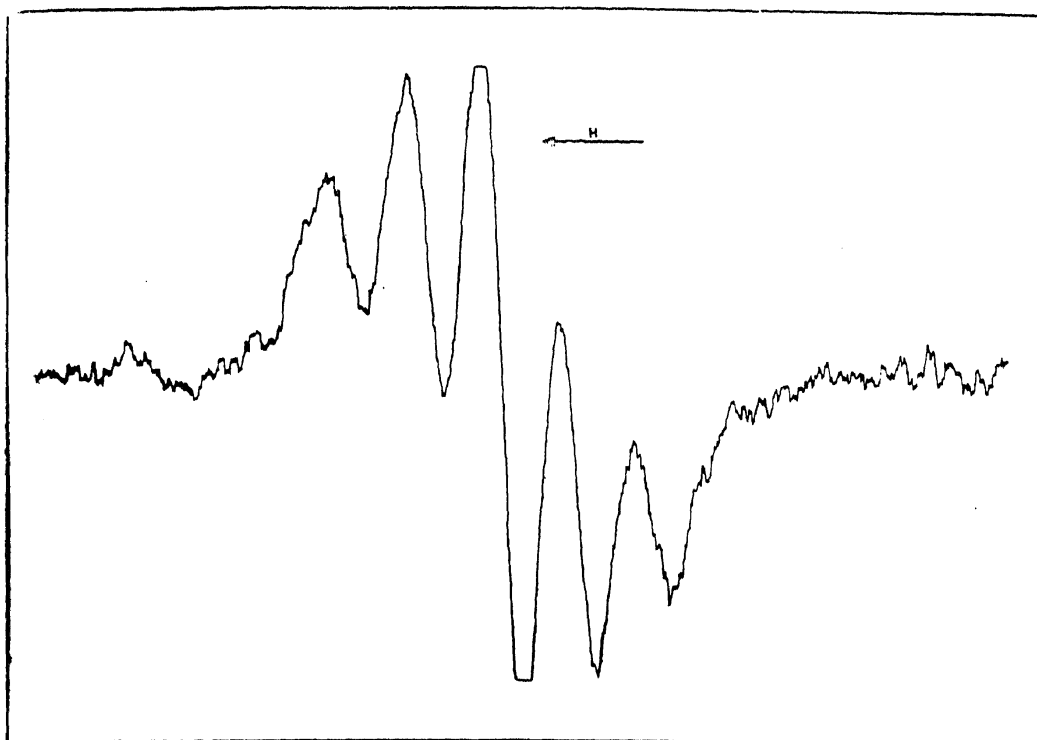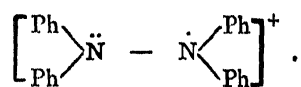


FIG. 2. Derivative of the electron spin resonance absorption from a solution of tetraphenylhydrazine in acetic acid heated and cooled. The radical is the tetraphenylhydrazinium radical,

$$\left[ \begin{array}{c} Ph \\ Ph \end{array} \!\!\! >\ddot{N} \;-\; \dot{N}\!\!\! < \begin{array}{c} Ph \\ Ph \end{array} \right]^{+}.$$

which had a *g*-value that differs distinctly from that of the diphenylamino radical, is believed to be due to the radical of the type,

$$\left[ \begin{array}{c} Ph \\ Ph \end{array} \!\!\! >\ddot{N} \;-\; \dot{N}\!\!\! < \begin{array}{c} Ph \\ Ph \end{array} \right]^{+},$$
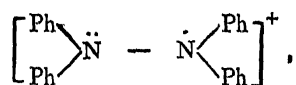
a radical similar to DPPH; the hyperfine structure arises from the interaction of the electron spin with the nuclear spins of the two equivalent nitrogen nuclei. The relative intensities of the hyperfine components also agree

A2

qualitatively with the expected ratio of 1:2:3:2:1. The experiment was repeated with $CH_3COOD$ and there was no change in the spectrum showing thereby that the fine structure does not arise from the protons derived from the carboxylic group of acetic acid.

4. When a freshly prepared solution of tetraphenylhydrazine in acetic acid was shaken for about ten minutes, the solution took a greenish tinge and showed a very poorly-resolved, weak, resonance absorption. The $g$-value of this differed from those of all the other spectra and the entire spectrum was spread over 50 gauss. A new radical species is formed, the nature of which could not be determined on account of the lack of detailed characteristics of the spectrum.

The same solution, however, when kept over for about a week turned dark brown and exhibited a strong, five-component, resonance line with a $g$-value agreeing with that of the radical obtained on heating a freshly prepared solution of tetraphenylhydrazine in acetic acid.

5. On oxidation of the solution of tetraphenylhydrazine in acetic acid with $PbO_2$, a strong absorption was obtained and the spectrum again showed five distinct lines, and its $g$-value agreed with that of the heated solution in acetic acid. The spectrum, however, was less resolved and was spread over a larger range; the spacing between the components was also different (*see* Fig. 3). The spectrum showed no change when $CH_3COOD$ was used instead of $CH_3COOH$.
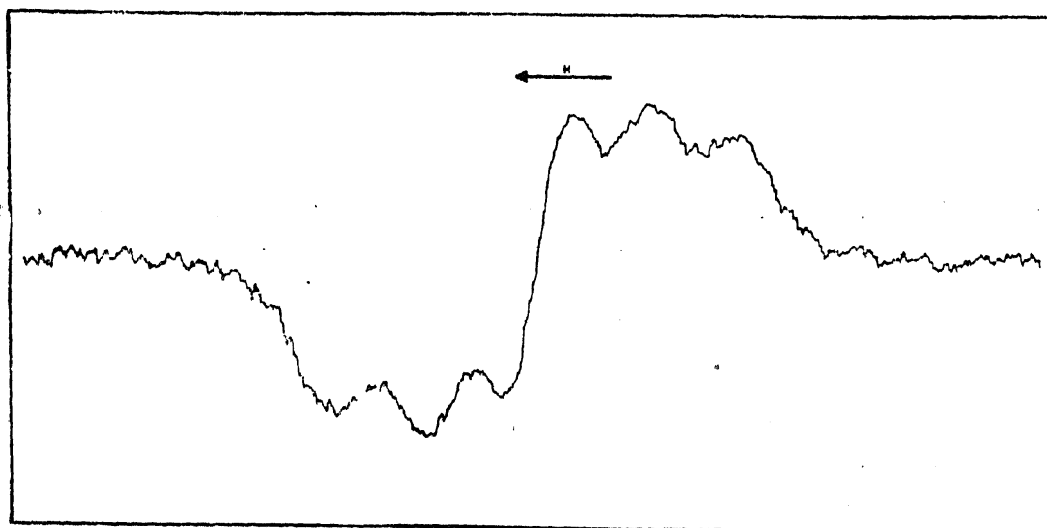


Fig. 3. Derivative of the electron spin resonance absorption from a solution of tetraphenyl-hydrazine in acetic acid treated with $PbO_2$.

6. A powdered sample of tetraphenylhydrazine, when treated with concentrated sulphuric acid, showed very rapid colour changes. There

was a deep violet colour that lasted for a very short time, followed by a longer blue which finally turned into pale green. All the colour changes were followed in the paramagnetic resonance spectrometer and only the violet phase showed the presence of free radicals. Initially, the concentration of radicals was very large but decreased very rapidly with no trace of resonance signal after ten minutes. The entire spectrum had to be scanned very rapidly using fast scanning techniques and short time constants. Steady flow techniques were not adopted because of certain experimental difficulties. The g-value measurements were made very hurriedly owing to the short life of the species and a precision greater than $\pm 0 \cdot 0007$ could not therefore be attained. The g-value was smaller than the free electron value of $2 \cdot 0023$ and the spectrum consisted of 5 components. Both the powdered tetraphenylhydrazine and the concentrated sulphuric acid were cooled to about $-5°$ C. before mixing to prolong slightly the life of the free radical phase.

7. The spectrum obtained from adding a drop or two of concentrated sulphuric acid to a freshly prepared acetic acid solution of tetraphenyl-hyrdazine was, however, very much different from those discussed earlier [Fig. 4 (a)]. When sulphuric acid was added to the acetic acid solution, there was a flash of violet colour followed quickly by blue, turning slowly into green. The violet phase was too short-lived for resonance studies and the blue phase exhibited no resonance. The green phase had a paramagnetic resonance spectrum, whose central portion showed a flat on the derivative curve indicating a trough rather than a peak at the centre. Since the hyperfine interaction with nitrogen $(I = 1)$ alone cannot under any conditions give a trough at the centre, it had to be concluded that some hyperfine structure due to protons also was being observed. (In the other spectra where the observed *hfs* has been attributed solely to nitrogen nuclei, any *hfs* due to protons might be unresolved.) To confirm this, the experiment was repeated with $CH_3COOD$ instead of $CH_3COOH$ and the resulting spectrum [Fig. 4 (b)] showed no trough at the centre. The trough at the centre was, therefore, caused by hyperfine interaction with the protons derived from the carboxyl group of acetic acid; and the deuteration of the carboxyl group led to a peak instead of a trough, as expected from a nucleus with $I = 1$. The g-values of the deuterated and undeuterated species agree with each other, though they differ from the g-values of the other radicals and fall below the free electron value. The spectrum of the deuterated species was split into five main lines and the spectrum of the undeuterated species apparently into six. The five main lines might be due to a larger nitrogen splitting over which smaller proton or deuteron splittings are superimposed. From the fact that some of the *hfs* is derived from the proton abstracted
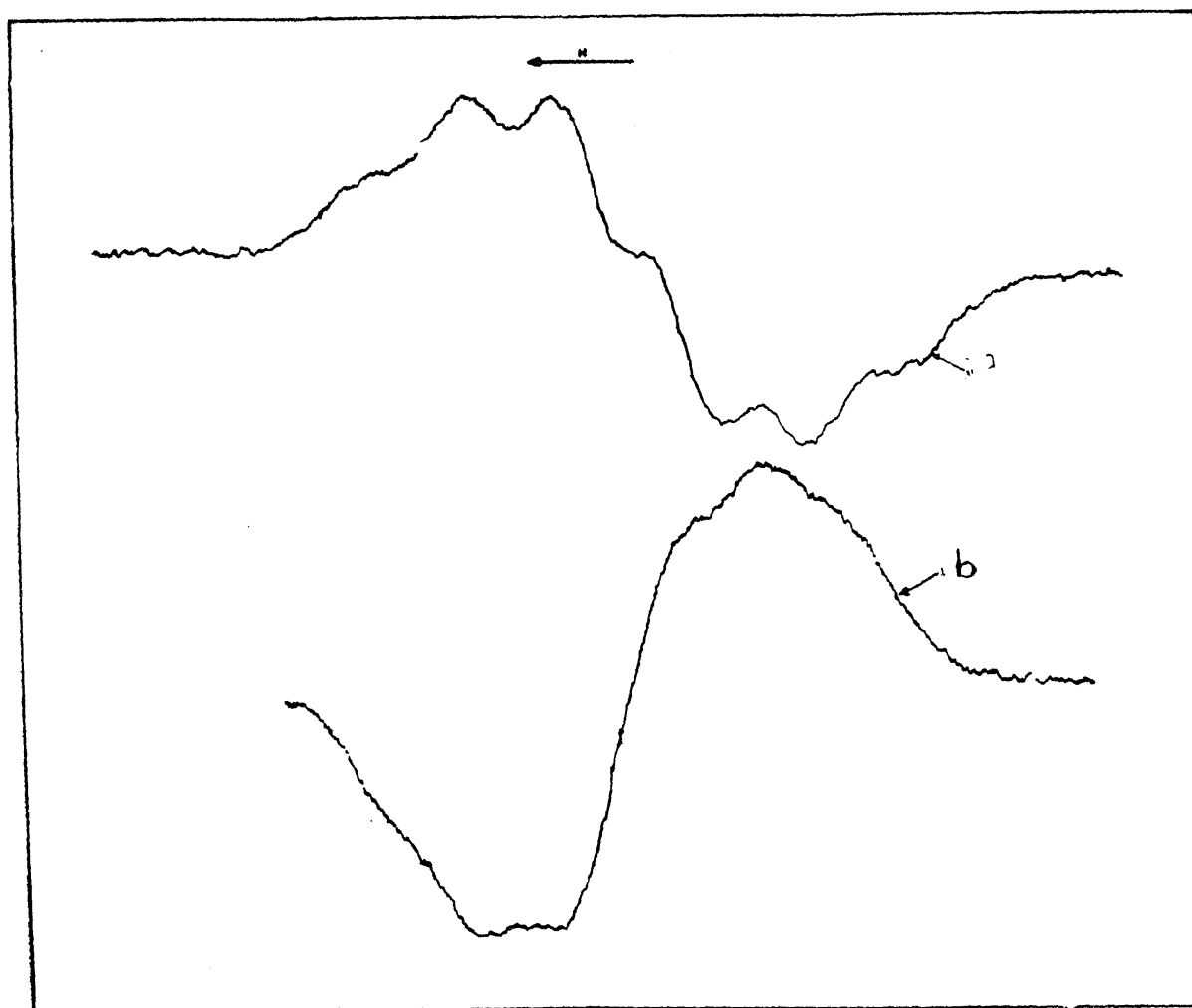
FIG. 4. (a) Derivative of electron spin resonance absorption from a solution of tetra-phenylhydrazine in acetic acid treated with a drop of sulphuric acid; (b) $CH_3COOD$ is used as the solvent instead of $CH_3COOH$.
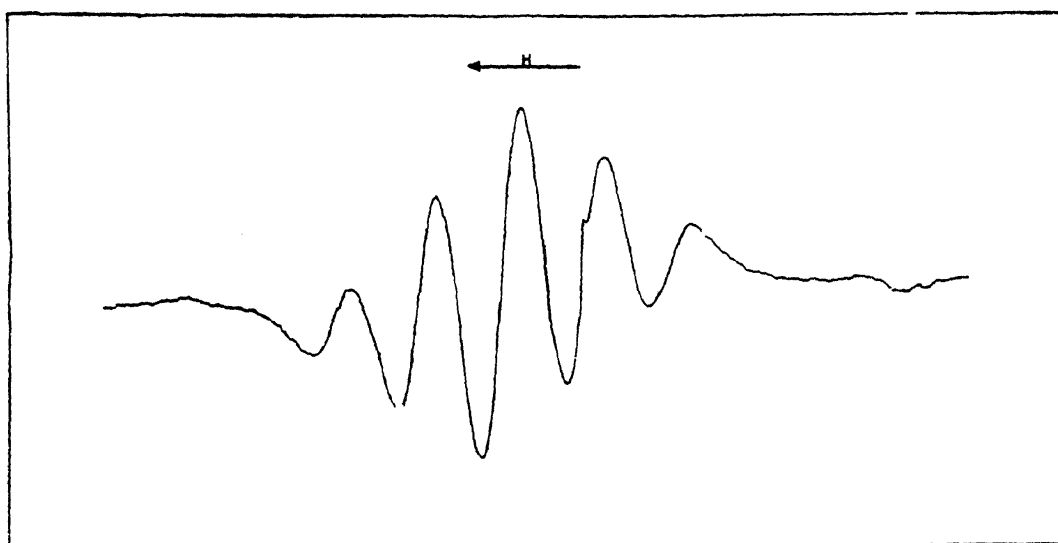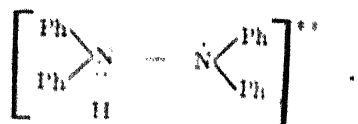


FIG. 5. Derivative of the electron spin resonance spectrum of a solution of dipyhenlamine in acetic acid treated with $PbO_2$. The radical is the same as that in Fig. 2.

from the carboxyl group of acetic acid, we are led to believe that the free radical formed is in all probability, the protonated tetraphenylhydrazinium radical,

$$\left[ \begin{array}{c} Ph \\ Ph \end{array} \!\!\!\! > \overset{..}{\underset{H}{N}} - \overset{.}{N} \!\!\!\! < \begin{array}{c} Ph \\ Ph \end{array} \right]^{++} .$$

*II. Studies on Diphenylamine.* The paramagnetic resonance studies were extended to a few reactions of diphenylbenzidine and diphenylamine, to ascertain whether diphenylamine and diphenylbenzidine would, under suitable conditions, yield the same radicals as those obtained from tetra-phenylhydrazine.

1. Diphenylamine was subjected to oxidation with $PbO_2$ in a polar medium, *viz.*, acetic acid. The resonance spectrum of the resulting mixture exhibited five components and the g-value, the line-widths of the components and *hfs* spacings agreed with those of the free radical obtained by heating a solution of tetraphenylhydrazine in acetic acid (Fig. 5). When deuterated acetic acid, $CH_3COOD$, was used there was no change in the spectrum.
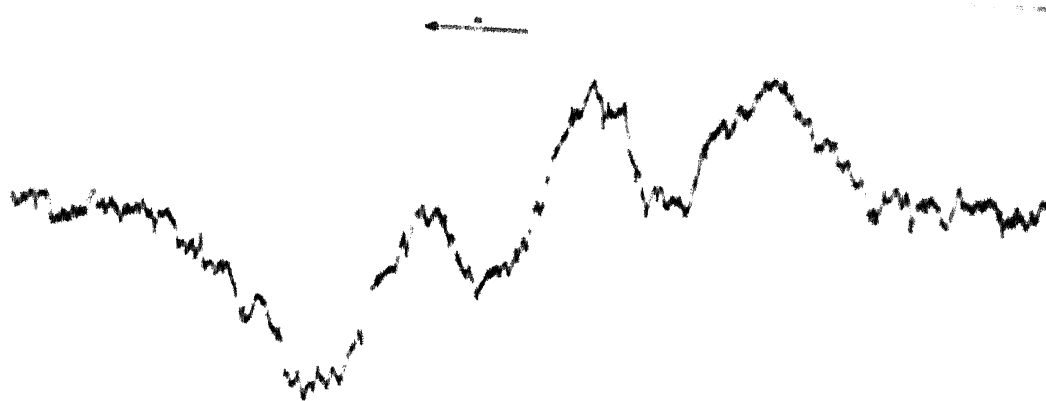


FIG. 6. Derivative of the electron spin resonance spectrum of the xylene extract of the produce obtained by the oxidation of diphenylamine with potassium permanganate in acetone and evaporating the acetone.

2. If, however, the oxidation was carried out with $PbO_2$ or AgO in xylene, a non-polar solvent, the resulting solution gave a very broad, weak resonance spectrum, whose characteristics could not be easily measured. Since, tetraphenylhydrazine is usually prepared by the oxidation of di-phenylamine with powdered potassium permanganate in acetone this system

was subjected to resonance studies. A solution of diphenylamine in acetone was shaken for about ten minutes with powdered potassium permanganate at room temperature and the acetone was evaporated with a jet of nitrogen. The residue—which on crystallization from a benzene-alcohol mixture yields tetraphenylhydrazine—was extracted with xylene in the cold and the xylene extract was examined in the spectrometer; a well-resolved three-line spectrum was found (Fig. 6). This spectrum resembled the spectrum of diphenylamino radical in its line-width and overall spread, but had a different g-value. The mother liquor from the crystallization of the crude tetraphenylhydrazine also gave a similar spectrum. The mechanism for the formation of tetraphenylhydrazine is presumed to be the oxidation of diphenylamine into diphenylamino radicals, two of which combine to form a molecule of tetraphenylhydrazine. The species, whose spectrum we have observed, might be that of the diphenylamino radical further oxidized; the presence of three components may be indicative of this radical containing only one nitrogen atom.

*III.  Studies on Diphenylbenzidine.*—1. Diphenylbenzidine behaved in a manner analogous to diphenylamine, when treated with acetic acid and $PbO_2$ (Fig. 7). The five-line resonance spectrum did not undergo any change when deuterated acetic acid, $CH_3COOD$, was used instead of $CH_3COOH$.
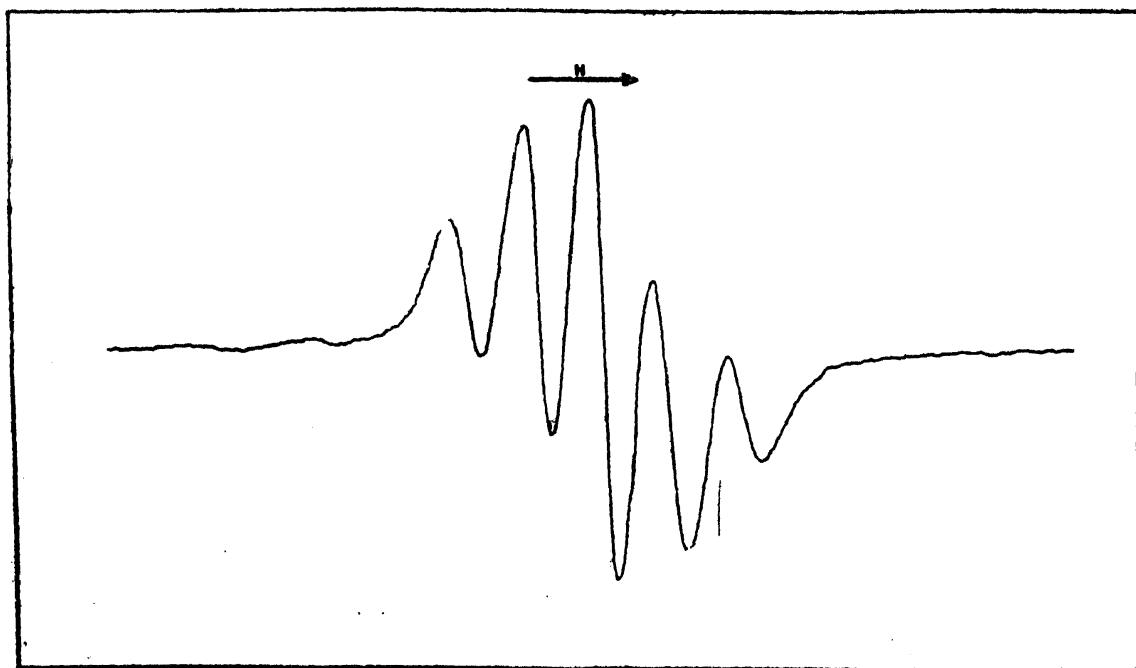


FIG. 7.  Derivative of the electron spin resonance spectrum of a solution of diphenyl-benzidine in acetic acid treated with $PbO_2$.  The radical is the same as that in Figs. 2 and 5.

2. In a non-polar solvent like xylene, the oxidation of diphenylbenzidine with $PbO_2$ or AgO, resulted in an asymmetric paramagnetic resonance spectrum (Fig. 8). It is believed that more than one radical is formed and the measurement of g-value has no meaning due to the ambiguous nature of the spectrum. The spectrum could be interpreted as consisting of a less intense line superimposed on a stronger three-line spectrum. If this interpretation is correct the g-value of the 3-component species is 2·0030 ±0·0005.
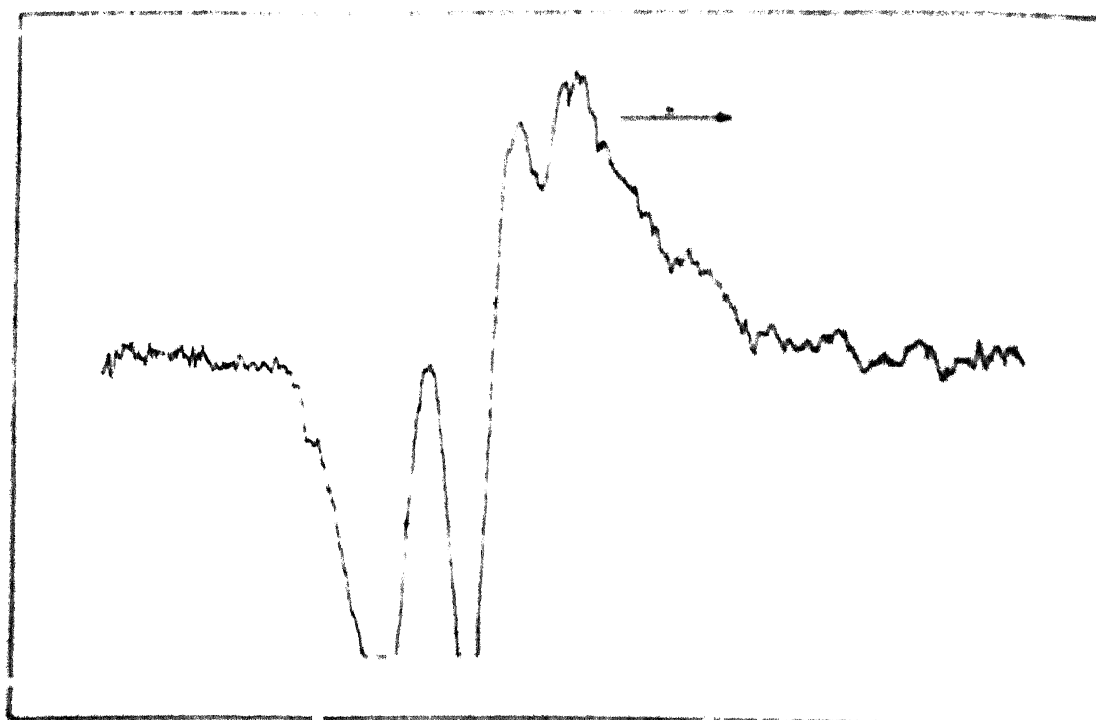


FIG. 8. Derivative of the electron spin resonance spectrum of a solution of diphenyl-benzidine in xylene oxidized with $PbO_2$.

## CHARACTERISTICS OF THE ELECTRON SPIN RESONANCE SPECTRA OF FREE RADICALS

The electron spin resonance spectra of organic free radicals are characterised by the g-values, the hyperfine structure and the separation between the hyperfine components, the line-widths of the components and the over-all spread of the spectra. Among these the g-values and the hyperfine structure are most useful in differentiating between radical species. The g-values of organic free radicals containing C, H, O and N have been found to cluster around the free electron value of 2·0023 and great precision in the determination of g-value is necessary for differentiating between organic free radicals only on the basis of their g-values. The almost

complete quenching of spin-orbit interaction in organic free radicals results in the isotropic part of the g-tensor (the part which is measured in solutions) being very close to the free electron value and the small deviations from the free electron value are presumably due to second order contributions from spin-orbit coupling.

The rich hyperfine structure usually observed in the electron spin resonance spectra of organic free radicals gives considerable information about the nature and structure of the free radical. It arises from the magnetic interaction of the electron magnetic moment with the magnetic moment of the nuclei, the magnitude of this interaction being reflected in the spacings between the hyperfine components. In solutions of low viscosity, the magnitude of the hyperfine interaction with a particular nucleus is directly proportional to the density of the unpaired electron at this nucleus,[18] and a study of the hyperfine pattern gives information on the distribution of the unpaired electron over the molecule. Most of the hyperfine structure observed in the radicals related to tetraphenylhydrazine has been attributed to interaction with nitrogen nuclei (except in the radical formed when a solution of tetraphenylhydrazine in acetic acid is treated with a drop or two of concentrated sulphuric acid). The magnitude of splittings measured are of the same order as those found for nitrogen splittings in other radicals (compare DPPH in benzene[19] or peroxylamine disulphonate ion[20]). The splittings due to protons in the phenyl rings of these radicals are usually very small and we have not observed them. The only proton splitting that has been observed in this study is due to the proton derived from the acidic medium, in the reaction between concentrated $H_2SO_4$ and tetraphenylhydrazine in an acetic acid medium; even here the proton is outside the phenyl ring.

The hyperfine structure spacings have been reported only for some of the radicals studied because of the large uncertainties involved in the overlap corrections when the individual components have line-widths comparable to the hfs separations. The hyperfine spacings in spectra, which are not sufficiently well resolved, are, therefore, less reliable criteria than the g-values for differentiation between radicals. In our investigation, we did not have to rely on hfs spacings for differentiation between radicals except in one instance, viz., the radical derived by the oxidation of tetraphenylhydrazine with $PbO_2$ in an acetic acid medium. It has five components and its g-value agrees with those of the other five-line radicals observed in this series; the spectrum, however, is very broad and spread over a larger region. The uncorrected hfs spacing of 9·1 gauss found for this radical is very much

different from the average of 7 gauss for the other five-line spectra. If there is an appreciable overlap between the components due to the larger line-widths of the components in this particular medium, the corrected *hfs* spacing would increase; hence, we are led to believe that we have here a radical, different from the radical which gives the same g-value but different *hfs* spacings.

The line-widths and the overall spread of the spectra depend considerably on the concentration of the radicals and the nature of the medium in which the radical is obtained. Whereas the isotropic part of the g-tensor and *hfs* spacings of radicals in solutions of low viscosity depend only on intra-molecular interactions and are hence independent of the medium, the line-widths and consequently the overall spread of the spectrum depend also on intermolecular interactions. The interaction of the radical with its neighbours (lattice) decides the spin-lattice relaxation time and hence the line-width of the individual components. The dipolar and the exchange interactions that govern the line shape and the line-widths are concentration dependent. (It should be pointed out that in very concentrated solutions the hyperfine structure might be completely lost due to the phenomenon of exchange narrowing.) In certain cases, the lifetime of the radical itself is made short by fast reactions in which the radical takes part and the line-width becomes dependent on the rate of this reaction, which in turn is controlled by the concentration of the radical and the other reactions.[21] For the reasons cited above, we have not relied on line-widths in making systematic differentiations between the radicals. The observed line-widths are a function of the amplitude of the magnetic field modulation and the overlap between the different components of the spectra. It was not always possible to operate at low field modulation amplitudes due to the low free radical concentration; in such cases the line-widths and *hfs* spacings have not been reported.

## CONCLUSION

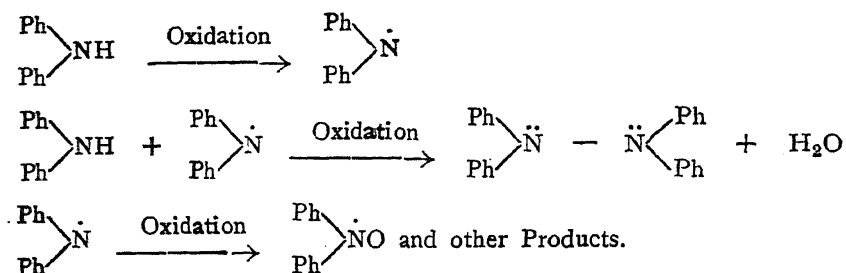Tetraphenylhydrazine has been known, from the time it was first prepared, to undergo a variety of reactions involving free radical intermediates. We have attempted in our studies to provide positive proof for the formation of these radicals and to identify the reactions that may involve common intermediates.

1. Among the radicals which have 3-line spectra, we have identified the diphenylamino radical.

which is obtained either by heating a solution of tetraphenylhydrazine in xylene or by keeping the solution for a week or by bubbling oxygen through it.

2. The three-line spectrum obtained from diphenylamine, on oxidation with potassium permanganate [See Table I–II (2)] in an acetone medium cannot be attributed to the diphenylamino radical. The free radical results, perhaps, from the successive oxidation of the diphenylamino radical by excess potassium permanganate:

$$\frac{Ph}{Ph}\!\!>\!\!NH \xrightarrow{\ Oxidation\ } \frac{Ph}{Ph}\!\!>\!\!\dot{N}$$

$$\frac{Ph}{Ph}\!\!>\!\!NH + \frac{Ph}{Ph}\!\!>\!\!\dot{N} \xrightarrow{\ Oxidation\ } \frac{Ph}{Ph}\!\!>\!\!\ddot{N} - \ddot{N}\!\!<\!\!\frac{Ph}{Ph} + H_2O$$

$$\frac{Ph}{Ph}\!\!>\!\!\dot{N} \xrightarrow{\ Oxidation\ } \frac{Ph}{Ph}\!\!>\!\!NO \ \ and\ other\ Products.$$

The spectrum reported by Hoskins for the radical obtained by passing oxygen through a hot solution of diphenylamine in a mixture of toluene and alkaline alcohol, and presumed to be diphenyl nitric oxide,

$$\frac{Ph}{Ph}\!\!>\!\!\dot{N}O,^{5}$$
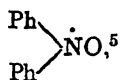
does not agree with our spectrum and the g-values are also different. The nature of the radical we have observed is, therefore, not well understood.

3. We believe that the asymmetric spectrum obtained by the oxidation of diphenylbenzidine with AgO or PbO$_2$ in a non-polar solvent [see Table I–III (2) and Fig. 8] is from more than a single radical species. The g-value of the major three-line radical does not agree with that of the diphenylamino radical, and the radical could either be Ph–Ṅ–Ph–Ph–NH–Ph, or the biradical, Ph–Ṅ–    h–Ṅ–Ph, obtained by the oxidation of either one or both of the imino groups of diphenylbenzidine, Ph–NH–Ph–Ph–NH–Ph, respectively. The biradical is rather unlikely to be formed on account of the higher stability of the diamagnetic quinonoid compound,

$$Ph-N\!=\!\!\bigcirc\!\!=\!\!\bigcirc\!\!=\!\!N-Ph.$$

In this connection, it may be mentioned that the carbon analogue of this compound, Chichibabin's hydrocarbon,

$$\frac{Ph}{Ph}\!\!>\!\!C\!=\!\!\bigcirc\!\!=\!\!\bigcirc\!\!=\!\!C\!\!<\!\!\frac{Ph}{Ph},$$
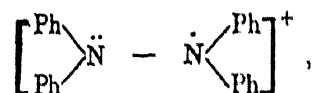
is found to be diamagnetic. Hutchison and co-workers and also later workers have observed electron spin resonance from the solution of this hydrocarbon, corresponding to this hydrocarbon existing in the biradical form
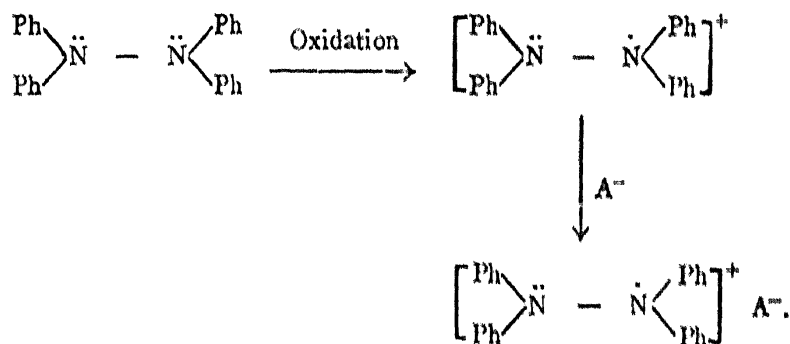
$$\underset{Ph}{\overset{Ph}{>}}\dot{C}-Ph-Ph-\dot{C}\underset{Ph}{\overset{Ph}{<}},$$
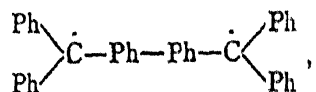
to about 4%.[22] Ingram, however, observes that the signal might have been due to an impurity.[23]

4. The radical,

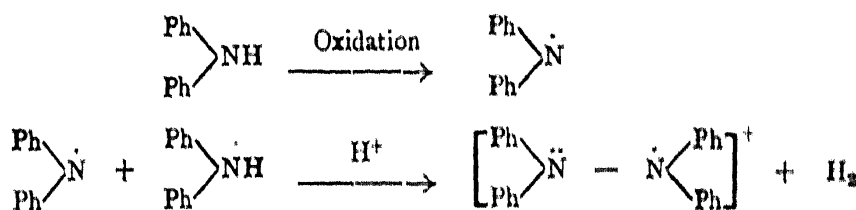$$\left[\underset{Ph}{\overset{Ph}{>}}\ddot{N} - \dot{N}\underset{Ph}{\overset{Ph}{<}}\right]^{+},$$

is formed under various conditions: (*a*) on heating a solution of tetraphenylhydrazine in acetic acid; (*b*) by the ageing of a solution of tetraphenylhydrazine in acetic acid; and (*c*) when diphenylamine or diphenylbenzidine is oxidized with $PbO_2$ in an acetic acid medium. Weitz and Schwecten have suggested that in acid solution this radical is formed by the removal of an electron from a molecule of tetraphenylhydrazine; the resulting cation can then form a salt with the anion of the acid.[a] A molecule of tetraphenylhydrazine itself can act as the oxidizing agent:

$$\underset{Ph}{\overset{Ph}{>}}\ddot{N} - \ddot{N}\underset{Ph}{\overset{Ph}{<}} \xrightarrow{\text{Oxidation}} \left[\underset{Ph}{\overset{Ph}{>}}\ddot{N} - \dot{N}\underset{Ph}{\overset{Ph}{<}}\right]^{+}$$

$$\downarrow A^{-}$$

$$\left[\underset{Ph}{\overset{Ph}{>}}\ddot{N} - \dot{N}\underset{Ph}{\overset{Ph}{<}}\right]^{+} A^{-}.$$

The formation of this radical on keeping an acetic acid solution of tetraphenylhydrazine is perhaps due to atmospheric oxidation. It is possible that the same radical is derived from diphenylamine and diphenylbenzidine in the following manner:

Diphenylamine:

$$\underset{Ph}{\overset{Ph}{>}}NH \xrightarrow{\text{Oxidation}} \underset{Ph}{\overset{Ph}{>}}\dot{N}$$

$$\underset{Ph}{\overset{Ph}{>}}\dot{N} + \underset{Ph}{\overset{Ph}{>}}NH \xrightarrow{H^{+}} \left[\underset{Ph}{\overset{Ph}{>}}\ddot{N} - \dot{N}\underset{Ph}{\overset{Ph}{<}}\right]^{+} + H_2$$

$$\downarrow \text{Oxidation}$$

**Diphenylbenzidine:**

$$
\text{Ph} - \overset{\overset{H}{|}}{N}: \qquad :\overset{\overset{H}{|}}{N} - \text{Ph} \qquad \xrightarrow{\text{PbO}_2} \qquad \text{Ph} - \overset{\overset{H}{|}}{N}\cdot\ + \qquad :\overset{\overset{H}{|}}{N} - \text{Ph}
$$

$$
\longleftrightarrow \qquad \left[\ \text{Ph} - \cdot\overset{\overset{H}{|}}{N}-\overset{\overset{H}{|}}{N} - \text{Ph} \quad + \ \right] \qquad \rightleftharpoons \qquad \left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}\!\!\!\!>\overset{\cdot}{N} - \overset{\cdot\cdot}{N}<\!\!\!\!\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \right]^{+}\cdot
$$
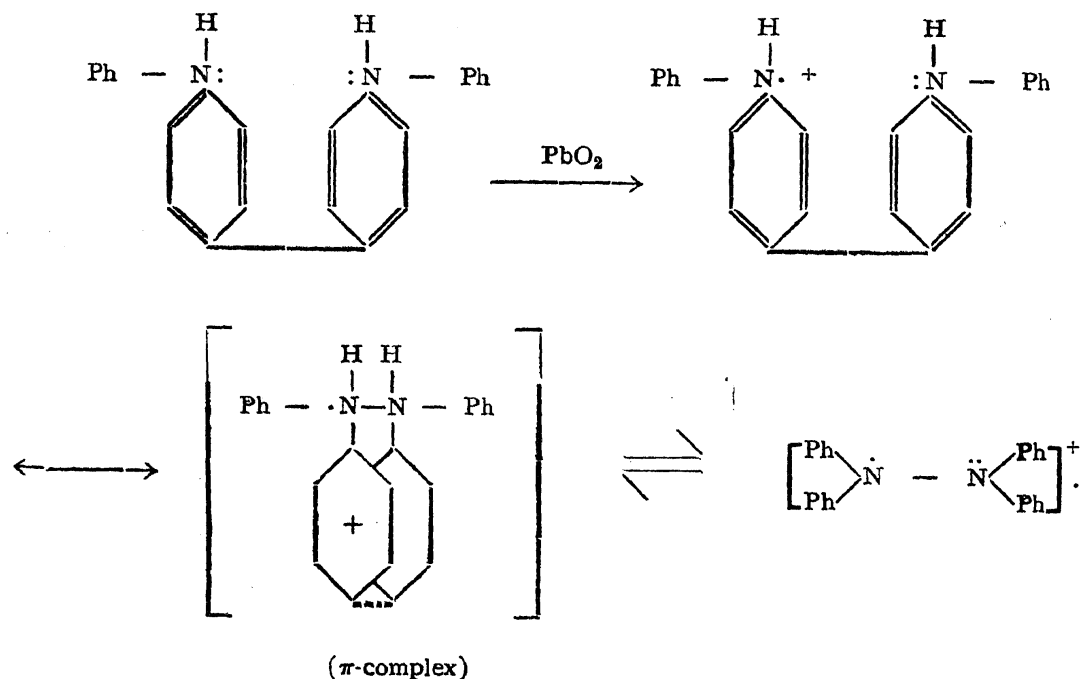
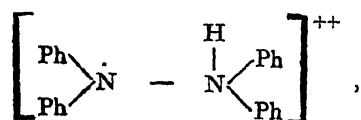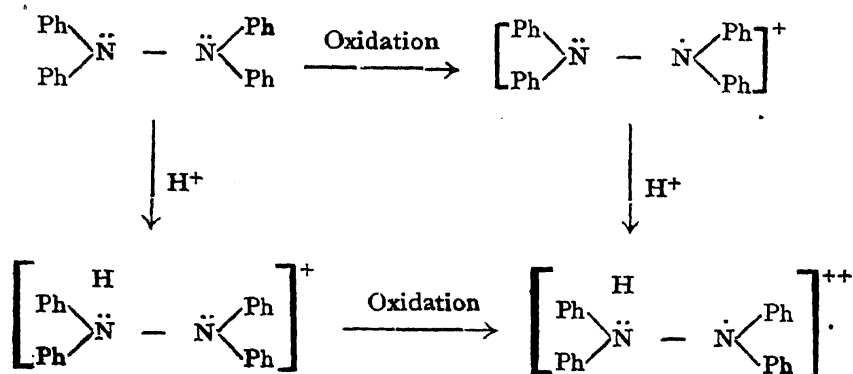(π-complex)

A similar π-complex is at present believed to be the transition state in the benzidine rearrangement.[24] The two aromatic rings fold on each other and the energy difference before and after the folding is extremely small;[24] and the formation of the tetraphenylhydrazinium radical is believed to be through a π-complex transition state and may be compared to the reverse of the benzidine rearrangement.

5. The protonated tetraphenylhydrazinium radical,

$$
\left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}\!\!\!\!>\overset{\cdot}{N} - \overset{\overset{H}{|}}{N}<\!\!\!\!\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \right]^{++}\ ,
$$

is obtained when a drop or two of concentrated sulphuric acid is added to a solution of tetraphenylhydrazine in acetic acid.

$$
\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}\!\!\!\!>\overset{\cdot\cdot}{N} - \overset{\cdot\cdot}{N}<\!\!\!\!\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \xrightarrow{\text{Oxidation}} \left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}\!\!\!\!>\overset{\cdot\cdot}{N} - \overset{\cdot}{N}<\!\!\!\!\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \right]^{+}
$$

$$
\Big\downarrow \text{H}^{+} \qquad\qquad\qquad\qquad \Big\downarrow \text{H}^{+}
$$

$$
\left[ \begin{array}{c} \text{Ph} \\ \cdot\text{Ph} \end{array}\!\!\!\!>\overset{\overset{H}{|}}{\underset{\cdot\cdot}{N}} - \overset{\cdot\cdot}{N}<\!\!\!\!\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \right]^{+} \xrightarrow{\text{Oxidation}} \left[ \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array}\!\!\!\!>\overset{\overset{H}{|}}{\underset{\cdot\cdot}{N}} - \overset{\cdot}{N}<\!\!\!\!\begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \right]^{++}\cdot
$$

6. We have not understood the nature of the radical formed when tetraphenylhydrazine is reacted with $PbO_2$ in acetic acid (Fig. 3); the radical is different from

$$\left[ \substack{Ph \\ Ph} \!\!> \!\ddot{N} - \dot{N} \!<\! \substack{Ph \\ Ph} \right]^{+} .$$
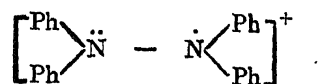
but the presence of a five-line structure indicates a $>N\!-\!\dot{N}<$ structure for this radical also.

7. On atmospheric oxidation of tetraphenylhydrazine in acetic acid, the radical formed as the initial step seems to be different from the tetraphenylhydrazinium radical,

$$\left[ \substack{Ph \\ Ph} \!\!> \!\ddot{N} - \dot{N} \!<\! \substack{Ph \\ Ph} \right]^{+} ;$$
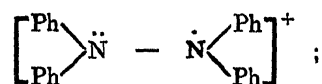
prolonged oxidation, however, leads to the formation of the tetraphenylhydrazinium radical. The nature of the radical formed as the first step is not well understood.

## SUMMARY

The free radicals obtained from tetraphenylhydrazine, diphenylbenzidine and diphenylamine under different conditions have been investigated with electron spin resonance techniques. The identification and differentiation between the radicals were done on the basis of their *g*-values and the line-widths and hyperfine structure exhibited by their spectra. The formation of the diphenylamino radical,

$$\substack{Ph \\ Ph} \!\!> \!\dot{N} ,$$
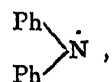
by the thermal dissociation of tetraphenylhydrazine in non-polar solvents has been confirmed. The same radical is obtained when tetraphenylhydrazine is subjected to atmospheric oxidation in a non-polar solvent. The tetraphenylhydrazinium radical ion,

$$\left[ \substack{Ph \\ Ph} \!\!> \!\ddot{N} - \dot{N} \!<\! \substack{Ph \\ Ph} \right]^{+} ;$$
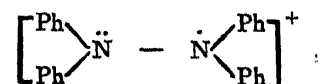
is formed (1) when a solution of tetraphenyl-hydrazine in acetic acid is subjected to prolonged atmospheric oxidation, (2) when a similar, freshly prepared solution is heated and (3) when diphenylamine or diphenylbenzidine is subjected to oxidation in an acetic acid medium. It is believed that the protonated hydrazinium radical,

$$\left[ \begin{array}{ccc} Ph & & Ph \\ & \overset{\bullet}{N} - \overset{\cdot\cdot}{\underset{H}{N}} & \\ Ph & & Ph \end{array} \right]^{++},$$
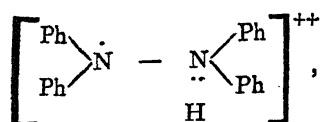
results if an acetic acid solution of tetraphenylhydrazine is treated with a few drops of concentrated sulphuric acid.

During the course of this investigation, the $g$-value of a $0 \cdot 002$ M solution of DPPH in xylene was measured to be $2 \cdot 00347 \pm 0 \cdot 00004$.

## Acknowledgements

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