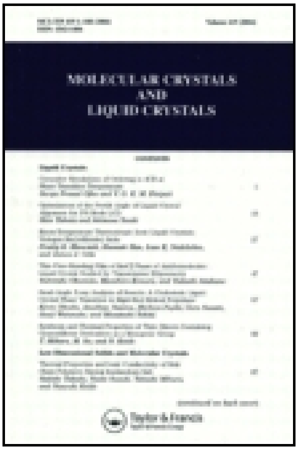

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Charge-Transfer Crystals with Ionic Triplet States: An ESR and ODMR Study of HMB-TCNB and HMBTCPA

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Charge-Transfer Crystals with Ionic Triplet States: An ESR and ODMR Study of HMB-TCNB and HMB-TCPA

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ESR and zero-field ODMR measurements were performed for charge-transfer single crystals of hexamethylbenzene (HMB) with tetracyanobenzene (TCNB) and of HMB with tetrachlorophthalic anhydride (TCPA). Both systems exhibit very high ionic (charge-transfer) character of the triplet excitation as deduced from the small S_1-T_1 separation and small fine structure parameters of $|D| = |0.0285$, $|E| = 0.0066\ \mathrm{cm}^{-1}$ (HMB-TCNB) and $|D| = 0.01525$, $|E| = 0.00342\ \mathrm{cm}^{-1}$ (HMB-TCPA). By comparison with the respective parameters of the neutrally excited acceptors a charge-transfer character is determined as $c_{CT}^2 \simeq 90\%$ and 100%, respectively. Delocalized states (triplet excitons) are detected in HMB-TCNB in a narrow temperature range (~140 K).

I. INTRODUCTION

Among the numerous crystals of weak organic charge-transfer (CT) complexes, the vast majority are characterized by a highly ionic lowest

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excited S_1 state (charge-transfer singlet state), however their lowest triplet state is mainly localized either on a donor or on an acceptor. The properties of the T_1 state of such a system usually resemble those of the respective component of the crystal. ESR spectra of the T_1 state have been studied so far only for very few crystals with high CT character of the T_1 state. It has been found that for phenanthrene-pyromellitic dianhydride (P-PMDA), the CT character of T_1 is 76%[1] and for fluorene-tetracyanobenzene (F-TCNB) it amounts to about 70%.[2] An even higher CT character of T_1 of about 86% has been inferred from ESR studies of the HMB-TCNB complex in low-temperature glassy solution.[3] Equally scarce optical investigations of such systems, like those of HMB-TCNB and HMB-TCPA crystals[4,5] strongly confirm the very high CT character of the T_1 state, for instance in the latter case a CT character of practically 100% has been suggested. Such a high CT character of the triplet state makes it interesting from the point of view of the excitation energy transfer in the crystal. As pointed out in Ref. 6 the properties of CT excitons are different from typical Frenkel-type excitons encountered in CT crystals with local triplet states. First, however, quantitative informations about the CT-character of the T_1 state have to be obtained. Since optical measurements do not yield this sort of information, in this work we report the results of the measurements of the zero-field-splitting (zfs) of the triplet state of HMB-TCNB and HMB-TCPA crystals employing magnetic resonance techniques, the method pioneered in Refs. 7 and 8.

II. EXPERIMENTAL

2.1. Crystal growing

The HMB-TCNB crystals were grown from acetone solution. HMB was first zone-refined, while TCNB, which cannot be zone-refined was repeatedly recrystallized from methanol. Pale-yellow crystals of typical dimensions of 3 × 2 × 0.5 mm^3 were obtained.

The HMB-TCPA crystals were grown using the plate-sublimation technique.[9] In this case both the donor and acceptor were zone-refined separately first, than also as a complex, which was placed in the sublimation ampoule. The crystals had similar color and size as HMB-TCNB.

2.2. Crystal structure

2.2.1. HMB-TCNB. The crystal structure of HMB-TCNB is known[10] in full detail. The crystal is monoclinic, space group $P2_1/n$.

The unit cell parameters are: $a = 15.07$, $b = 8.92$, $c = 7.41$ Å, and $\beta = 104.9°$. There are two complexes per unit cell, which form two stacks of magnetically non-equivalent molecules. The stack axis is the c axis. The TCNB molecules in a stack are inclined to the c axis by 19°, the HMB molecules are parallel to them within 2°. For a detailed orientation of the TCNB molecules in the crystal, see Table I.

2.2.2. *HMB-TCPA.* The structure of HMB-TCPA has been only recently solved and will be published elsewhere.[11] The crystal is monoclinic, space group $P2_1/m$, unit cell parameters are: $a = 9.22$, $b = 13.37$, $c = 8.89$ Å and $\beta = 119.1°$. The stack axis is the b axis. There are two complexes per unit cell, but only one stack, due to a special position of the TCPA molecule, which lies in a mirror plane.

2.3. Magnetic resonance experiments

The zero-field ODMR equipment used in the experiments was described in more detail elsewhere.[2] For the excitation of the HMB-TCNB into the CT band the 457.9 nm line of a Spectra Physics Mod. 164 argon-ion laser was chosen. In exciting HMB-TCPA, which has a higher-lying CT state, the 441 nm line of Spectra Physics Mod. 185 helium-cadmium laser was used alternatively with a HBO 100 high-pressure mercury lamp with suitable filters.

The ESR experiments were performed with a Varian Century line E109 X-band spectrometer equipped with an Oxford Instruments E900 variable temperature unit. The excitation conditions were the same as in the ODMR, except that a XBO 1600 lamp was used instead

TABLE I

Orientation of the TCNB molecule in the HMB-TCNB crystal relative to the crystal axes (in degrees, calculated from Ref. 10).

	a^*	b	c	a^*	b	c
x	16	105	87	164	105	93
y	76	24	71	76	156	71
z	98	108	19	98	72	19

Orientation of the zfs tensor of the HMB-TCNB crystal relative to the crystal axes (in degrees)

	a^*	b	c	a^*	b	c
x	32	120	82	148	120	98
y	65	36	66	65	144	66
z	108	107	25	108	73	25

of the HBO 100. The crystals were oriented for the high-field measurements using a "Laue live-TV" equipment described in Ref. 12.

III. RESULTS

3.1. HMB-TCNB

Typical emission spectra of HMB-TCNB crystal at low temperature are given in Figure 1. They are in general agreement with previously reported findings[4] that the optical emission of HMB-TCNB consists of two strongly overlapping, broad and weakly structured bands, which were identified as the fluorescence (with maximum at ~19000 cm^{-1}) and phosphorescence (with maximum at ~17900 cm^{-1}) originating from shallow triplet X-traps.

In the zero-field ODMR experiments the phosphorescence was monitored at its maximum while microwaves were swept. Two signals

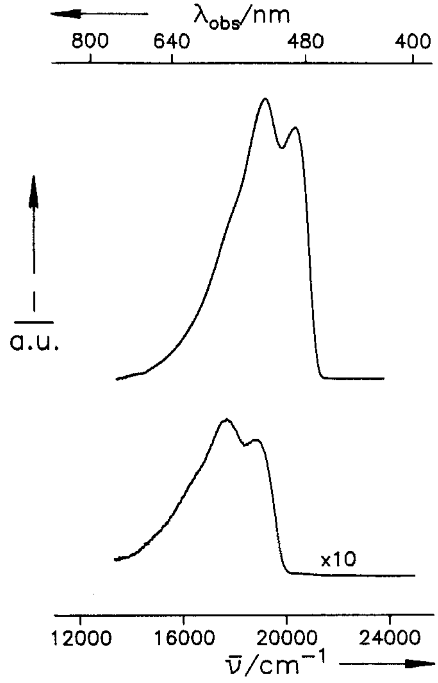

FIGURE 1 Fluorescence (top) and phosphorescence (bottom) spectra of the HMB-TCNB crystal at 4 K.

were detected at 656 and 1052 MHz, both corresponding to an increase of phosphorescence intensity at resonance (Figure 2). The width of the signals is about 30 MHz (FWHM), and they are inhomogeneously broadened, as proved by hole-burning.

All attempts to find the third transition either at the sum or difference of the recorded frequencies by double resonance techniques failed so far. Comparison with the results of ODMR experiments conducted on the isolated complex in glass[3] yield good agreement (see discussion) and suggested that the missing transition lies at the difference rather than the sum of the observed frequencies. The signal at 656 MHz corresponds therefore to the $D - |E|$ and the one at 1052 MHz to the $D + |E|$ transition.

The calculated zfs parameters D and E of the standard zero-field spin Hamiltonian:

$$\mathcal{H} = D\,(S_z^2 - 2/3) + E\,(S_x^2 - S_y^2)$$

are presented in Table II.

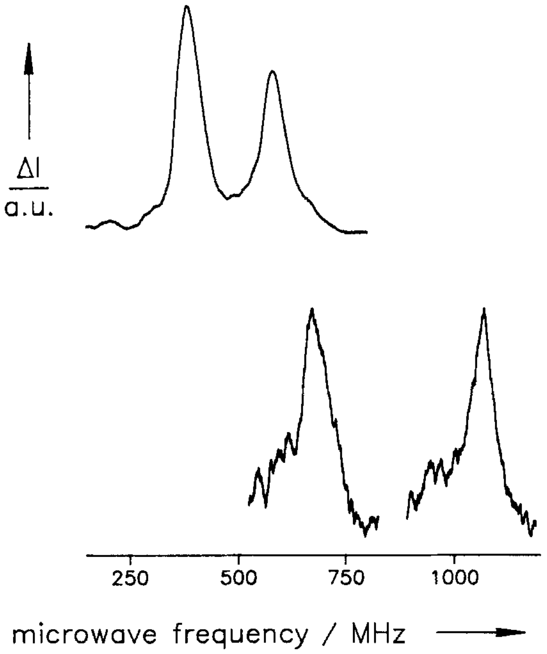

FIGURE 2 ODMR spectra of the HMB-TCPA (top) and HMB-TCNB (bottom) crystals at 1.2 K.

TABLE II

Zfs parameters of the HMB-TCNB and HMB-TCPA crystals

Crystal	Method	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})
HMB-TCNB	zf-ODMR	0.0285(1)	0.0066(1)
	ESR	0.0286(3)	0.0067(3)
HMB-TCPA	zf-ODMR	0.01525(5)	0.00342(5)
	ESR	⩾0.0145	—

The ESR spectrum of HMB-TCNB at low temperature consists of 2 sets of 2 signals each, as expected from the crystal structure. All signals are absorptive and about 15 G broad (depending on orientation, Figure 3). No hyperfine structure could be resolved. The decay time of the signals was found to be 0.60 ± 0.05 s at 6 K.

The signals are highly anisotropic, their angular dependence is shown in Figure 4. The crystal was rotated around all three of its axes. Due to the crystal symmetry only one set of signals is recorded during rotation about the *b* axis.

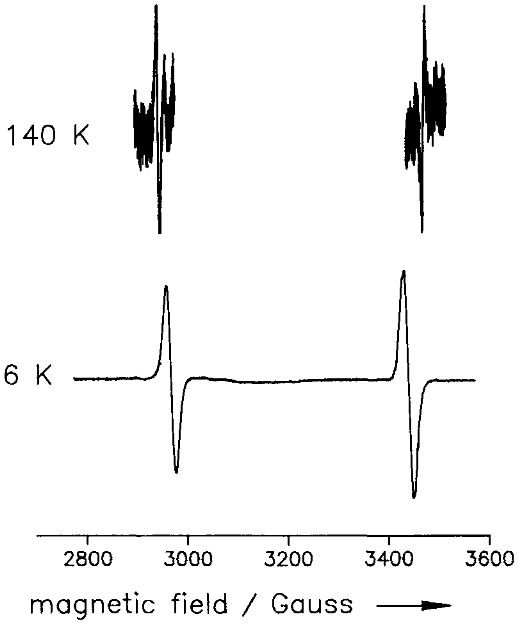

FIGURE 3 ESR spectra of the HMB-TCNB crystal at different temperatures. Magnetic field parallel to the *c* crystal axis (for this particular orientation only one pair of signals is recorded—see text). The signals at 140 K were averaged 10 times. ν_{rf} = 8.998 GHz.

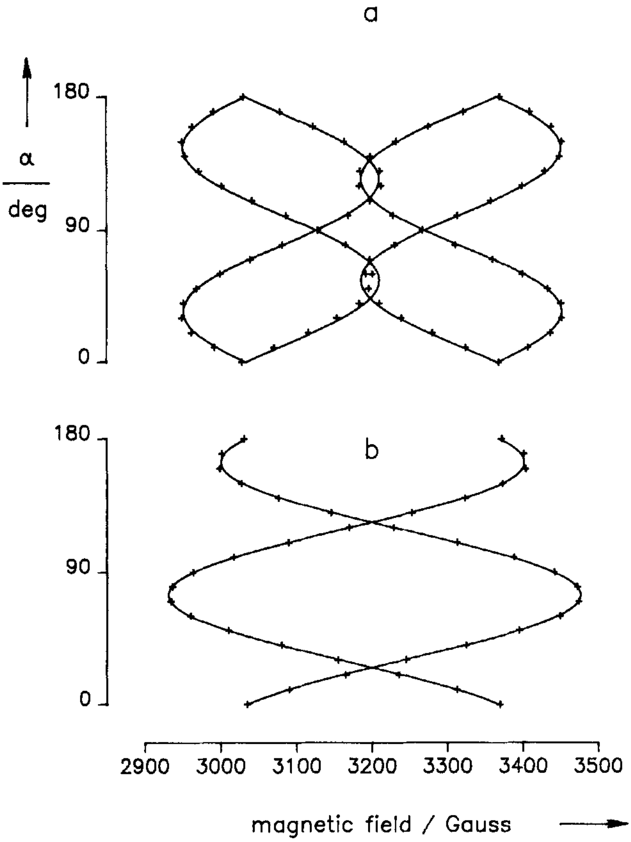

FIGURE 4 Angular dependence of ESR signals of the HMB-TCNB crystal at 6 K. Rotation about: *c* axis (a) and *b* axis (b). The crosses represent experimental points while the curves were drawn using the best-fitted zfs parameters from Table II.

From the rotational patterns, the zfs parameters *D* and *E* as well as the orientation of the two zfs tensors relative to the crystal axes (Table I and II) could be obtained by a numerical fit. The zfs parameters agree within the experimental error with those obtained from the ODMR spectra, proving that the same state is observed by ESR and ODMR.

Upon increasing the temperature the intensity of the ESR signals decreases with an activation energy of 80 ± 20 cm^{-1} and the signals disappear above 40 K.

At about 120 K a new set of signals, different from those observed at low temperature, appears (Figure 3). They are less than 3 G broad, and are spin-polarized. Unfortunately, the intensity of these signals was very low in all crystals examined, so not much information could be gained from them. They could be observed only while rotating the crystal around the *b* axis, and only in the vicinity of the *c* axis, therefore only one pair of signals could be observed. Nevertheless, despite the narrow angular region in which the signals appeared we could observe that their zfs tensors differ in orientation from the low-temperature ones by about 5°. Above 160 K the ESR signals disappear totally.

3.2. HMB-TCPA

The optical emission spectrum of HMB-TCPA crystal is composed of prompt fluorescence and of long-lived emission, which at low temperature is the phosphorescence of trapped excitons.[5] Both emissions have identical spectral position (onset at 22500, maximum at 19600 cm^{-1}) and can be resolved only in the time domain. Time-resolved studies of long-lived emission have revealed the presence of E-type delayed fluorescence for temperatures above 40 K.[13]

In the ODMR experiments at 1.2 K, phosphorescence at its maximum was monitored. Two strong signals at 355 and 560 MHz were found (Figure 2). The signals are 25 MHz broad (FWHM) and are inhomogeneously broadened. In order to find the third signal, the EEDOR technique was employed with saturating either of the observed transitions. The third signal was found at 205 MHz and attributed to the $2|E|$ transition. The zfs parameters inferred from the spectra are presented in Table II.

The ESR spectrum of HMB-TCPA at 3.8 K consists of one pair of signals, symmetrically placed about a very intense $g = 2$ line, which is clearly of photochemical origin (a stable, light-induced $S = 1/2$ state) (Figure 5). The signals are about 15 G wide, and are spin-polarized.

The very intense radical signal made it impossible to follow the full angular dependence of the weak $S = 1$ signals, particularly as the latter's splitting is very small. The maximum splitting of the lines was measured at an orientation close to $B_0//b$, and was found to be 313 G. The D value calculated from this splitting agrees very well with the ODMR results (Table I).

Above 4.2 K the ESR signals disappear and can not be found at higher temperatures.

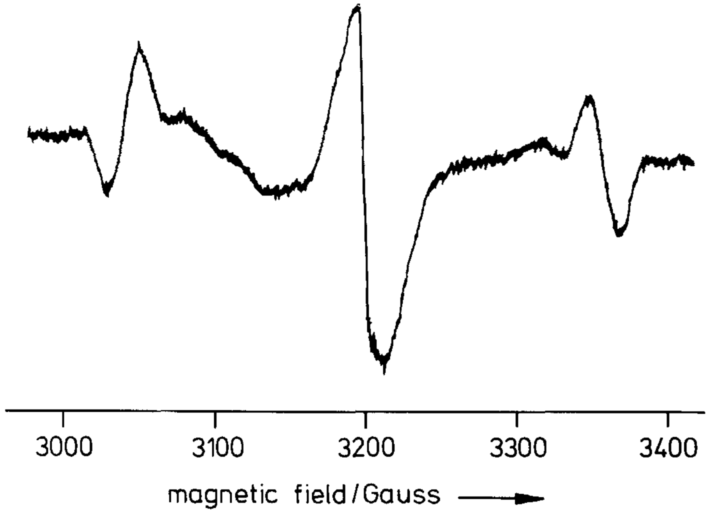

FIGURE 5 ESR spectrum of the HMB-TCPA crystal at 3.8 K. Magnetic field parallel to the *b* crystal axis. ν_{rf} = 8.998 GHz.

IV. DISCUSSION

The most striking feature of the results presented above are very small values of the zfs parameters D and E of HMB-TCNB and particularly HMB-TCPA (Table II) in comparison with the respective parameters of the acceptors ($D = 0.1243$, $E = 0.0136\ \text{cm}^{-1}$ for TCNB[3] and $D^* = \sqrt{D^2 + 3E^2} = 0.1419\ \text{cm}^{-1}$ for TCPA.[14] The zfs parameters obtained by us for the HMB-TCNB crystal agree rather well with the values in Ref. 3 for the isolated complex in low-temperature glass, which are somewhat larger, as it was observed also for other CT systems.[8] The zfs parameters of the pentamethylbenzene-TCNB complex present as a trap in the naphtalene-TCNB crystal ($D = \pm 0.021$, $E = \mp 0.010\ \text{cm}^{-1}$),[15] are also quite similar to the parameters of the HMB-TCNB crystal.

The zfs parameters can be a measure of the CT character of the triplet state. A widely accepted way of expressing the zfs tensor of a triplet state is:[1,6–8]

$$F_{ij}^{\text{exp}} = c_1^2\, F_{ij}(D^+A^-) + c_2^2\, F_{ij}(DA^*) + c_3^2\, F_{ij}(D^*A) \qquad (1)$$

where:

F_{ij}^{exp}—the experimentally determined tensor of the T_1 state,
$F_{ij}(D^+A^-)$—the tensor of the ionic (CT) form of the complex,

$F_{ij}(DA^*)$ and $F_{ij}(D^*A)$—the tensors of the locally excited triplet states of the acceptor and the donor, respectively.

In our case the contribution of the locally excited triplet state of HMB can be neglected, as it lies much higher on energy scale than those of the acceptors (TCNB, TCPA). The coefficient c_1^2 is defined as the CT character of the T_1 state, and can be calculated according to the formula:

$$c_{CT}^2 = \frac{F_{ij}(DA^*) - F_{ij}^{exp}}{F_{ij}(DA^*) - F_{ij}(D^+A^-)} \tag{2}$$

The most troublesome values in this expression are usually the elements of the zfs tensor of the ionic form, (D^+A^-), as they are not accessible experimentally. This problem is usually solved in two alternative ways:

—by neglecting the zfs tensor of the ionic form altogether; this was done in Ref. 8 for a series of complexes, but is justified only in case of a triplet state of small CT character (F_{ij}^{exp} of the order of $F_{ij}(DA^*)$),

—by theoretical calculations of the zfs tensor of the (D^+A^-) form; this was the approach in Ref. 7 and a series of following papers; the authors calculated the zfs parameters of the ionic forms of complexes of methylated derivatives of benzene with TCNB and TCPA using the known geometry of the HMB-TCNB complex in crystal. Unfortunately only the mean zfs parameter D^* was given as the result of those calculations. The most refined attempt so far was made for the crystalline complex P-PMDA.[1] In this outstanding work the complete zfs tensor of the ionic form of this complex was calculated together with its orientation in respect to the molecular axes, and used to calculate the CT character of the T_1 state.

In our case the only theoretical values available for comparison with our experimental results are the D^* values of the ionic forms of HMB-TCNB and HMB-TCPA obtained in Refs. 7 and 14, respectively:

$$D^*(HMB^+TCNB^-) = 0.0222\ cm^{-1}$$
$$D^*(HMB^+TCPA^-) = 0.0250\ cm^{-1}$$

Using the first of these values we can estimate according to formula (2) the CT character of the T_1 state of HMB-TCNB as about 90%, in agreement with the results on the isolated complex.[3] We are aware of the error possibly caused by using the D^* parameter instead of

D or *E*, as pointed out in Ref. 8, and also by some crude approximations made in the calculation of the D^* parameter of the ionic form.

The errors made by those approximations become particularly visible in the case of HMB-TCPA. When the *D* and *E* values from our experiment are recalculated into the D^* value it turns out that it is smaller ($0.0164\ \mathrm{cm}^{-1}$) as compared to the above quoted $0.0250\ \mathrm{cm}^{-1}$ for the ionic form, which could mean that the latter value is wrong. Another possibility is that the *D* parameters of the complex and its ionic form have different signs, as suggested in Refs. 16 and 17. It is therefore not possible to give a certain value of the CT character of the T_1 state of HMB-TCPA, but it must be very close to 100%, that is its triplet state is almost of pure ionic character. To our best knowledge, this is the first CT crystal with such a property.

As a consequence of the high CT character of the T_1 state of HMB-TCNB, the principal axes of the zfs tensor do not coincide with the symmetry axes of the component molecules (Table I) as was also observed in P-PMDA.[1,16] The known orientation of the zfs tensor of TCNB can be a starting point for more precise calculations of the CT character, similar to those in Ref. 1 for P-PMDA. One has to bear in mind, however, that the triplet states observed by us are trap states. This is quite obvious when regarding the ODMR and ESR linewidths and inhomogenous behaviour, as well as the long decay time of the signals in case of HMB-TCNB. The question in as much a trap state can represent the general properties of the crystal appears often. On one side, the results on P-PMDA show almost no difference of trap and excitonic zfs tensors. On the other hand, our rather scarce data on excitons in HMB-TCNB show a difference between the tensor of about 5° in the ac plane. One would wish to get more informations about the mobile excitons. It seems, however, that the inherent property of excitons of very high CT character is the difficulty in observing them by magnetic resonance. In the case of HMB-TCPA all attempts to detect them have failed so far, in HMB-TCNB they are barely visible in a narrow temperature and angular range (the weak signals in Figure 3).

The reason for these difficulties can be seen in the very small S_1–T_1 energy gap, which in emission spectra demonstrates itself as a very small spectral shift between fluorescence and phosphorescence bands. Small S_1–T_1 separation is leading at higher temperatures to a very effective process of thermal activation of triplet excitons from the T_1 to S_1 band, thus reducing the steady-state concentration as well as the lifetime of triplet excitons. This was proved experimentally by studies of emission spectra,[4,5,13] as well as their kinetics.[18]

Acknowledgments

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