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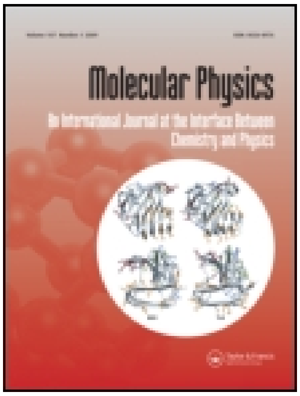

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Molecules and ions in a donor acceptor complex

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Molecules and ions in a donor acceptor complex[†]

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(*Received* 8 *May* 1967)

This paper reports the results of an x-ray analysis, electron spin resonance, electrical conductivity, u.v. and visible spectroscopic measurements on TMPD-chloranil. The results can be explained by assuming a molionic lattice, i.e. a crystal lattice built up of neutral TMPD and chloranil molecules together with bi-valent positive TMPD ions and bi-valent negative chloranil ions. Elementary excitations creating (chloranil$^-$ . . . TMPD^{++} . . . chloranil$^-$) are presumed to be responsible for the measured paramagnetism.

It was found that two modifications of TMPD-chloranil exist, which at room temperature are only distinguishable by the anisotropy of their E.S.R. linewidth. At low temperature both modifications suffer a phase transition, as observed on x-ray Weissenberg photographs and confirmed by E.S.R. measurements.

1. Introduction

Although in the past 10 years the properties of the solid complexes of aromatic diamines and halogenated quinones have been investigated intensively, little progress has been made in their theoretical understanding (for reviews of this kind of donor–complexes see for example [1]). The main problem has been the lack of reliable experimental data, most of these having been determined using compressed powders.

In our laboratory we have succeeded in preparing single crystals of the N,N,N′,N′-tetramethyl-p-phenylene-diamine chloranil (TMPD-chloranil) complex. These crystals were stable at room temperature over a period of more than 2 days. This paper reports the results of a preliminary x-ray analysis, electron spin resonance, electrical conductivity and u.v. and visible spectroscopic measurements on these crystals. All of the results obtained can be explained by assuming a molionic lattice, i.e. a crystal lattice built up of neutral TMPD and chloranil molecules, together with bi-valent positive TMPD ions and bi-valent negative chloranil ions. Elementary excitations creating (chloranil$^-$ . . . TMPD^{++} . . . chloranil$^-$) are presumed to be responsible for the measured paramagnetism in E.S.R.

It was found that two modifications of TMPD-chloranil exist, which at room temperature are only distinguishable by the anisotropy of their E.S.R. linewidth.

At low temperature both modifications suffer a phase transition. This was first observed on x-ray Weissenberg photographs and has been confirmed by E.S.R. measurements.

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2. Experimental

2.1. *Materials*

TMPD-2HCl was obtained from the British Drug Houses Ltd. After dissolving this salt in water, the amine was precipitated with NaOH and sublimed twice *in vacuo*. Chloranil (tetrachlorobenzoquinone) was obtained from Fluka A.G. and purified by two recrystallizations from pure benzene. For the preparation of the complex, spectrograde benzene was used as a solvent. The mono-negative and bi-negative ions of chloranil were prepared by electrolytical reduction of a 0·01 molar solution of chloranil in acetonitrile with $NaClO_4$ as a supporting electrolyte. The applied voltage on the platinum electrodes was 1·9 v.

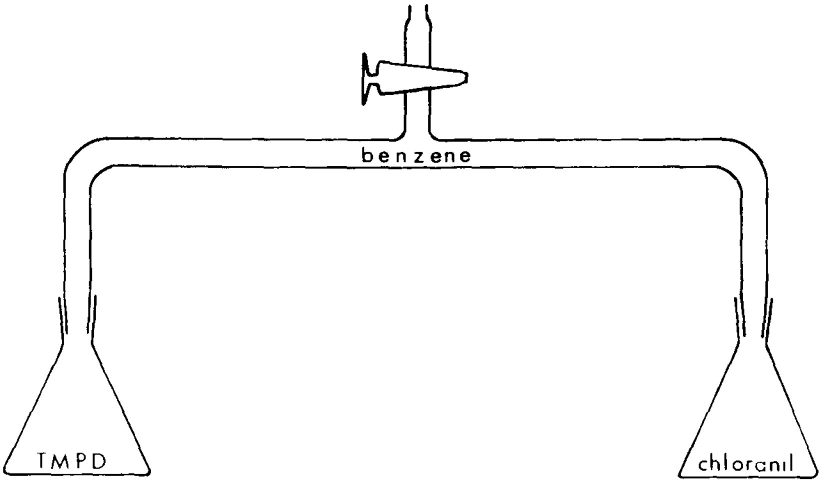

Figure 1. Crystal growth apparatus.

TMPD-chloranil crystals were prepared in the following way: A 50 ml. erlenmeyer was filled with a saturated solution of chloranil in benzene (about 0·20 mole/litre), another 50 ml. erlenmeyer was filled with a 0·094 molar solution of TMPD in benzene. The two erlenmeyers were connected with a glass tube of 40 cm length and 1 cm inner diameter as illustrated in figure 1. Pure benzene was added through the stopcock until the glass tube was filled. Then the stopcock was closed and the apparatus turned through 120° so that the plane through both erlenmeyers and the glass tube made an angle of about 30° with the horizontal plane. Under these circumstances, chloranil and TMPD diffused towards each other and after about 15 to 30 min crystals were formed in the glass tube. After 2 hours the contents of the tube were filtered and the crystals were washed with benzene. The temperature was maintained at 20°c.

As will be shown later there are two modifications of TMPD-chloranil, TMPD-chloranil-A (TC-A) and TMPD-chloranil-B (TC-B). The elemental analysis of TC-A and TC-B agrees within the errors of the analysis with the theoretical values for a 1 : 1 complex. Which of the modifications is formed, appears to be accidental. It was found, however, that in each case all crystals formed were either of form A or form B, a mixture of both modifications never being found. Although many conditions such as concentration, purity, temperature and geometry of glass tube and erlenmeyers were varied it was not possible to find the conditions under which always either type A or B formed, though the probability of the formation of B could be increased by lowering the TMPD concentration. The crystals were stored at liquid nitrogen temperature.

2.2. *Experimental techniques*

E.S.R. measurements were carried out with a Varian V4502 E.P.R., X-band spectrometer and associated 12 in. electromagnet. The Varian V–4560/100 kHz field modulation unit was used in conjunction with the V–4531 multi-purpose cavity. For accurate integration of the E.S.R. signal the detection part of the V–4502 apparatus was replaced by an integrating circuit which allowed digital registration of the paramagnetic intensity [2]. In this way the determination of the relative magnetic susceptibility could be performed with an accuracy of better than 3 per cent.

The optical absorption spectra were taken with a Cary recording spectrophotometer model 14. For measuring the conductivity of TMPD-chloranil the crystals were suspended on thin copper wires in a dry nitrogen atmosphere. Electrical contact was made with a ' Silver Dag ' dispersion. The leads to the crystal were connected to an electric circuit consisting of a battery, a Keithley 200B vacuum tube voltmeter with model 200B decade shunt. The applied field was 10 v per cm.

3. RESULTS

3.1. *Crystal structure*

The room temperature crystal structure of TC has been determined by de Boer [3]. He kindly consented to let us use his preliminary results in this paper.

Examination of single crystals of TC-A and TC-B show these to be monoclinic. By visual inspection no differences were observed for the Weissenberg photographs of the two forms. It was therefore assumed that the room temperature structures of both forms are essentially identical. During the structure determination the space group C 2/m was adopted.

The unit cell data were found to be:

$a = 16\cdot32 \pm 0\cdot03$ Å,
$b = 6\cdot57 \pm 0\cdot02$ Å, $\beta = 111\cdot9 \pm 0\cdot1°$, $Z = 2$ (TC units),
$c = 8\cdot81 \pm 0\cdot02$ Å.

Figure 2 shows the (010) plane of the unit cell of TC-A. A standard deviation of 0·02 Å was assigned to the bond lengths given.

A complication in the determination of the crystal structure turned out to be the instability of the complex. Freshly prepared crystal yield clearly defined spots in a Weissenberg photograph, while these become very diffuse for crystals of a few days old, kept at room temperature. Until 2 days after the preparation, however, the decomposition of the crystals was still small as is demonstrated in figure 3. This figure gives a plot of I_t/I_0 versus time of the reference reflection 600 where I_0 is the intensity of this reflection at time $t=0$, and I_t, (at time is t), measured with a counter technique. Although the intensity decrease of this reflection is not necessarily an exact representation of the intensity dependence of all other reflections, it gives an impression of the decomposition rate of the crystals. From the diagram it appears that the crystals are more or less stable during 2 days after which follows an accelerated decomposition.

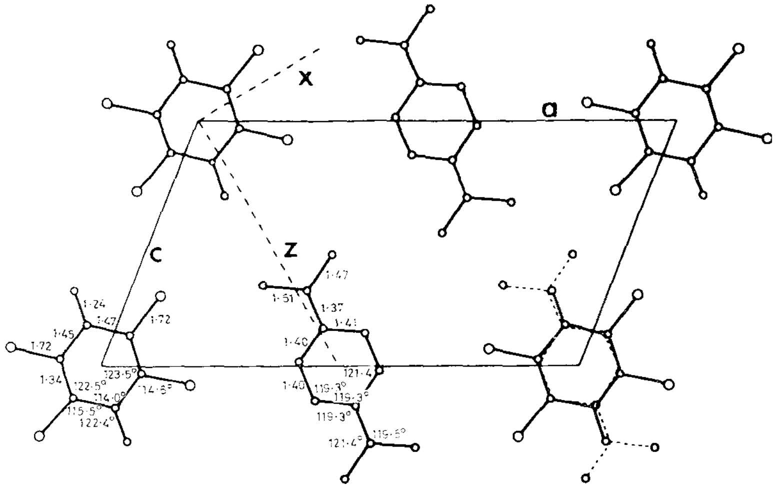

Figure 2. (010) plane of the crystal structure of TMPD-chloranil. The dotted lines are principal axes of the g tensor. This figure is based on preliminary results of J. L. de Boer.

The bond angles and bond lengths of chloranil in the TC complexes agree with those measured on pure chloranil [4]. This suggests that chloranil in TC is molecular. The bond lengths and angles of TMPD in the TC complex also suggest a molecular structure. $TMPD^{+}$ and $TMPD^{2+}$ ions are expected to have a more quinone-like structure as calculated by Monkhorst and Kommandeur [5]. The large thermal parameters observed indicate either a large thermal motion of the atoms or the presence of a minority of TMPD and chloranil ions (up to some 20 per cent) statistically distributed in the crystal. From the x-ray analysis one can conclude to the presence of TMPD and chloranil molecules but not to the absence of TMPD and chloranil ions. The number of ions, however, if present, must be substantially smaller than the number of molecules.

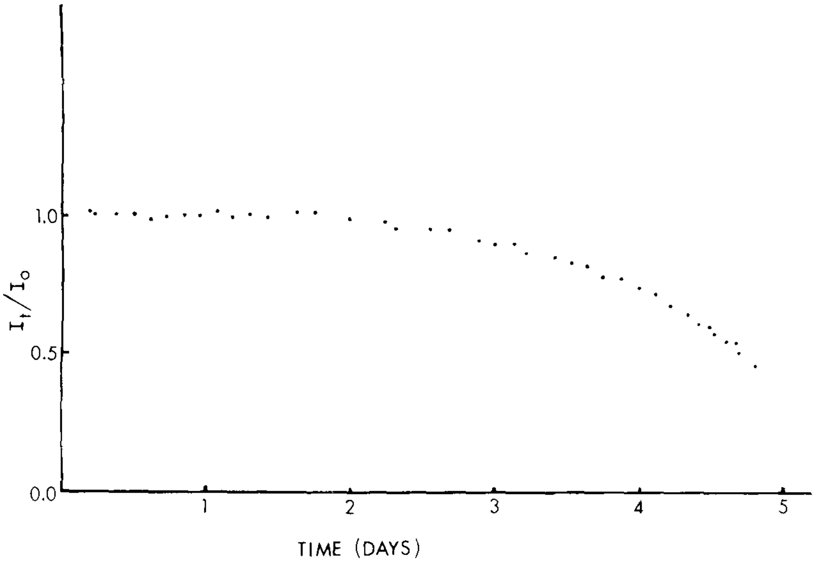

Figure 3. Relative intensity of reference reflection 600 versus time.

Both modifications TC-A and TC-B suffered a phase-transition at low temperatures which was readily seen in *h* 1 *l* Weissenberg photographs taken at 100°K. The splitting of the spots, due to the twinning of the crystals after the phase transition increased with decreasing temperature. The single crystals could be taken through the phase transition repeatedly.

3.2. *The anisotropy of the g value*

TC-A and TC-B both were found to be weakly paramagnetic showing a very narrow anisotropic E.S.R. signal.

Orientation of the needle shaped TC crystals in the magnetic field was easily performed because they have clearly identifiable flat sides, the needle axis coinciding with the crystallographic *b* axis. The orthogonal principal axes x, y and z of the g tensor are shown in figure 2 (dotted lines).

The components of the g tensor are for both TC-A and TC-B:

$$g_{xx}=2\cdot0062\pm0\cdot0002,$$
$$g_{yy}=2\cdot0021\pm0\cdot0002,\quad g_{\mathrm{av}}=2\cdot0052\pm0\cdot0002,$$
$$g_{zz}=2\cdot0072\pm0\cdot0002.$$

The g value of TMPD$^+$ in an alcoholic solution was measured to be 2·0033 and the g value of the chloranil semi-quinone in acetonitrile was 2·0056. This latter value is in agreement with that reported in the literature [6]. Because the average g value, g_{av}, of TC is close to the g value of the chloranil negative ion in solution it is highly likely that the unpaired electron is mainly localized on the chloranil molecule. The large g values in the x and z direction are then due to the large spin–orbit coupling in the chlorine atoms in these directions [7]. In impure crystals, grown from solutions containing excess TMPD two signals can be obtained, one corresponding with the g value of TMPD$^+$ and one with the g value of chloranil (figure 4). In pure crystals, however, no E.S.R. signal near $g=2\cdot003$ is observed, therefore TMPD$^+$ is absent. Electro-neutrality then necessitates the presence of TMPD^{++} ions.

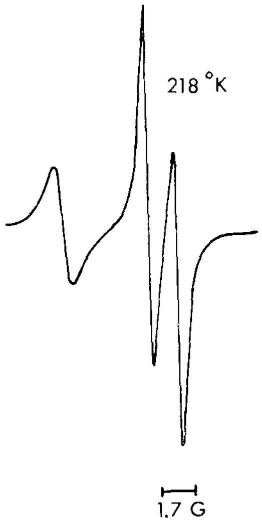

Figure 4. E.S.R. spectrum of an ' impure ' crystal of TMPD-chloranil-B. Except for the split line normal for TC-B at 218°K, a broader line near $g=2\cdot003$ is observed.

Since the g tensor axes do not coincide with the chloranil molecular axes it is likely that the chloranil ions are tilted somewhat in the (010) plane until the O–O axis of chloranil coincides with the z axis (dotted line in figure 2). The number of chloranil ions, however, is so small as to make the tilting unobservable in X-ray analysis. This distortion may be caused by a Coulomb attraction between a chloranil ion and a TMPD^{++} ion positioned on either end of the dotted line representing the z axis in figure 2.

3.3. *Anisotropy of the linewidth*

In addition to the g value anisotropy a remarkable linewidth anisotropy was observed, which was different for TC-A and TC-B crystals. Figure 5 (*a*) gives the E.S.R. signals found for a TC-A crystal at different orientations of the y axis with respect to the external magnetic field. The crystal was rotated about the x axis. Outer spectra correspond with orientations of the magnetic y axis perpendicular and parallel with the external field respectively while the spectrum in the middle corresponds with an orientation where a minimum linewidth was observed. For these crystals the y axis makes an angle of 55° with the magnetic field direction. Figure 5 (*b*) gives the E.S.R. lines for different orientations of the TC-B crystal. The minimum linewidth orientation now corresponds with an angle between the y axis and the magnetic field of 45°. For both crystals the minimum peak to peak linewidth was about 300 mGauss. This narrow line in TC is caused by the long spin–lattice relaxation time (as also evidenced by the rapid saturation) and by the absence of strong broadening effects. The line

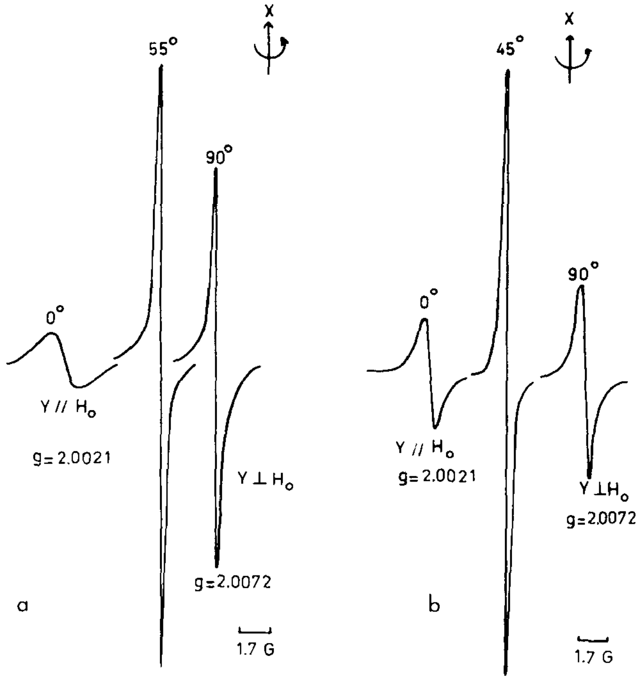

Figure 5. (*a*) E.S.R. signals of a TC-B crystal at three orientations of the y axis with respect to the external magnetic field. (*b*) E.S.R. signals of a TC-A crystal, at three orientations of the y axis with respect to the external magnetic field.

broadening is mainly caused by the anisotropic interaction with the protons and nitrogen nuclei of neighbouring TMPD molecules or ions. The difference in linewidth anisotropy for TC-A and TC-B is possibly due to slightly different orientations of the $N(CH_3)_2$ groups in the neighbourhood of a chloranil ion.

After powdering the crystals the *g* value and the linewidth anisotropy were lost and a symmetrical relatively broad line of about 7 Gauss peak to peak width was observed. Samples powdered under liquid nitrogen still showed some *g* value and linewidth anisotropy but $\frac{1}{2}$ hour after powdering the line was also broadened to about 7 Gauss. This illustrates the instability of powdered samples. The *g* value and linewidth anisotropy of single crystals remained observable until 2 days after the preparation, in agreement with the stability shown by X-ray data.

3.4. *The twinning of the TC complex*

On cooling TC-B crystals below 250°K a splitting of the E.S.R. line was observed. The splitting was anisotropic and increased with decreasing temperature. Figure 6 shows some E.S.R. spectra taken at different temperatures in the orientation of maximum splitting. Because the average components of the *g* tensor did not change significantly in lowering the temperature, the splitting may be due to chloranil ions having slightly different orientations in the crystal lattice. Line splittings are also observed in a few other organic and semi-organic compounds like Wurster's blue perchlorate [8] and some TCNQ complexes [9].

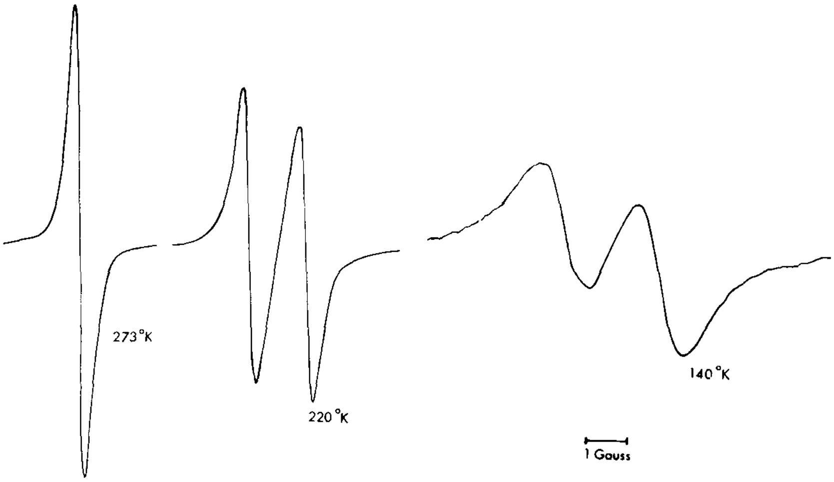

Figure 6. Temperature dependence of the E.S.R. absorption of a crystal of TC-B in the orientation of maximum splitting. The spectra were obtained with different spectrometer gain settings at the different temperatures.

It is well established that in these compounds the splitting is due to electron dipole–dipole interactions. Benderskii *et al.* [10] reported a line splitting in p-phenylene-diamine-chloranil (composition 5 : 3) at temperatures below 150°K. They attributed this splitting also to an electron spin–spin interaction. In this complex, as in TC-B, the splitting is of the order of a few Gauss. We have also observed such a splitting in PPD-chloranil (1 : 1) below 120°K, which was however accompanied by an ' impurity ' signal as is shown in figure 7.

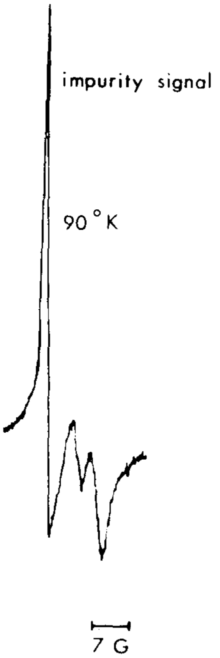

Figure 7. The split E.S.R. signal of p-phenylene-diamine-chloranil (1 : 1) at 90°K accompanied by an impurity signal.

Measurements at 10 and 35 GHz microwave frequency were then performed†. The line splitting in TC-B was found to be proportional to the microwave frequency and was thus due to species having different orientations in the lattice. In order to have two orientations at low temperature the crystal must have suffered a phase transition. From the plot of the line splitting versus temperature (figure 8) it follows that when the temperature is lowered the crystal transforms gradually into the other phase. The angle between the two chloranil ions in the transformed crystal was calculated from the following data. No splitting was observed with the magnetic field in the xy and xz planes. The magnitude of the splitting versus the rotation angle on rotating the crystal about the x axis is plotted in figure 9. The anisotropic g values, g_{xx}, g_{yy} and g_{zz} are independent of temperature. With these data one obtains for the magnitude of the splitting for rotation about the x axis:

$$\Delta g=(g_{xx}-g_{yy})\sin 2\phi^\circ \sin \Delta\phi^\circ, \quad \vartheta'=\vartheta''=90^\circ,$$

where

$$\phi^\circ=\tfrac{1}{2}(\phi'+\phi''), \quad \psi'=\psi''=0^\circ$$

and

$$\Delta\phi^\circ=\tfrac{1}{2}(\phi'-\phi''),$$

ϕ', ϑ', ψ' and ϕ'', ϑ'', ψ'' being the Eulerian angles for the two differently oriented chloranil ions. The maximum splitting, obtained for $\phi=45^\circ$ is 2·2 Gauss giving $\Delta g^{45^\circ}=1\cdot 36\times 10^{-3}$ and $\Delta\phi^\circ=7\cdot 8^\circ$. The solid curve in figure 9 represents a $\sin 2\phi$ function showing that the magnitude of the splitting is indeed proportional to $\sin 2\phi$.

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† Measurements at 35 GHz microwave frequency were performed on the Varian V-4503 E.P.R. spectrometer of the Technical University Twente in Enschede.

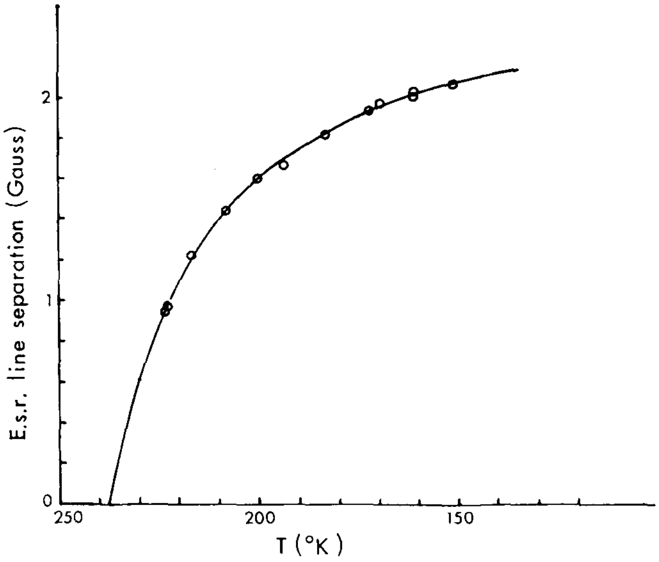

Figure 8. E.S.R. line separation versus temperature for TC-B.

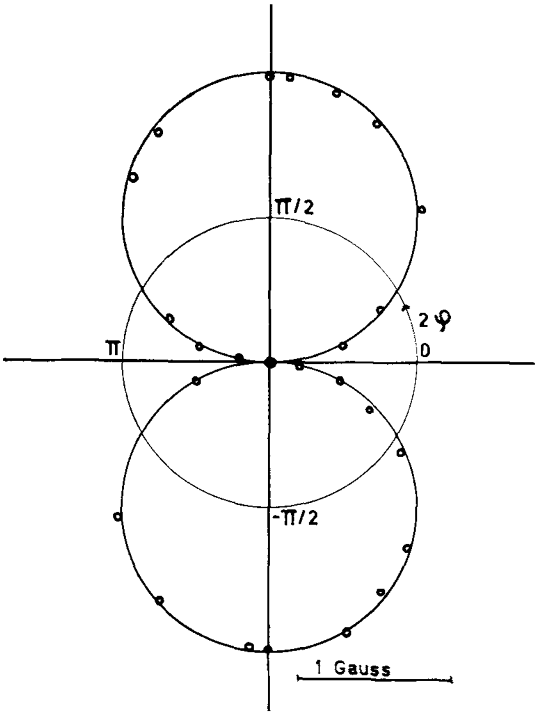

Figure 9. The magnitude of the E.S.R. line splitting versus the angle between the TC-B x axis and the external magnetic field (points). The solid curve represents a polar plot of sin 2ϕ.

From the crystallographic and E.S.R. data it thus follows that the TC-B crystals at low temperatures twin about the magnetic x axis with the chloranil$^-$ ions rotated $+7\cdot8°$ and $-7\cdot8°$ about this axis.

In addition to the splitting the lines were broadened at low temperature. The line broadening could be due to the stopping of the rotational motion of the $N(CH_3)_2$ groups at low temperature. At room temperature the CH_3 groups may perform a hindered rotation as has been evidenced by the observation of a relatively narrow N.M.R. line (about 4 Gauss). The N.M.R. linewidth of a non-rotating CH_3 group is about a factor three larger [11 (*a*)].

E.S.R. signals from TC-A did not show such well resolved splittings. The E.S.R. line remained single at temperatures down to 180°K, then became asymmetrical and showed some evidence for splitting below 140°K. The splitting was badly resolved because at this temperature the lines are broad with respect to the magnitude of the splitting. It thus appears that the TC-A complex also transforms in another phase but as far as E.S.R. measurements are concerned, the transition temperature is much lower for TC-A than for TC-B.

3.5. *Optical absorption spectra*

Well defined absorption spectra of the solid were obtained in two experiments, both giving the same results. Firstly, very small crystals were compressed in KBr, yielding almost completely transparent green pellets from which the absorption spectrum could be measured. Secondly TMPD-chloranil was carefully powdered on a small matted quartz plate. Through the roughness of the surface a substantial amount of powder remains on the quartz plate when it is mounted vertically in the spectrophotometer.

The electronic absorption spectrum of solid TMPD-chloranil is shown in figure 10 (A). This spectrum is in agreement with the single crystal reflection spectra, recently published by Anex and Parkhurst [11 (*b*)], who also give the polarization of the broad band at 10 000 Å. According to their measurements this band is polarized at right angles to the molecular planes, i.e. along the crystal *b* axis (figure 2). The spectra of TC-A and TC-B were qualitatively identical. Also, lowering the temperature to 100°K produced no changes in the spectra. As is shown there are four absorption bands, two in the U.V. region, one near 5 000 Å and a very broad band near 11 000 Å, the latter being a charge-transfer band as evidenced by its polarization. The absorption near 5 000 Å was also observed in solid TMPD-bromanil and in some TMPD complexes with di-halogen substituted quinones [12, 13] and in the low temperature phase of Wurster's blue perchlorate [14, 15]. In the latter this band was ascribed to a charge-transfer modified $TMPD^{2+}$ absorption [15]. In donor–acceptor complexes with donors other than TMPD the 5 000 Å absorption was not observed [11 (*a*)]. Chloranil and its ions have no such low energetic absorptions. Therefore it is likely that the 5 000 Å absorption in TMPD-chloranil is due to the presence of $TMPD^{2+}$ ions. If $TMPD^{2+}$ ions are really present electro-neutrality requires the existence of chloranil ions. As will be shown, the number of paramagnetic mono-negative chloranil ions is less than 1 per cent at room temperature and decreases very strongly with decreasing temperature. The 5 000 Å absorption band, however, does not change with temperature. Therefore, the most important counter ions for $TMPD^{2+}$ are probably the bi-negative chloranil ions. The absorption spectrum of TMPD-chloranil was compared with the spectra of the chloranil

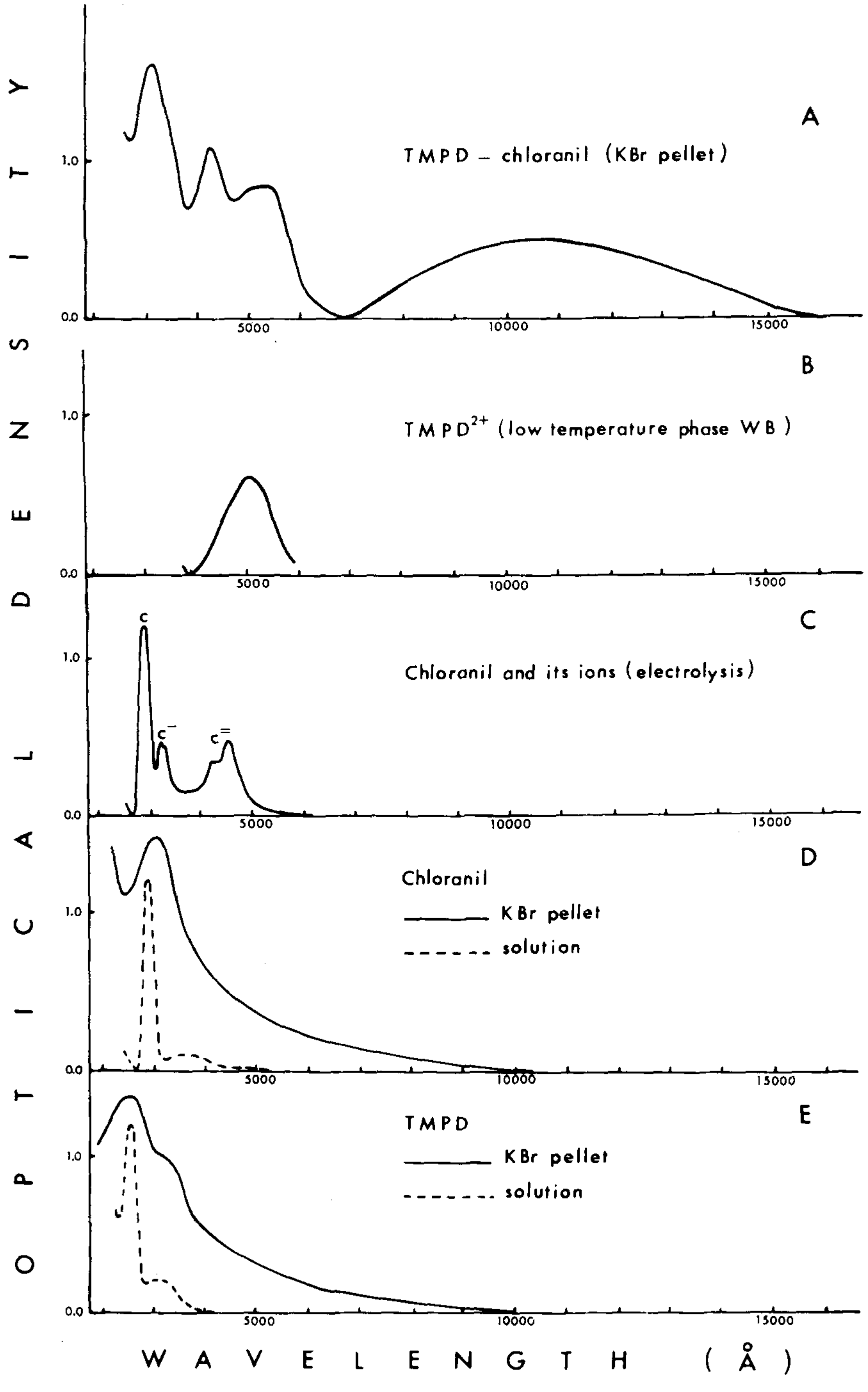

Figure 10. Electronic spectra of the separate entities occurring in TMPD-chloranil (B, C, D and E). Spectrum A can be seen as a superposition of B, C, D and E with an additional charge-transfer band.

mono- and bi-negative ions (figure 10 (C)) prepared electrolytically. For this purpose a solution of chloranil was electrolysed in the E.S.R. cavity, at first yielding a rapidly increasing signal of mono-negative chloranil ions, which then decreased after a few seconds through the formation of bi-negative chloranil ions. This electrolysis was also performed in the spectrophotometer. When the wavelength scale was fixed at 3 200 Å the absorption increased very rapidly as soon as the current was switched on, and then decreased as is typical for an intermediate product (figure 11, curve *a*). The wavelength scale fixed at 4 300 Å yielded a more slowly increasing absorption (figure 11, curve *b*). Thus the 3 200 Å and 4 300 Å band as shown in figure 10 (C) are due to mono-negative and bi-negative chloranil ions, respectively. The decrease of the latter absorption after a few minutes is probably caused by polarization of the electrodes together with diffusion and convection through the solution. Comparison of the chloranil$^{=}$ band with the TC spectrum shows evidence for the presence of bivalent chloranil ions in the complex. Figure 10 (D) shows the spectrum of chloranil pressed in a KBr pellet. In this case the 4 200, 5 000 and 11 000 Å bands are absent and therefore originate in the complex.

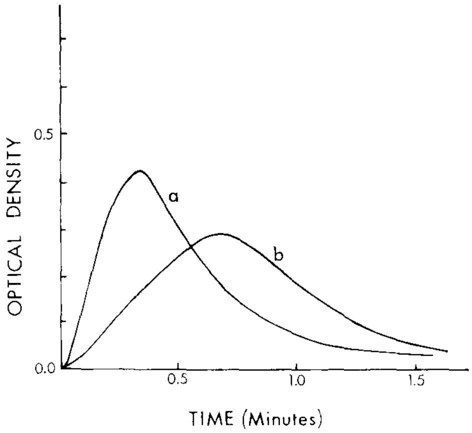

Figure 11. The optical density versus time for the 3200 Å absorption (curve *a*) and the 4300 Å absorption (curve *b*).

Figure 10 (D) also shows the spectrum of chloranil in acetonitrile. Although the absorption band in solution is narrowed with respect to that from the solid, it appears that the shift in its location relative to that in the solid is small. Finally, figure 10 (E) gives the spectrum of TMPD in KBr pellet and in solution. Looking at all spectra of figure 10 the absorption spectrum of TMPD/chloranil can be regarded as the sum of the spectra of the neutral molecules and the bi-valent ions of TMPD and chloranil. Unfortunately, quantitative measurements could not be performed and from the absorption spectra given above it is impossible to make estimates of the number of ions in the solid.

3.6. *Quantitative measurements of the paramagnetic susceptibility*

E.S.R. signal intensity measurements were performed using an accurate integration technique [2]. The percentage chloranil^{-} ions at 25°c with respect to the number of TC pairs was measured to be 0·80 (±0·15) per cent in TC-B. A plot of the logarithm of the number of unpaired electrons versus the reciprocal temperature for TC-A and TC-B is given in figures 12 and 13. As is shown, the chloranil$^-$ ions are thermally accessible species. Since the formation of a doublet state in the TC complex can only originate from an electron transfer and since a TMPD$^+$ signal is not observed the only possible elementary excitations forming chloranil$^-$ ions lead to:

$$C^- --- T^{++} --- C^-.$$

There seems to be no evidence for exchange coupling between the spins of the two chloranil ions, therefore the excited states have a fourfold degeneracy and

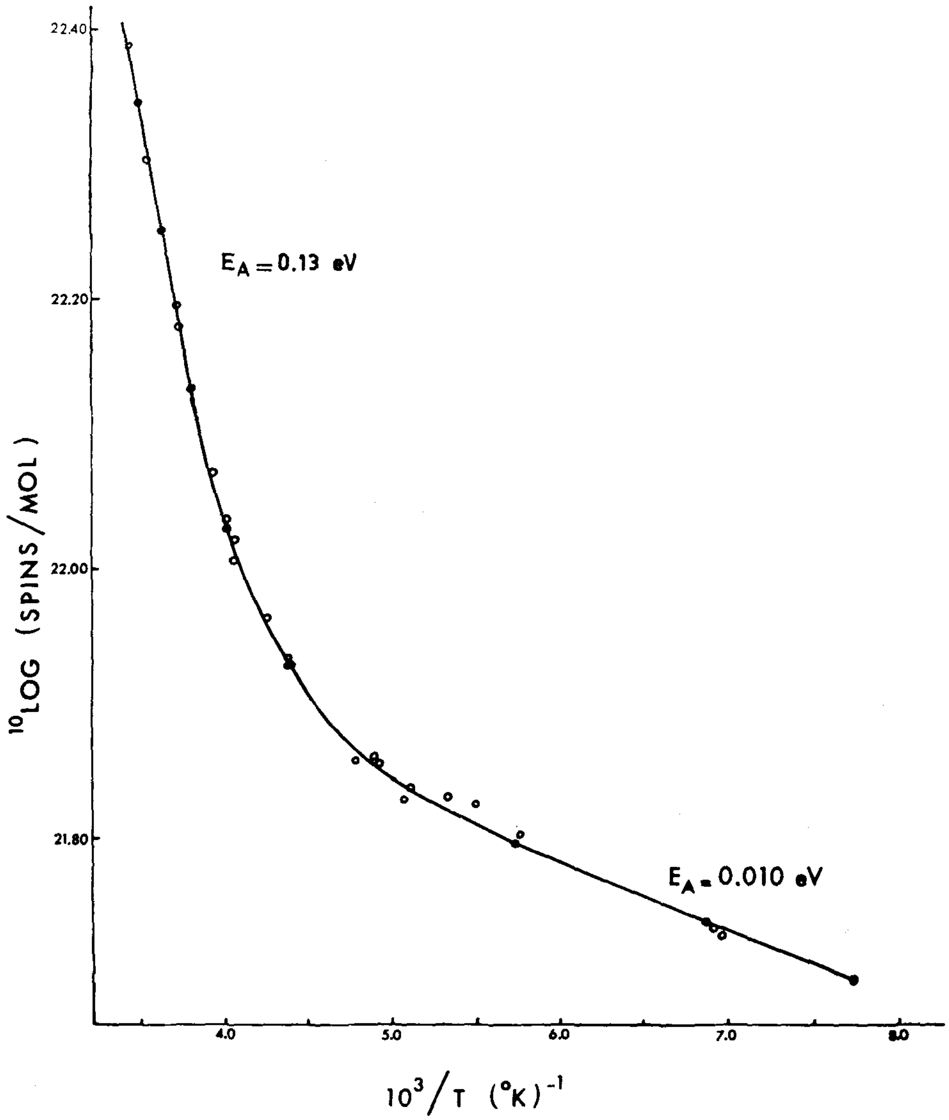

Figure 12. The logarithm of the number of spins versus the reciprocal temperature for TC-A.

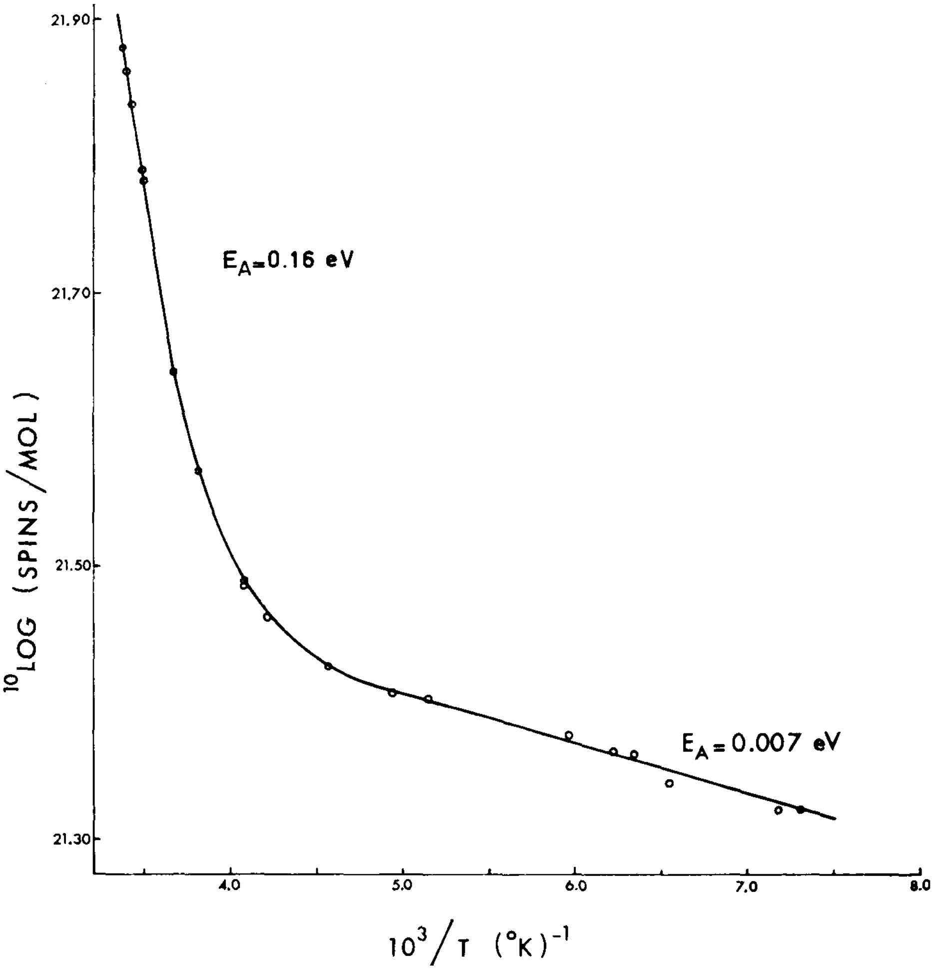

Figure 13. The logarithm of the number of spins versus the reciprocal temperature for TC-B.

for low spin concentration the temperature dependence of the number of chloranil$^-$ ions should obey the relation:

$$\frac{N}{N_0'}=2\cdot\frac{4\exp(-E/kt)}{1+4\exp(-E/kt)},$$

where N is the number of paramagnetic ions and N_0' a constant. The activation energy for the upper curves calculated on this basis is $0\cdot 165\pm 0\cdot 004$ ev for TC-B, and $0\cdot 134\pm 0\cdot 002$ ev for TC-A. From these data the number of chloranil molecules in the ‘ ground state ’ partaking in these excitations are calculated as $N_0'=0\cdot 55\ (\pm 0\cdot 20)\ N_0$ for TC-B and $0\cdot 20\ (\pm 0\cdot 06)\ N_0$ for TC-A, where N_0 is the total number of TC pairs.

Thus, not every TC pair can be thermally excited. This is understandable since part of the lattice sites appear to be occupied by bi-valent chloranil and TMPD ions. Moreover, the environment of all molecules is not identical and the excitation energies will differ. This could also explain the breaks in both curves of figures 12 and 13, although the possibility that the break is due to the phase transition cannot be ruled out. The low activation energy at low temperature cannot be explained by the assumption that doublet state impurities are present, since their susceptibility would follow Curie's law. Also, an impurity concentration of at least 0·1 per cent would be required, which is improbable in the samples used for the paramagnetic intensity measurements. Furthermore, crystals can be grown, in which two E.S.R. signals can be detected at low temperatures, one with the g value of 2·0033 (TMPD$^+$) and one with $g = 2{\cdot}0052$ (chloranil$^-$). The TMPD$^+$ ion gives a non-temperature activated signal, thus providing an internal standard for the chloranil$^-$ E.S.R. intensity at low temperatures. Comparison of both signals shows the chloranil$^-$ absorption still to be decreasing even below 240°K, where the breaks in the exponential curves occur. The TMPD$^+$ ions are probably misfits occurring at sites, where the donation of another electron becomes impossible. This is in accordance with the fact that the TMPD$^+$ concentration increases when the crystals are prepared at a higher temperature. All other measurements reported here were performed on crystals free from these defects.

3.7. *Electrical conductivity*

In lattices of species having mixed valences, like TMPD-chloranil where at room temperature there are neutral molecules and bivalent ions of TMPD and chloranil as well as chloranil mono-negative ions, one might expect semiconductivity. Such a conductivity was indeed observed. The room temperature resistivity was measured to be 500 Ω cm^{-1}. A plot of the logarithm of the conductivity versus $1/T$ is shown in figure 14 (TC-A) and figure 15 (TC-B). It is most likely that the break in the curve for TC-B is due to the phase transition. The room temperature resistivity and activation energy were almost equal for both modifications.

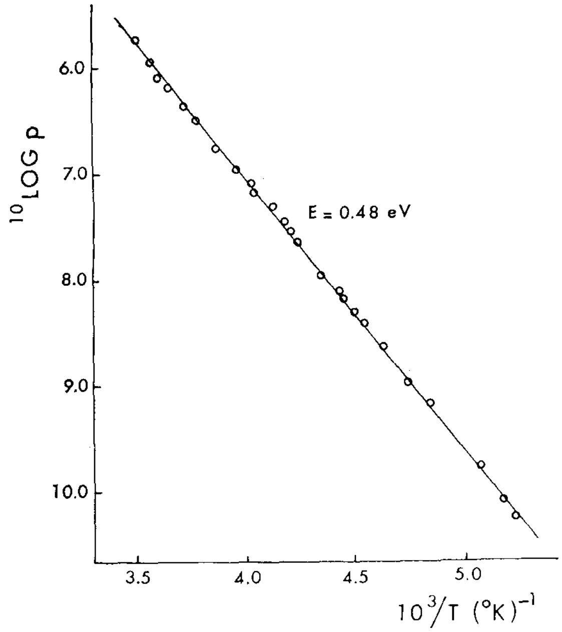

Figure 14. The logarithm of the conductivity versus the reciprocal temperature for TC-A.

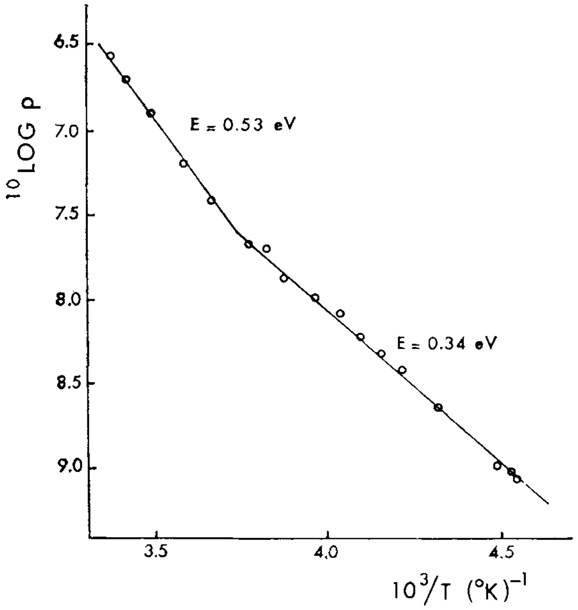

Figure 15. The logarithm of the conductivity versus the reciprocal temperature for TC-B.

Previously, some authors have reported much lower conductivities [16, 17]. Our measurements were, however, made on single crystals and after the crystals deteriorate the conductivity decreases sharply.

4. Discussion

The experimental results reported in the previous sections all point to a lattice composed of molecules and bivalent ions. Specifically the x-ray data suggest the lattice to be molecular, the absorption spectra show evidence for the presence of bivalent ions, while the E.S.R. measurements show chloranil mono-negative ions to be present. For a molionic lattice to be stable with respect to the completely ionic and the completely molecular lattice a relatively high value of $I-A$ (the difference between the ionization potential of the donor and electron affinity of the acceptor), and a high polarization energy are required. For earlier calculations on a molionic lattice, we have assumed the formation of mono-negative and mono-positive ions [18]. There is no objection to carrying this calculation further to the bi-valent ions as seems to be the case in TMPD-chloranil. Indeed, the polarization energy due to a bi-valent ion, as well as the total Madelung energy, will be increased by a factor of four which will suffice to offset the extra energy required for the double ionization. Thus the TMPD-chloranil system appears to be a good example of a molionic lattice.

From the length of the *b* axis it follows that the intermolecular distance in a stack of TMPD-chloranil molecules is only 3·28 Å, which is considerably smaller than the normal van der Waals distance of about 3·40 Å, as found for instance in the N-N-dimethylaniline-chloranil complex [19]. This short distance may be caused by the bi-valent ions. These will exert a force on each other, thus compressing the whole chain. An order of magnitude estimate of this effect can be obtained as follows: the force two bi-valent ions exert on each other will be $F=4e^2/r^2$, where r is the ion separation in a TC chain. This force can be converted into a pressure by dividing through the surface area (S) of a stack in the *ac* plane. Thus $p=4e^2/Sr^2$. With the fractional decrease of the intermolecular separation:

$$\frac{dl}{l}=28\times10^{-7}p-45\times10^{-12}p^2,$$

as found between the layers in graphite [20], and $S\simeq20$ Å^2, and

$$dl/l=0\cdot115/3\cdot40=0\cdot034$$

we find a distance between two bivalent ions of 16·7 Å, which being about a fivefold of the intermolecular separation, means a bivalent ion concentration per chain of 20 per cent. This fraction, although high, may be reasonable. If the contraction in the chain is explained on this basis we arrive at the following order in the chains:

$D^{++}ADADA^{=}DADAD^{++}ADADA^{=}$ for this donor(D)-acceptor(A)complex.

Another interaction playing a role may be the charge-transfer interaction, but it is hard to estimate its effect. The charge transfer does lead to a low lying electronic state, which is observed in the optical spectra, as discussed before. From the E.S.R. measurements we conclude to the existence of two types of TMPD-chloranil complexes, although they are stoichiometrically, crystallographically and optically completely identical. The only difference is found in the anisotropy of the E.S.R. linewidths of the thermally generated chloranil ions. An explanation may be found in the bivalent ions. One can think of various ways of ordering these ions. If they occur at say every fifth site in a chain, then one can still shift the chains along each other and thus obtain different ' super ' lattices. Both the number and the sites of the chloranil molecules partaking in the excitation to chloranil ions may be effected by this ordering, since this will depend critically on the potentials in the lattice.

In conclusion it can be said that the properties of the TMPD-chloranil complex such as its spectrum, its structure, its magnetic properties and its conductivity can be explained on the model of a molionic lattice, containing neutral molecules as well as bi-valent ions, while monovalent chloranil ions are excited thermally.

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