

Finally we note that the gross charge Q obtained as prescribed by Mulliken⁸ gave the charges, $+0.19$, -0.19 , -0.19 , $+0.19$ for the first, second, third and fourth carbon atoms in C_4 .⁹ This might be compared with the charges $+0.20$, -0.40 ,

- (8) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338 (1955).
 (9) E. Clementi and H. Clementi, to be published.

$+0.20$ on the first, second and third carbon atoms in C_3 .⁸

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Electron Spin Resonance in Molecular Complexes. I. Electronic Splitting and Hyperfine Interactions in the Solid State

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The resolution of the e.s.r. absorption of several amine-quinone complexes in the solid state establishes the existence of uncoupled spins as a rather general feature of these materials. Hyperfine structure has also been observed. A delineation and discussion of the respects in which the amine-quinones differ from the paramagnetic hydrocarbon-halogen complexes is given. The relationship of e.s.r. data to information regarding electronic conduction in the same materials is also discussed.

I. Introduction

Electron spin resonance (e.s.r.) has been observed in amine-quinone² and hydrocarbon-halogen^{3,4} molecular complexes. Kainer, *et al.*,² explain the observed paramagnetism in terms of an ionic ground state for this strong donor-acceptor (D-A) interaction. The free ions, D^+ and A^- , would each have an unpaired electron, each be in a doublet state and give two independent spins unless they interact strongly in the complexes to give splitting into a diamagnetic singlet and a paramagnetic triplet state.

Bijl, *et al.*,^{2b} in a study of several amine-quinone complexes found a single absorption line in all but one case, the *p*-phenylenediamine-bromanil complex, which had two unresolved lines with g values of 2.0095 and 2.005 at 90°K. Matsunaga⁵ reports clear resolution for *p*-phenylenediamine-chloranil and correlation of the resonance lines with those independently observed for the component ions; he also notes that absorption for N,N,N',N' -tetramethyl-*p*-phenylenediamine-chloranil is highly asymmetric.

We have found similar results for *p*-phenylenediamine-chloranil^{6c}; in this paper the successful resolution of the resonance absorption of several molecular complexes, and several cases of hyperfine structure in these solids are reported.

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(2) (a) H. Kainer, D. Bijl and A. C. Rose-Innes, *Naturwissenschaften*, **41**, 303 (1954). (b) D. Bijl, H. Kainer and A. C. Rose-Innes, *J. Chem. Phys.*, **30**, 765 (1959).

(3) Y. Matsunaga, *ibid.*, **30**, 855 (1959).

(4) L. S. Singer and J. Kommandeur, *ibid.*, **34**, 133 (1961); J. Kommandeur and Frances R. Hall, *ibid.*, **34**, 129 (1961).

(5) Y. Matsunaga and C. A. McDowell, *Nature*, **185**, 916 (1960).

(6) (a) M. M. Labes, R. Sehr and M. Bose, *J. Chem. Phys.*, **32**, 1570 (1960); (b) M. M. Labes, R. Sehr and M. Bose, *ibid.*, **33**, 868 (1960); (c) R. Sehr, M. M. Labes, M. Bose, H. Ur and F. Wilhelm, "Proc. Conference on Electronic Conductivity in Organic Solids," Durham, N. C., April 20-22, 1960, Interscience Publishers, Inc., New York, N. Y., to be published (1961); (d) M. M. Labes, R. Sehr and M. Bose, "Proc. International Conference on Semi-conductor Physics," Prague, Czechoslovakia, August 29-September 2, 1960, 850 (1961).

The hydrocarbon-halogen complexes also exhibit paramagnetism but Matsunaga's,³ Singer and Kommandeur's⁴ and our own work^{6c} have uncovered no cases of structure in the resonance spectra. This and other differences in the two types of complexes will be discussed in detail.

II. Experimental

Materials.—The preparation of the complexes and starting materials from which they are derived has been described in previous papers,⁶ with the exception of diaminodurene and N,N,N',N' -tetramethyl-*p*-phenylenediamine. The former was prepared in a manner analogous to that described by Smith,⁷ m.p. 147-148° after two recrystallizations from alcohol. The latter amine after liberation from the dihydrochloride obtained from British Drug House was sublimed three times *in vacuo*, m.p. 46-48°.

Spin Resonance Measurements.—Initial spin resonance experiments were carried out with the standard Varian V4500 EPR spectrometer operating in the X band. The Varian V4560 100 kc. field modulation unit was used in the later stages in conjunction with the Varian V-4531 multi-purpose cavity which enabled the sample temperature to be varied from room down to liquid nitrogen temperatures. The increase in sensitivity and resolution obtained at this higher modulation frequency is obvious in Fig. 1. The spectra were recorded using a very low modulation field and a slow scanning rate. The g values were estimated by comparison with either α,α -diphenyl- β -picrylhydrazyl (DPPH) or with ultramarine. The line widths reported are between points of maximum slope.

Preliminary studies on some samples indicated that the resonance absorption was not affected by atmospheric oxygen. However, as a precautionary measure, all the samples were studied *in vacuo*. It was necessary however, to use fresh samples as the absorption was found to be modified considerably on storage in some cases. All measurements were performed on microcrystalline material.

III. Results

Figure 1 shows the e.s.r. spectra of *p*-phenylenediamine-chloranil at room temperature. Figure 1a, obtained with a modulation frequency of 400 c./sec. and an amplitude of modulation field of approximately 0.2 gauss, exhibits two absorption peaks with g values of 2.0026 and 2.0056, respectively, corresponding to the uncoupled spins of the donor and acceptor ions (*cf.* Matsunaga).⁵ Figure

(7) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 254.

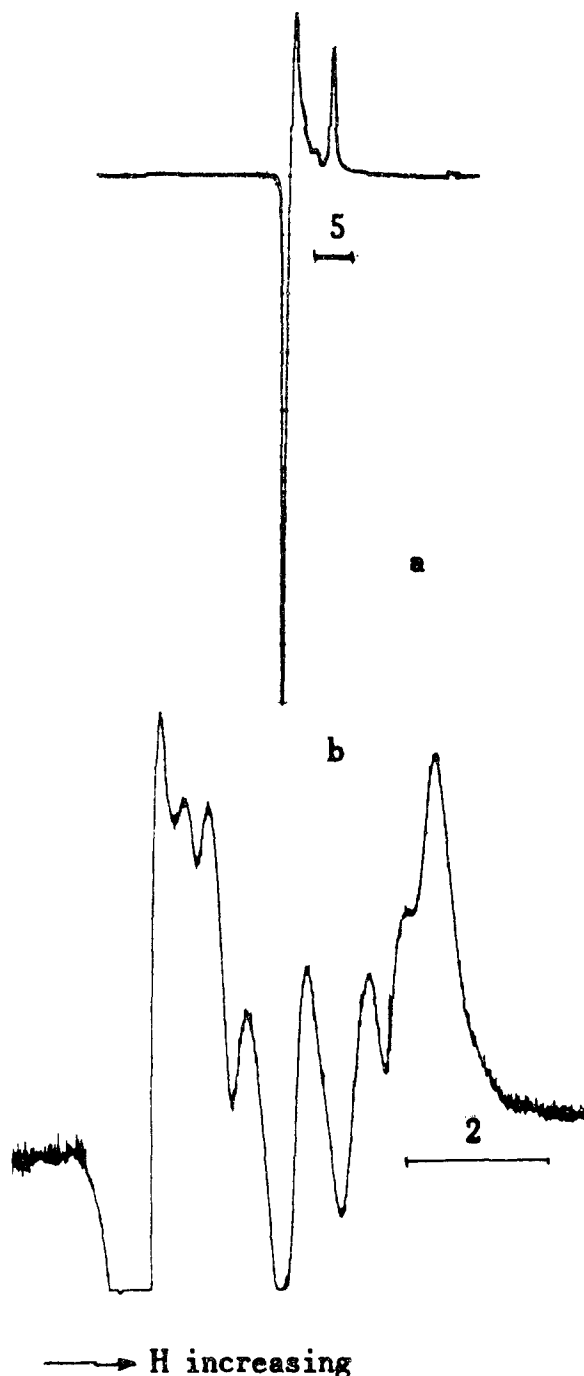


Fig. 1.—First derivative of e.s.r. absorption of *p*-phenylenediamine-chloranil at 294°K.: (a) modulation frequency, 400 cps.; (b) modulation frequency, 100 kc./sec.

1b is the same complex examined at a modulation frequency of 100 kc./sec. and a depth of modulation of 0.025 gauss approximately. This spectrum shows hyperfine structure in the individual electronic levels. Though the number of hyperfine lines remained more or less the same for different preparations of the complex, the width and height of the hyperfine lines varied to some extent from sample to sample.

Figure 1b is one of the best resolved hyperfine spectra obtained with this complex. It is an eight

line spectrum which might be divided into a five line spectrum corresponding to the donor at higher field value and a three line spectrum corresponding to the acceptor at lower field value. The lines in each group are roughly equidistant. In the former the splittings are of the order of 0.8 gauss as compared to 0.4 gauss in the latter. Chloranil semiquinone ion in solution has no hyperfine structure,⁸ but the Wurster's salt⁹ derived from *p*-phenylenediamine shows a rich hyperfine spectrum. In this case the primary resolution is due to the protons of the amino group or the methyl substituted amino group and the secondary splittings arise from the ring protons. The splittings due to the vanishingly small nitrogen hyperfine interaction have finally been observed by Hausser.¹⁰ Hyperfine coupling constants observed were 1.9 gauss for the aromatic ring protons, 6.8 gauss for the methyl protons and 0.28 gauss for N¹⁴ nuclei. Very recently Melchior and Maki¹⁰ have been able to resolve the hyperfine lines in *p*-phenylenediamine positive ion in solution, the splitting parameters being 5.29 gauss for N, 5.88 gauss for the amino protons and 2.13 gauss for the ring protons, respectively. However, their results on perdeuterio-*p*-phenylenediamine indicate that the line positions are not favorable for the resolution of N¹⁴ interaction alone. Thus both from Wurster's salt studies and the result from *p*-phenylenediamine positive ion, the strongest interaction appears to be that due to the amino protons; our results on the solid complexes seem to be consistent with this picture. In the *p*-phenylenediamine-chloranil complex we tentatively suggest that the donor ion splittings into five component lines are in all probability due to the four amino protons, the other splittings not being observed.

This suggestion is supported by the lack of greater resolution in diaminodurene-chloranil (Fig. 2c) which should have had a richer hyperfine structure, if the 12 extra methyl protons were effective. Further, for N,N,N',N'-tetramethyl-*p*-phenylenediamine-chloranil, though we do not have the expected increase in the number of hyperfine lines, the number is greater than for *p*-phenylenediamine-chloranil. The chloranil negative ion exhibits no fine structure in solution, but in the solid molecular complex the situation is different. In the crystal the *p*-phenylenediamine and chloranil molecules are in all probability stacked alternately.^{6b} Here one has to consider the dipole-dipole interaction between the spins on the oxygen in chloranil and the protons of the amino group. As there is the possibility of rotation of the amino group around the C-N bond, both protons would be effective, thus producing a triplet.

Figure 3 shows the effect of lowering of temperature on the hyperfine structure of *p*-phenylenediamine-chloranil. One finds the hyperfine components broadening out, resulting in a loss of structure. Thus going from 294° to 241°K., we pass from an 8-9 line spectrum to a 5-6 line one, then

(8) J. E. Wertz and J. L. Vivo. *J. Chem. Phys.*, **23**, 2441 (1955).

(9) S. I. Weissman, M. G. Townsend, D. E. Paul and G. E. Pake, *ibid.*, **21**, 2227 (1958); S. I. Weissman, *ibid.*, **22**, 1135 (1954); T. R. Tuttle, *ibid.*, **30**, 331 (1959).

(10) M. T. Melchior and A. H. Maki. *ibid.*, **34**, 471 (1961).

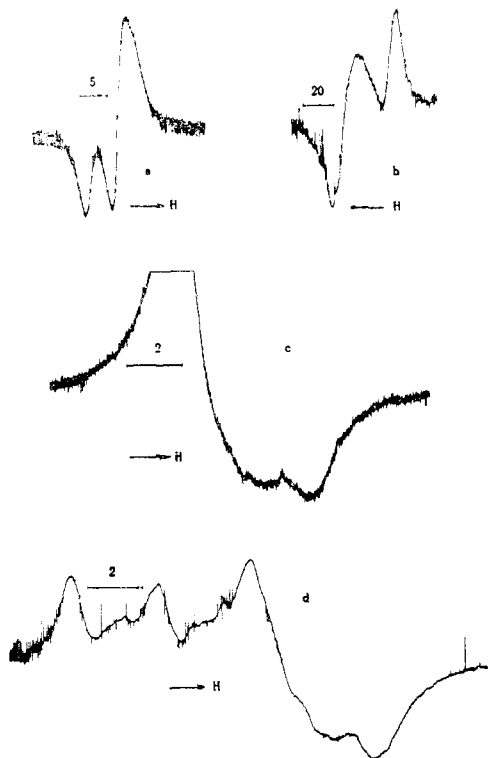


Fig. 2.—First derivative of e.s.r. absorption at 294°K. with modulation frequency of 100 kc./sec.: (a) *p*-phenylenediamine-bromanil; (b) *p*-phenylenediamine-iodanil; (c) diaminodurene-chloranil; (d) *N,N,N',N'*-tetramethyl-*p*-phenylenediamine-chloranil.

at 215°K. we have a 3 line spectrum and at 144°K. we have a single symmetrical broad absorption line without any trace of structure. Similar behavior also has been observed with diaminodurene-chloranil. This loss of structure with temperature possibly is due to the freezing out of the internal rotational motion of the amino groups. It is relevant to point out that proton resonance line width transitions in benzidine¹¹ occurred around 238°K. and the magnitude of the line width change indicated that this was also brought about by a rotational motion of amino groups about their two-fold axes, though of course much lower frequencies of motion are required for narrowing of n.m.r. than of e.s.r. lines.

The *g* values and the total line width of e.s.r. absorption are presented in Table I.

The above results were obtained with microcrystalline materials. Recently we have succeeded in preparing single crystals of some of these complexes; preliminary resonance studies on single crystals of diaminodurene-chloranil indicate the presence of a definite hyperfine axis; the appearance of hyperfine structure depends on the orientation of the crystal in the magnetic field.

IV. Discussion

Hyperfine structure is observed in solids only under special situations and, to the best of our knowledge, the results herein presented are the first such observations made on molecular com-

(11) R. Kromhout and W. Moulton, *J. Chem. Phys.*, **23**, 1673 (1955).

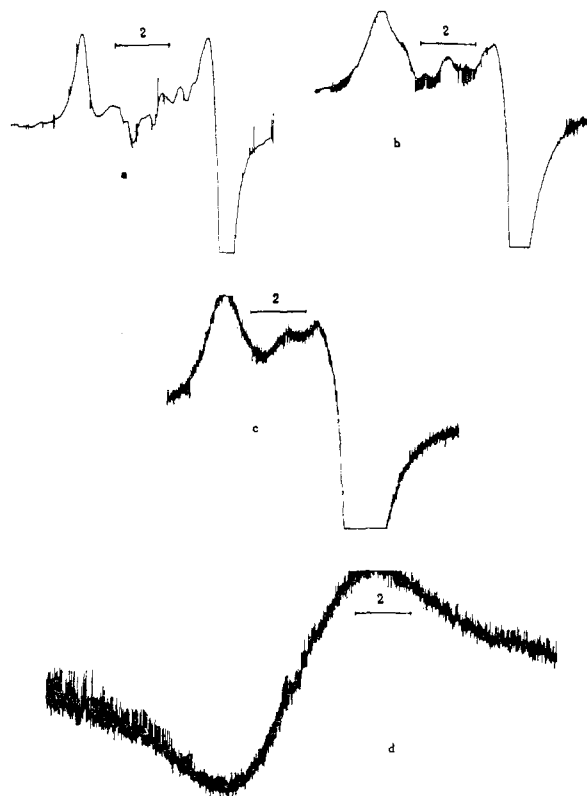


Fig. 3.—Temperature variation of e.s.r. spectra of *p*-phenylenediamine-chloranil: (a) 294°K., (b) 241°K., (c) 215°K., (d) 114°K.

plexes. Usually dipole-dipole (spin-spin) interaction leads to line broadening in solids. However, when free radicals produced by irradiation¹² are trapped in a solid matrix at a sufficient distance apart, hyperfine structure is observed. DPPH¹³

TABLE I
LINE WIDTHS AND *g* VALUES OF E.S.R. ABSORPTION FOR AMINE-QUINONE COMPLEXES

| Name of complex | Temp., °K. | Total line width (gauss) | <i>g</i> values | | Number of lines |
|---|------------|--------------------------|-----------------------------------|-----------------------------------|------------------------|
| | | | <i>g</i> _{D⁺} | <i>g</i> _{A⁻} | |
| <i>p</i> -Phenylene-diamine-chloranil | 294 | 5.2 | 2.0026 | 2.0056 | 8 |
| | 241 | 5.2 | | | 5-6 |
| | 215 | 5.2 | | | 3 |
| | 114 | 5.5 | | | 1 |
| <i>p</i> -Phenylenediamine-bromanil | 294 | 8.2 | 1.9926 | 2.0044 | 2 |
| <i>p</i> -Phenylenediamine-iodanil | 294 | 43.2 | 2.0036 | 2.0058 | 2 |
| Diaminodurene-chloranil | 294 | 5.4 | | | 6 |
| | 140 | 6.5 | | | (Poor resolution) 1 |
| <i>N,N,N',N'</i> -tetramethyl- <i>p</i> -phenylenediamine-chloranil | 294 | 10.9 | | | 10 |

(single crystals of α,α -diphenyl- β -picrylhydrazine containing approximately 0.1% DPPH) and di-*p*-

(12) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Butterworths Scientific Publications, London, 1958, Ch. VI.

(13) R. W. Holmberg, R. Livingston and W. T. Smith, *J. Chem. Phys.*, **33**, 541 (1960).

anisyl nitric oxide¹⁴ (25% solid solution in a plastic medium) in solid solution have also been found to give hyperfine structure. It seems likely, therefore, that in the molecular complexes studied with 0.1–5% free radical character, we have to consider the radical centers as being dispersed with order in a non-paramagnetic matrix where the radicals are far enough apart for dipole–dipole broadening to be minimal. Matsunaga's recent observation¹⁵ of hyperfine structure in mesonaphthodianthrene, and its quinone is, we believe, another example of the same type of effect.

E.s.r. studies show clear differences between the amine–quinone and hydrocarbon–halogen complexes. The former often have structure; no examples of structure in the latter have been observed. Studies on the temperature dependence of spin concentration indicate that the amine–quinones² generally follow the Curie law ($1/T$ dependence), whereas the hydrocarbon–halogens⁴ show an exponential dependence on temperature in agreement with the activation energy for electronic conduction. Recently, however, Chesnut and Phillips¹⁶ have observed that diaminodurene–chloranil follows a temperature dependence of a triplet state (exponential dependence) contaminated by about 0.04% doublet state impurity, whereas Huggins and LeBlanc¹⁷ have reported that the β -carotene–triiodide ion complex exhibits a weak and substantially temperature independent e.p.r. signal intensity. The temperature variation of line width is also different for the types of complexes. For the perylene–iodine complexes the line width decreases from 8 oersteds at room temperature to 2.5 oersteds at 77°K. Similar behavior has been observed with pyrene, pyranthrene and violanthrene complexes.¹⁵ For the amine–quinone complexes the situation seems reversed. The hyperfine lines become broader and broader with lowering of temperature and all traces of structure disappear giving a single broad symmetric line. The difference in behavior in the two groups of complexes is also reflected in the g values, hydrocarbon–halogen complexes having g values very close to that of the free electron (2.0023) while the g values corresponding to the acceptor ions in amine–quinones (Table I) show considerable departure from that of the free electron. One may be dealing with delocalized electrons in the former case and localized electrons in the latter, as suggested by Holden, *et al.*,¹⁸ in a study of some organic free radicals.

(14) G. Berthet, *Arch. Sci.*, **10** (Special), 101 (1957).

(15) Y. Matsunaga, *Canad. J. Chem.*, **38**, 323 (1960).

(16) D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

(17) C. M. Huggins and O. H. LeBlanc, Jr., *Nature*, **186**, 552 (1960).

These results appear to be consistent with the picture of ionic molecular complexes with little $D^+ A^-$ interaction in the amine–quinones, but strong $D^+ A^-$ interaction in the hydrocarbon–halogens. In the latter complexes a delocalized π electron from the hydrocarbon goes over to a vacant antibonding orbital in the iodine molecule. This antibonding orbital has a large radius and since both the hydrocarbon and the iodine molecules are highly polarizable, it is not unlikely that in spite of the electron transfer, there is quite a bit of orbital overlap between the donor and acceptor ions leading to the case of considerable orbital interaction (singlet–triplet condition). In the amine–quinones the presence of bulky groups, amino or alkylamino in the donor and halogen in the acceptor, possibly produces steric conditions which do not allow very close approach of the component ions preventing strong $D^+ A^-$ interaction.

The two groups differ also in their electrical behavior. For the amine–quinones the Seebeck coefficient^{6a,c} was always positive indicating that conduction was predominantly by holes, whereas for perylene–iodine the Seebeck coefficient was negative indicating that current carriers were primarily electrons.

The correlation or lack of correlation of e.s.r. information with studies of electronic conduction in these solids is in an interesting but uncertain state. We have pointed out that there is no simple correlation^{6c} between spin concentration and conductivity at room temperature for several complexes, indicating that the unpaired electrons might not have anything to do with the conduction process. However, from the agreement between the activation energies of spin concentration and conduction for the hydrocarbon–halogen complexes, it has been argued that the unpaired spins are the charge carriers.⁴ For the diaminodurene–chloranil complex¹⁶ e.s.r. studies give a singlet–triplet separation energy (J) of 0.16 e.v. which is not the same as the activation energy of 0.26 e.v. for electrical transport. Further studies of temperature dependence of both type of complexes are needed before the relationship of unpaired electrons in an organic matrix to charge transport is fully understood.

V. Acknowledgments.—The authors are indebted to Dr. A. Neaves for his kind help in the e.s.r. measurements, to Mrs. H. Ur for assistance in the preparation of materials and to Dr. R. Bersohn of Columbia University for a helpful discussion.

(18) A. N. Holden, W. A. Yager and F. R. Merritt, *J. Chem. Phys.*, **19**, 1319 (1951).