On Hyperfine and Fine Structure of Excited Charge-Transfer-Complexes

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The charge-transfer (CT)-crystal naphthalene (N)-1,2,4,5-tetracyanobenzene (TCNB) was doped with various guest acceptors. CT-complexes of these acceptors with N are formed acting as a triplet energy trap in the crystal. This provides a method to investigate oriented CT-complexes ESR-spectroscopically. In favorable cases the hyperfine structure (Hfs) in the ESR-spectra can be resolved and interpreted. The Hfs of the complexes N-hexacyanobenzene and N-pentacyano-toluene show that in the crystalline complex the triplet electrons are distributed over no more than two molecules. This finding suggests a strong exciton-phonon-coupling which causes a breakdown of the inversion symmetry upon excitation. The spectra of naphthalene-s-trinitrobenzene (TNB) yield the spin density on the three equivalent protons of TNB and demonstrate that the triplet electrons are also equally distributed over the three nitrogen atoms.

As further systems, complexes of extremely large CT-character, c_1^2, in the triplet state are studied (e. g. N-chloranil).

The data obtained from the measurements of the Hfs- and of the zero-field-splitting (ZFS)-parameters are compared, proving that previous models and approximations in deriving c_1^2 are essentially correct. It is also shown that the ZFS-parameter D $(A^+ D^+)$ of the hypothetical purely ionic state is negative and for different complexes its value is very close to that obtained in earlier theoretical calculations (-0.027 cm^{-1}).

I. Introduction

Considerable effort and progress has been made in understanding the excited states of the so-called weak charge-transfer (CT)-complexes which are non-ionic in their ground states while in their lowest excited singlet states they contain considerable ionic contributions. However there is still some uncertainty about the nature of the lowest excited triplet states in these complexes. The problems connected with the investigation of these states arise mainly from the fact that the phosphorescence spectra are generally very broad and difficult to interpret. Therefore, the most important tool for a study of these states has become ESR-spectroscopy [1-4] and related methodologies (e. g. ODMR) [5, 6] that measure the dipolar interaction of the triplet electrons as characterized by the ZFS-parameters, D and E. Measurements of these parameters indeed show that, depending on the kind of donor and acceptor, there exists a variety of triplet states whose amount of charge delocalization (CT-character) differs between 5% and 80%.

The feasibility of applying the ZFS-parameters in determining the CT-character is based on the fact that the dipolar interaction strongly depends on the

distance between the two unpaired electron spins. Therefore, the D-value is reduced significantly when the triplet electrons are delocalized over more than one molecule. However, serious difficulties arise in determining the electron distribution in CT-triplet states from the ZFS-parameters. The difficulties arise from the fact that

a) the relation between the CT-character and the ZFS-parameters was derived using a model that could not be tested by any other method,

b) there existed no other equally accurate method to furnish a comparative study of triplet states,

c) the D-value of the purely ionic CT-state, which is necessary for an exact treatment, is not available experimentally.

To some extent these difficulties have been overcome, since in the last year we have been able to resolve the hyperfine structure in the triplet ESR-spectra of CT-complexes [7, 8]. As these measurements yield the electron density near each interacting nucleus, we have obtained another independent method to investigate CT-complexes, thus enabling us to examine the existing models and their neglections.

The previous experiments were carried out by doping the CT-crystal naphthalene-1,2,4,5-tetra-cyanobenzene (TCNB) with another donor [4, 7, 8]. The guest donor forms a CT-complex with the host acceptor TCNB acting as a triplet energy trap in the

crystal. After optical population of the trap, triplet states of CT-complexes in fixed and well defined configurations could be studied.

In this publication we report about measurements performed on the CT-crystal naphthalene (N)-TCNB doped with different guest acceptors. The experiments were carried out mainly to answer the following three questions:

(1) Are (in a crystal) the triplet electrons of a CT-complex distributed over two or over three molecules (see III. 1.)?

(2) How can one describe the triplet state of CT-complexes with acceptors other than TCNB? We will subsequently report about studies of complexes with acceptors having a higher electron affinity than TCNB.

(3) How large are the Hfs-coupling constants of the acceptor nuclei in a CT-complex? Because we can not observe the small coupling constants of TCNB, we have extended our studies to complexes where we can observe the couplings of the acceptor nuclei.

We should also mention that further data on the hyperfine structure of CT-complexes are of interest in light of recent experiments showing a hyperfine modulated ion recombination in solution [9].

II. Experimental

TCNB was purified by recrystallization and sublimation. Naphthalene was zone-refined. The dopands were used without further purification. Hexacyanobenzene (HCNB) and pentacyanotoluene were a gift from Dr. N. Karl of the Kristallabor Stuttgart.

ESR-measurements were made with a Bruker X-band spectrometer equipped with an NMR-magnetometer and a variable temperature unit.

Optical excitation was achieved with a high pressure mercury lamp using suitable filters. The small signal-to-noise ratio in some of the spectra is due to the poor quality of the dewars provided by the manufacturer. The spectra were simulated using a Bruker program and a Bruker BNC 12 computer.

The host crystal used was naphthalene-d_8 (or-h_8)-TCNB. It consists of stacks of alternating donor and acceptor molecules with the molecular planes perpendicular to the stack axis [10]. The crystals grow needle-like, the needle axis being the stack axis. Thus it is quite easy to find the canonical orientations of the molecules in an ESR-experiment. On rotating the magnetic field in the plane perpendicu-

lar to the needle axis, the extrema of the resonance field strength yield the two canonical in plane orientations (x and y). The orientation perpendicular to the molecular plane (z) is obtained from measurements with the magnetic field parallel to the needle axis.

It can be shown that within an accuracy of $1°$ a guest donor assumes the same orientation as the host donor [11]. An analogous behavior may also be expected from the guest acceptors used in our experiments. For the interpretation of the spectra we only needed to make the trivial assumption that due to the dense packing along the stack axis the molecular planes of guest and host molecules are mutually parallel. The good resolution in the ESR-spectra shows also that the guest acceptors are oriented very homogeneously in the CT-crystal.

III. Results and Discussion

III.1. The Complex Naphthalene-hexacyanobenzene (N-HCNB)

Having a much larger electron affinity than TCNB, HCNB is assumed to form with N a CT-complex that is energetically lower in its lowest excited states than N-TCNB [12]. Thus the excited states of N-HCNB act as energy traps in the crystal N-TCNB. The observed ESR-spectra of the HCNB doped CT-crystal are, therefore, ascribed to the N-HCNB complex. The ZFS-parameters are given in Table 1.

Table 1. ZFS-parameters D, E and $D^* = (D^2 + 3 E^2)^{1/2}$ of the CT-complexes studied in this work and CT-character c_1^2 derived from Eq. (1), using $D(A^- D^+) = 0.027 \text{ cm}^{-1}$.

Complex	D [cm^{-1}]	E [cm^{-1}]	D^* [cm^{-1}]	c_1^2 (D)
N-HCNB	± 0.066	∓ 0.011	0.069	0.27
N-HCNB (in solution)			0.063	≈ 0.3
N-Penta-cyanotoluene	± 0.0667	∓ 0.0114	0.0696	0.26
N-TNB	± 0.0670	∓ 0.0134	0.0709	≈ 0.5
N-chloranil	± 0.0081	∓ 0.0011	0.0083	0.76
N-riboflavin	± 0.0405	∓ 0.0238	0.0577	0.1
N-FAD	± 0.0646	∓ 0.0113	0.0675	0.05
coronene-TCNB	± 0.0484	∓ 0.0033	0.0487	0.39
hexamethyl-benzene-TCNB	± 0.0110	∓ 0.0087	0.0187	0.75

Figure 1 shows the ESR-lines for the three canonical orientations. For the two in-plane orientations (Fig. 1 a and b) one observes a well resolved hyperfine structure which is undoubtedly due to the
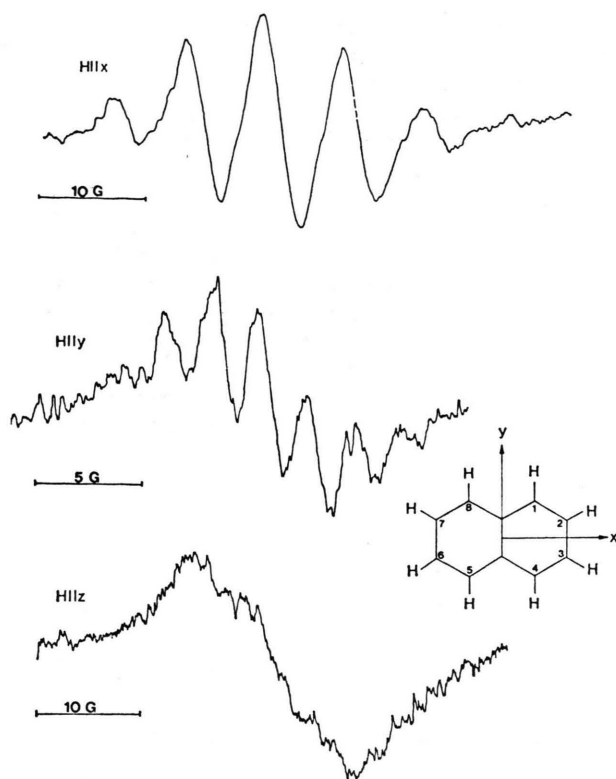
Fig. 1. Triplet-ESR-lines of the complex N-h_8-HCNB for the three canonical orientations. $T = 140$ K, $\nu = 9190$ MHz, $H_0 = 3805$ G ($H \parallel x$), $H_0 = 3430$ G ($H \parallel y$), or $H_0 = 3982$ G ($H \parallel z$).

naphthalene protons *. It was shown recently (see also III.5) that, due to complex formation, all the coupling constants of a molecule in its triplet state are reduced by the same ratio [7]. Knowing this the interpretation of the Hfs is analogous to the one done by Hutchison and Mangum [14] and by Schwoerer and Wolf [15] for the uncomplexed naphthalene molecule.

For the orientation $H \parallel x$ these authors observe 5 equidistant lines with an intensity ratio of about 1:4:6:4:1 and a splitting of 8.05 Gauß. This is due to the 4 equivalent α-protons on positions 1, 4, 5 and 8 (c. f. Figure 1). The couplings of the residual (β-)protons are too small to be resolved.

This is very similar to our experimental findings for the complex N-HCNB. The five equidistant lines in Fig. 1a have an intensity ratio of 1.2 : 4.6 : 6.0 :

* It is well known that the coupling constants of the protons as well as the nitrogen atoms of the TCNB-anion are smaller than 1.2 Gauß [13]. Consequently, these couplings as well as those of the nitrogen atoms of HCNB are not expected to be resolved in our spectra.

4.3 : 1.2. Their distance is reduced to 7.0 Gauß. From this reduction the CT-character, c_1^2, is calculated according to Equation (4). A value of $c_1^2 = 26\%$ is obtained.

A similar explanation holds for the spectrum in Fig. 1b, taken for the magnetic field parallel to the short in-plane axis y of naphthalene. It shows 7 lines with intensity ratios of 0.8 : 2.5 : 5.1 : 7.0 : 5.8 : 2.8 : 0.5 and with (within our experimental accuracy) an equal spacing of 2.05 Gauß. For this orientation of the uncomplexed donor, one observes the couplings of all 8 naphthalene protons. The most accurate data of the coupling constants are those obtained by ENDOR-experiments [16] yielding 2.6 Gauß for the β-protons and 2.3 Gauß for the α-protons. We simulated the spectra using the same ratio of the coupling constants of α- and β-protons for the complex. The resulting intensity ratio in the computed spectra is 0.5 : 2.3 : 5.4 : 7.0 : 5.4 : 2.3 : 0.5. This is very close to the experimental results, proving again that the Hfs is, indeed, due to the α- and the β-protons of naphthalene. We obtained coupling constants of 1.9 Gauß and 2.2 Gauß for α- and β-protons, respectively, corresponding to a CT-character of 33% [from Equation (4)].

The spectra just interpreted are also pertinent to answer another interesting question. Since, in the crystal, the acceptor is sandwiched between two donors, does the electron transfer (in the triplet state) occur from one molecule or from two naphthalene molecules? This question cannot be answered by investigating the ZFS-parameters of the complex. However, an inspection of the hyperfine structure yields an unequivocal answer which is subsequently shown.

With respect to the couplings, the above question reduces to: Is the observed Hfs due to the 8 protons of one naphthalene molecule with the coupling constants A_{xx}^i ($i = 1, \ldots, 8$), or is the Hfs due to the 16 protons of 2 donors with the coupling constants $\frac{1}{2} A_{xx}^i$ ($i = 1, \ldots, 16$)? There are two facts which show that the triplet electrons of the complex are distributed over only one donor.

1) The number of observed lines and their intensity ratios can be interpreted only on the basis of the protons of only one naphthalene molecule.

2) Upon complex formation the coupling constants of the donor (and the acceptor) cannot become larger [7, 8]. The assumption of an electron distribution over two donors would, therefore, lead

to coupling constants larger than $2 \cdot 7.0 = 14$ Gauß for the uncomplexed donor for the orientation $H \| x$. This is in contrast to the results obtained in the literature for the naphthalene triplet state [14-16].

There may be two reasons for the observed breakdown of the inversion symmetry in the triplet state of the crystalline CT-complex.

(1) The experiments are carried out on traps which are by themselves distortions of the lattice. The HCNB molecule replacing TCNB may assume a position, slightly different from that of the host, where the interaction with one donor is larger than with the other neighboring donor.

However the distortion on doping is not supposed to be very efficient since the shapes of the guest and the host acceptor are very similar. Furthermore, the observation of a well resolved Hfs demonstrates that the crystals are not seriously distorted by the dopand.

(2) A more probable explanation for the breakdown in the inversion symmetry is that the exciton-phonon interaction tends to stabilize an asymmetric triplet state. A possible explanation for this is that, once the acceptor has moved closer to one donor, the Coulomb forces in the CT-triplet state attract it even more to this side and thus favour the asymmetric position. Since the efficiency of this interaction depends on temperature [17], we have to stress that our results hold in the temperature range between 90 K and 170 K, where we were able to resolve the Hfs. However, we cannot rule out that at higher temperatures the triplet electrons might be distributed over more than two molecules.

These experiments are also relevant with respect to the discussion concerning exciton motion in CT-crystals, since part of the primary processes in exciton hopping might also be observable in the trapped system. A fast jump of a hole from the donor on one side of the (guest) acceptor, to the other side would consequently lead to contributions of two donors to the Hfs in the ESR-lines. This jumping process has to be considered if exciton motion along the donor-acceptor chain occurs via a successive change in the dipole moment according to $D^+ A^- D A \xleftarrow{1} D A^- D^+ A \longleftrightarrow D A D^+ A^-$ as is discussed for singlet excitons [18]. Therefore, we conclude that either exciton motion (and therefore process 1) are very slow in this crystal or they occur without a change in dipole moment according to

$D^+ A^- D A \longleftrightarrow D A D^+ A^-$. The latter process, involving simultaneously the second acceptor molecule, would not be observable in our experiment.

Finally, we should point to one unresolved problem connected with the comparison of the CT-characters of the guest and host complexes. The CT-character of the host, measured in solution, can be estimated close to 50% [3]. However, the ZFS- as well as the Hfs-parameters of N-HCNB consistently yield a CT-character near 30% (c. f. Table 2). This is surprising since the larger electron affinity of HCNB (2.54 eV compared to 2.21 eV of TCNB) [19] is supposed to cause a more ionic complex triplet state [20]. On the other hand, as expected from the larger electron affinity, N-HCNB forms a trap in the crystal, proving its lower triplet energy as compared to that of N-TCNB.

One might argue that the ESR-signal is due to an impurity in the crystal. This possibility is not considered very probable, because in solutions containing N and HCNB, we have observed a $\Delta m = 2$-ESR-signal ascribed to the complex N-HCNB. But even so, the Hfs in the ESR-spectra clearly shows that the triplet electrons are mainly localized on the naphthalene molecule. Therefore, an impurity could only be an acceptor and it would still be necessary to explain why the CT-complex of N with an impurity acceptor has a lower triplet energy but also a lower CT-character.

On the other hand, one may speculate that besides the purely electronic properties of the complexing molecules, their steric properties are also important in determining the ionicity and the energies of the excited states of the complexes. We should mention that a similar behavior is also observed for the complex of N with another stronger acceptor, s-trinitrobenzene, which is discussed in the next paragraph. This suggests that in the triplet state the interaction of N with acceptors of more than twofold symmetry is not very favorable.

III.2. The Complex Naphthalene-pentacyanotoluene (PCNT)

The ZFS-parameters of the complex N-pentacyanotoluene, obtained on doping the host crystal N-h_8-TCNB with PCNT are quite similar to those obtained for the complex N-HCNB (c. f. Table 1). The Hfs in the spectra could also be well resolved for the two canonical in-plane orientations and is — analogous to the procedure in III.1. — interpreted

on the basis of the protons of one naphthalene molecule. For $H \parallel x$ one observes 5 equidistant lines with a coupling constant of 7.0 Gauß, corresponding to a CT-character of 26%. For $H \parallel y$ one obtains 7 equidistant lines with a splitting of 2.15 Gauß, yielding a CT-character of 26%, too.

III.3. The Complex Naphthalene-s-trinitrobenzene (TNB)

TNB is also an acceptor of higher electron affinity than TCNB [21] and, therefore, one may assume that the complex N-TNB forms a trap in the TNB doped CT-crystal. We have observed the ESR-spectra of one kind of trap, described by the ZFS-parameters $D = \pm 0.0670 \text{ cm}^{-1}$; $E = \mp 0.0134 \text{ cm}^{-1}$; $D^* = 0.0709 \text{ cm}^{-1}$.

It is evident from the discussion of the Hfs in the spectra that the ESR-lines are, indeed, due to a CT-complex of N with TNB. The ZFS-values are rather large for a CT-complex, indicating a triplet state of

low polarity. This surprising behavior was already discussed in paragraph III.1).

The use of the acceptor TNB has the advantage that, judged from the ESR-spectra of the TNB-anion, one expects to observe the rather large couplings of the acceptor nuclei in the complex [22]. This was not possible with all the other acceptors used. But this acceptor has the disadvantage that basically nothing is known about its lowest excited triplet state: neither the triplet energy, nor the ZFS-parameters, nor the Hfs-parameters. Therefore, a quantitative evaluation of the CT-character is not possible.

Figure 2 a shows the ESR-spectrum of the complex N-d_8-TNB for the one orientation that we could clearly resolve. It contains 25 lines that are due to the nitrogen atoms as well as the protons of the TNB-molecule. We simulated the spectrum using Lorentzian line shapes of the components and obtained as best fit the spectrum in Figure 2 b. The agreement between calculation and experiment is even better if one compares the stick diagrams corresponding to Figs. 2 a and 2 b [**]. This indicates that the coupling constants thus determined are essentially correct, the main error in the calculation is very probably the result of using an incorrect line shape. The coupling constants are $a(\text{N}_3) = 4.97 \text{ G}$, $a(\text{N}_1) = a(\text{N}_5) = 3.65 \text{ G}$, $a(\text{H}_6) = 2.75 \text{ G}$, $a(\text{H}_2) = a(\text{H}_4) = 1.36 \text{ G}$.

This result is pertinent to one question associated with the interpretation of the Hfs in CT-triplet states: How much does the proximity of the donor in the CT-complex distort the electron distribution on the acceptor?

The TNB anion seems to be very sensitive to these distortions since, depending on the environment, its ESR-spectrum is ordered into one of two distinct groups [22] (classes):

(1) The electron distribution is not distorted. The ESR-spectrum consists of couplings of three equivalent nitrogen atoms and three equivalent protons.

(2) The electron distribution is strongly distorted. The electron density on two of the nitrogen atoms is zero with the three protons still equivalent. This situation is observed in solutions containing group
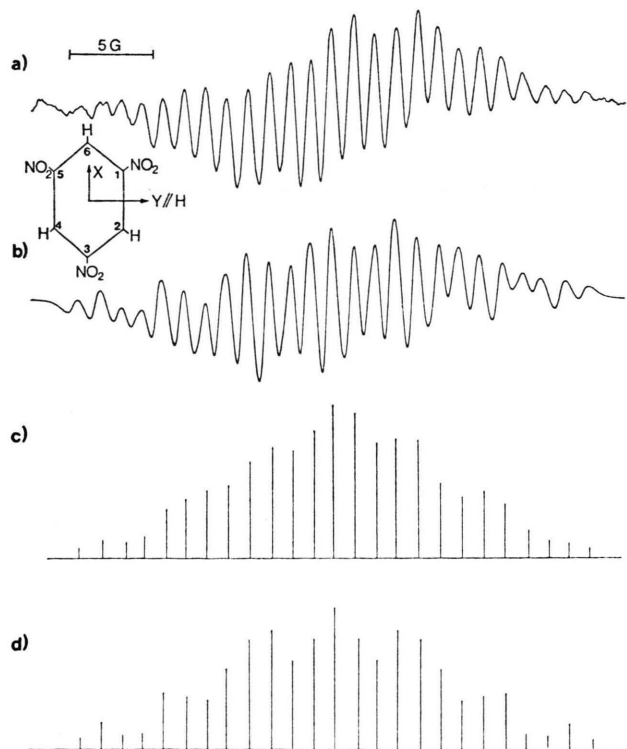
Fig. 2. Triplet-ESR-lines of the complex N-d_8-TNB for the orientation $H \parallel y$, Fig. 2 a: Experimental spectrum, $H_0 = 3428 \text{ G}$, $\nu = 9184 \text{ MHz}$, $T = 150 \text{ K}$. Fig. 2 b: Calculated spectrum using the parameters given in the text. Figures 2 c and 2 d show the stick diagrams corresponding to the experimental and the calculated spectrum, respectively.

[**] The stick diagrams in Figs. 2 c and 2 d consistently reveal the existence of seven groups of lines. This is due to the three nitrogen nuclei. The further splitting within these groups is brought about by the TNB-protons.

II cations and is essentially understood as follows: The small cations are bound to one NO_2-group, thereby attracting the excess electron of the anion to this part of the molecule.

As the classification is very sharp, it is quite obvious that in our case the complex belongs to the first class. The deviations in the coupling constants on different nuclei are sure to be due to the anisotropy of the Hfs-constants. This proves that, even in such a sensitive case, the acceptor is not affected by the donor.

This was implicitly assumed in deriving the CT-character from the Hfs-constants and is justified by this experiment [see also IV(3)].

Furthermore one can derive the spin density, ϱ, on the carbon atoms next to the (equivalent) protons of TNB [23] and obtain $\varrho = 0.077$. Unfortunately, the relationship between the spin density and the nitrogen coupling constant is not yet clear. Therefore, the spin density on the residual nuclei of TNB cannot be calculated.

III.4. The Complex Naphthalene-chloranil

The homogeneous orientation of CT-complexes also permits the investigation of system with very short triplet lifetimes. An example of this is the complex N-h_8-chloranil, studied on doping the crystal N-TCNB with chloranil. Figure 3 shows the ESR-lines of the complex for two canonical orientations. For each orientation one observes an ab-

Fig. 3. Triplet-ESR-lines of the complex N-h_8-chloranil for the two canonical in-plane orientations. $T = 165$ K, $H_0 = 3270$ G, $\nu = 9164$ MHz. Since the radical line in the centre is absorptive, one clearly observes the high-field line for $H\|y$ and the low-field line for $H\|x$ to be emissive. The Hfs is not resolvable.

sorption and an emission line of about equal intensity (without resolved Hfs), indicative of optical spin polarization. This requires a very short triplet lifetime ($\lesssim 1$ ms)[24, 25] so that the Boltzmann equilibrium is not established among the triplet sublevels.

The corresponding ZFS-parameters are $D = \pm 0.0081$ cm^{-1}, $E = \mp 0.0011$ cm^{-1}, $D^* = 0.0083$ cm^{-1}, the smallest (to our knowledge) that have been reported for weak CT-complexes. To calculate the CT-character, we have to use the D-value of chloranil $D = +0.1176$[26] and obtain $c_1^2 = 76\%$ (c. f. Table 1). This shows that the triplet state is extremely polar.

III.5. CT-stacks as Host Matrices for Biomolecules

We also doped the CT-crystal with biologically relevant molecules, e. g. riboflavin, that are supposed to have a low triplet energy. The optical spectra show that these molecules are indeed incorporated in the crystal. The ESR-spectra even reveal a resolved Hfs[11]. The resolution of the Hfs, however, was not good enough for an interpretation. On the other hand, this also proves that these guest molecules are oriented homogeneously, although their shapes are quite different from that of the hosts. This suggests that CT-crystals are suitable matrices to study the ESR-spectra of large oriented molecules. The ZFS-parameters obtained on doping with riboflavin and flavin-adenosine dinucleotide are almost identical to those of the guest acceptors[27], indicating an only slight interaction with the host donor, naphthalene.

Another very large dopand, which is also soluble in the crystal, is the donor coronene. The triplet state of this guest complex is expected to be, to a large extent, a locally excited donor state, since coronene has a very low triplet energy[28]. This is also found for the complex coronene-tetrachlophthalic anhydride in solution[29]. However, as is also found in many other systems[4], in the crystal the ZFS-parameters are considerably reduced. Furthermore, it is observed that in the complex the sixfold symmetry of coronene is not present ($E \neq 0$). This is ascribed to the interaction with the acceptor.

Table 1 summarizes the ZFS-parameters and the corresponding CT-characters c_1^2 of the complexes studied in this work.
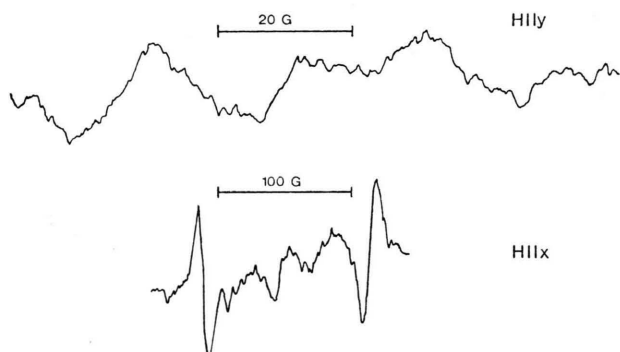
IV. Comparison of the Results Obtained from the Measurements of the ZFS- as well as the Hfs-Parameters

Usually the triplet state of a CT-complex is described as a superposition of a CT-state (where one electron is transferred from the donor to the acceptor) and locally excited donor and acceptor triplet states. One obtains the following relations for the ZFS-parameters, D and E [1-4], and for one diagonal element, A_{ii} [7,8], of the Hfs-tensor of the complex:

$$D_{exp} = c_1^2 D(A^- D^+) + (1 - c_1^2) D_{loc}, \qquad (1)$$

$$A_{ii}(exp) = c_1^2 A_{ii}(A^- D^+) + (1 - c_1^2) A_{ii}(loc) \qquad (2)$$

$D(A^- D^+)$, $A_{ii}(A^- D^+)$ are the corresponding parameters of the CT-state. D_{loc}, $A_{ii}(loc)$ are the values of the lowest excited triplet state of either the donor or the acceptor, whichever is lower in energy.

The advantage in measuring the Hfs-parameters to prove the model is mainly based on the fact that there exist $3 N$ Eq. (2) where N is the number of nuclei interacting with the triplet electrons. For those complexes, which will be subsequently discussed, we could resolve only the couplings of the donor protons. Therefore, if the lowest locally excited state is that of the acceptors, the interaction with the donor protons accurs solely in the CT-state and Eq. (2) reduces to

$$A_{ii}(exp) = c_1^2 A_{ii}(A^- D^+). \qquad (3)$$

In that case one is able to measure the electron distribution in the CT-state directly [8]. This is a great benefit since it is this hypothetical state that causes most of the problems in interpreting the spectra. To discuss the Hfs-parameters one approximates this state by that of a biradical in the fast exchange limit. One therefore expects $A_{ii}(A^- D^+)$ to be half of the coupling constants of the donor cation $[A_{ii}(D^+)]$ [30]. Since the donors used in our experiments are alternating hydrocarbons, these values are almost identical with those of the donor triplet and one finally obtains from Eq. (2)

$$A_{ii}(exp) = [1 - \tfrac{1}{2} c_1^2] A_{ii}(D) \qquad (4)$$

or from Eq. (3)

$$A_{ii}(exp) = \tfrac{1}{2} c_1^2 A_{ii}(D^+). \qquad (5)$$

Equation (4) is valid if the lowest locally excited state is that of the donor, whereas Eq. (5) holds in the case where the lower triplet energy is that of the acceptor.

For both types of complexes one expects a reduction of the Hfs-parameters of the uncomplexed molecules. And since all Hfs-parameters are reduced by the same ratio, one expects essentially the same profile of the ESR-spectrum of the complex as that of the free donor, but with smaller splittings.

Regarding the ZFS-parameters, one is unable to obtain the ZFS-parameters of the CT-state $D(A^- D^+)$ experimentally. Neglecting this expectedly small value yields an equation

$$D_{exp} = (1 - c_1^2) D_{loc} \qquad (6)$$

that can serve for a rough estimate of the CT-character. We will now summarize the most important neglections in deriving Eq. (3) to (6) and comment on these from the vantage point of the new results obtained from the measurements of the Hfs in the ESR-spectra.

1) The triplet state is described as a superposition of only two wave functions. Contributions of locally excited states other than the lowest one are neglected. Table 2 presents a comparison of the CT-characters where enough experimental data

$$[A_{ii}(loc), D_{loc}]$$

Table 2. CT-characters determined by different methods. The second column contains the average value determined from Hfs-measurements, the values in the last column are obtained by applying Eq. (1) using $D(A^- D^+) = -0.027 \text{ cm}^{-1}$.

Complex	c_1^2 (Hfs)	c_1^2 (D) [Eq. (6)]	c_1^2 (D) [Eq. (1)]
pentamethylbenzene-TCNB	0.74	0.83	0.69
phenanthrene-TCNB	0.47	0.64	0.51
naphthalene-HCNB	0.29	0.33	0.27
naphthalene-HCNB	0.26	0.32	0.26
anthracene-TCNB	0.05	0.03	0.03

are available on the uncomplexed molecules. Therefore, the CT-characters can be derived from the Hfs-parameters as well as from the ZFS-parameters. One observes that the CT-characters obtained by both methods are essentially in agreement. It is easily shown that contributions of locally excited states of the second molecule would lower c_1^2 determined from the Hfs-parameters. Since this would worsen the agreement between the values in the different columns, we may conclude that contributions of a second locally excited state are indeed very small.

2) The Hfs-parameters $A_{ii}(A^- D^+)$ of the CT-state are approximated by that of a biradical in the fast exchange limit [7,8]. This requires the exchange

integral between the triplet electrons in this state to be sufficiently large ($\gg 10^{-3}$ cm^{-1}). This approximation is valid; otherwise, for complexes with the alternating hydrocarbons naphthalene and phenanthrene, the Hfs-parameters would remain unchanged upon complex formation. This is in contrast to our results (for these molecules the coupling constants of cation and triplet state are almost equal).

3) The electron distribution of the ions of the biradical is assumed to be equal to that of the ions in solution. This assumption is not as trivial as one might initially expect since the discussion about the TNB-anion (see III.3) showed that a different environment can very well cause drastic changes in the electron distribution of the ion [22]. However, we could demonstrate that in the CT-complex the distortion due to the presence of the complex partner is very weak. The most striking examples of this proof are the complexes N-TNB and pentamethylbenzene (PMB)-TCNB. For the former complex we could show that the three nitrogen nuclei are equivalent in contrast to some measurements of the TNB anion in solution. In the complex PMB-TCNB we could measure the CT-state directly [8] and demonstrate the validity of Equation (5). In this case the Hfs is due to the four methyl groups of PMB. These 12 protons remain equivalent in the complex, as they do in the cation in solution [31].

4) To derive the CT-character from the ZFS-parameters one needs to know the corresponding parameters D (A$^-$ D$^+$) and E (A$^-$ D$^+$) of the CT-state. One can either neglect this value, as we did in deriving Eq. (6), or one can calculate it theoretically. There exists one calculation of the D- and E-values of CT-complexes between substituted benzenes [32].

For a distance of 3.4 Å between the complexing molecules, values of D(A$^-$ D$^+$) $= -0.027$ cm^{-1} and E(A$^-$ D$^+$) $= -0.004$ cm^{-1} were obtained. It is important to note that the calculated D-values are negative, whereas those of the uncomplexed molecules are positive.

In agreement with this is another calculation of the D^*-value of 0.023 cm^{-1} for the complex benzene-TCNB [2]. However, it is incorrect to use the D^*-value to evaluate the CT-character because it is not an eigenvalue of the spin-Hamiltonian [33]. Since for many molecules the approximation $|D^*| \approx |D|$ holds, one could still use this value if the signs of

D^* and D were equal in the locally excited as well as in the purely ionic state. Although there is still some discussion about the sign of D (A$^-$ D$^+$) [5], we will show that, at least in our complexes, it is negative and in agreement with the calculations of de Jong *.

Rearranging Eq. (1) yields a form

$$D_{\text{exp}} - (1 - c_1{}^2) D_{\text{loc}} = c_1{}^2 D(\text{A}^- \text{D}^+) . \qquad (7)$$

Therefore a plot of the left-hand-side of Eq. (7) against $c_1{}^2$, determined from the Hfs-parameters, yields a straight line through the origin with the slope D (A$^-$ D$^+$). Figure 4 contains the measured points obtained from Eq. (7) and from an equivalent equation for E.
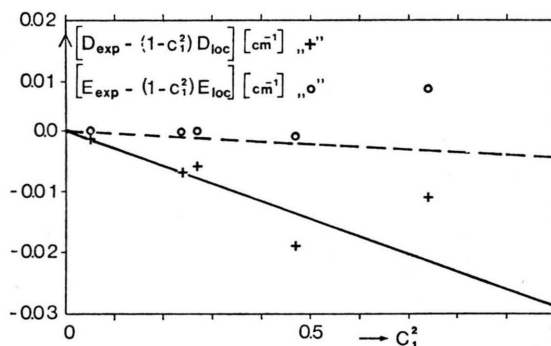

Fig. 4. Plot of the left-hand-side of Eq. (7) versus $c_1{}^2$, determined from Hfs-measurements. The complexes used are those given in Table 2. The straight lines are obtained theoretically using the data of de Jong [32].

The lines in Fig. 4 are obtained theoretically using the values of de Jong. Although the error in the measurements is rather large ($\approx 40\%$), since they result from a subtraction of two large quantities, one clearly observes a scattering of the values close to the theoretical curve. That all values in Fig. 4 are not on one straight line is not surprising since one cannot expect the parameters D(A$^-$ D$^+$), E(A$^-$ D$^+$) to be equal for different complexes. From Fig. 4 it follows that -0.015 cm$^{-1} > D$(A$^-$ D$^+$) > -0.040 cm^{-1}. This clearly shows that D(A$^-$ D$^+$) is negative and, for many complexes, close to the theoretical values. Therefore, the derivation of the

* That D(A$^-$ D$^+$) is considerably smaller than $+0.02$ cm^{-1} also follows from our measured D-values of N-chloranil ($D = \pm 0.0081$ cm^{-1}) and of hexamethylbenzene-TCNB ($D = \pm 0.011$ cm^{-1}). Since D can only become smaller for complexes with $c_1{}^2 = 1$, the measured values represent an upper limit for D(A$^-$ D$^+$).

CT-character from the ZFS-parameters can be improved by using Eq. (1) with $D(A^- D^+) = -0.027$ cm^{-1}. The values in the last column of Table 2 are thus obtained. The improvement is seen by comparing these CT-characters with those obtained from the Hfs-measurements.

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