The Problematic Charge-Transfer Triplet State of Electron-Donor-Acceptor-Complexes[1]

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Iwata, Tanaka and Nagakura, and Hayashi, Iwata and Nagakura have observed in ethylether-isopentane solutions (1 : 1) at 77 °K, in the case of the complexes of tetracyanobenzene (TCNB) as the electron acceptor with the electron donors mesitylene (Me), durene (Du) and hexamethylbenzene (HMB), an unstructured long-lived, long-wave emission band by exciting the complexes in the charge transfer (CT) band. They interpreted the ll, lw band as a CT-phosphorescence of a charge transfer triplet excited state $|\overset{\uparrow}{D^+}\overset{\uparrow}{A^-}|$. This would be of considerable theoretical interest and significance also for an interpretation of photochemical processes.

In the present communication, we report results which lead us to a different interpretation of the ll, lw emission band under discussion.

The emission spectra of the complexes of tetracyanobenzene (TCNB) with the electron donors toluene (To), p-xylene (Xy), mesitylene (Me), durene (Du) and hexamethylbenzene (HMB) were studied in glassy solutions in propylether at 100 °K. In the case of TCNB-To, -Xy, -Me and -Du, when the complexes were irradiated in the CT-band so that the complex *components were not excited,* we observed either the structured phosporescence band of TCNB which originates from a locally excited triplet state of complexed TCNB or, at large donor concentrations, the unstructured long-lived, long-wave emission band within the green spectral range. In the case of TCNB-HMB, only the ll, lw emission may be observed.

The ll, lw unstructured emission superimposed on the structured TCNB phosphorescence may also be observed when TCNB, singly soluted in glassy solvents or crystallized, is irradiated in the 31,600 cm^{-1} ($S_1 \leftarrow S_0$) peak. Obviously, the ll, lw emission band *may not be characteristic of the complexes* of TCNB.

Simultaneously with the ll, lw emission, a new molecular species X can be identified by a new absorption spectrum after irradiating either TCNB itself within the $S_0 \rightarrow S_1$ 31,600 cm^{-1} peak or the TCNB-complexes within the CT-absorption band. X is formed by a reaction of the triplet excited TCNB.

The excitation in the long-wave absorption peak of X at about 21,000−22,000 cm^{-1} gives rise to an emission with a maximum in the same spectral range as the ll, lw emission band. Accordingly, we interpret the ll, lw emission as a delayed emission of X due to an energy transfer from the triplet excited TCNB.

1. Introduction

IWATA, TANAKA and NAGAKURA (ITN)[2a] and HAYASHI, IWATA and NAGAKURA (HIN)[2b] have studied luminescence spectra of the EDA-complexes of 1,2,4,5-tetracyanobenzene (TCNB), pyromellitic-dianhydride (PMDA) and tetrachlorophthalic-anhydride (TCPA) as electron acceptors with various donors, e. g. hexamethylbenzene (HMB), durene (Du), mesitylene (Me), xylene (Xy), toluene (To), benzene (Bz), etc., in glassy solutions in ethylether-isopentane (1 : 1) (EP) at 77 °K.

By exciting in the CT-absorption band of the complexes, ITN and HIN observed long-lived, long-wave (ll, lw) emission spectra different from the phosphorescence spectra of the free acceptor and free donor. ITN and HIN assigned the unstructured long-lived emission to a straightforward charge transfer phosphorescence due to an excited triplet charge-transfer state $|\overset{\uparrow}{D^+}\overset{\uparrow}{A^-}|$ of the EDA complexes[3]. They also studied the triplet state by means of ESR spectra[2b, c]. Unequivocal evidence of a charge transfer triplet state would be of general interest[4].

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[1] See also G. BRIEGLEB and D. WOLF, Z. Angew. Chem. Internat.-Ed. Vol. **9**, 171 [1970].

[2] a) S. IWATA, J. TANAKA, and S. NAGAKURA, J. Chem. Phys. **47**, 2203 [1967]. b) H. HAYASHI, S. IWATA, and S. NAGAKURA, J. Chem. Phys. **50**, 993 [1969]. c) H. HAYASHI and S. NAGAKURA and S. I. IWATA, Mol. Phys. **13**, 489 [1967].

[3] See also a) N. MATAGA and Y. MURATA, J. Amer. Chem. Soc. **91**, 3144 [1969], and b) R. POTASHNIK, C. R. GOLDSCHMIDT, and M. OTTOLENGHI, J. Phys. Chem. **73**, 3170 [1969].

[4] S. P. MCGLYNN and J. D. BOGGUS, J. Amer. Chem. Soc. **80**, 5096 [1958]. — S. MULLIKEN, Proceedings of the R. A. WELCH Foundation Conferences on Chemical Research XI Radiation and Structure of Matter 1967, p. 109. — G. D. SHORT, Chem. Commun. **23**, 1500 [1968].

The results of this present work yield evidence that one may have doubts about the interpretation that the long-lived unstructured emission of the weak EDA complexes under discussion is a charge transfer triplet phosphorescence.

First, we would like to report investigations of emission spectra of TCNB, soluted in rigid glass at $T = 100$ °K.

2. Tetracyanobenzene

Figure 1 (1) shows the absorption spectrum of TCNB in rigid glassy solutions in n-propylether (nPE) at $T = 100$ °K. An excitation of TCNB in the first $S_0 \rightarrow S_1$ absorption peak at 31,600 cm^{-1} causes the structured fluorescence of TCNB within the frequency region 26,000 – 30,000 cm^{-1} [Fig. 1 (2)] and, furthermore, a blue phosphorescence within the frequency region at about 19,000 – 23,000 cm^{-1} [Fig. 1 (3)] [$\tilde{\nu}(10^3\ \text{cm}^{-1}) = 22.6$, 21.9, 21.1, 20.4 and 19.6]. The lifetime is $\tau = 2.7$ sec at 100 °K. After an irradiation for only a few minutes, a gradual transmutation of the "blue" *phosphorescence* [Fig. 1 (3)] into the spectra of Fig. 1 (4), 1 (5) and 1 (6) with a shift of the maximum intensity toward longer wave lengths in the green spectral region may be observed.

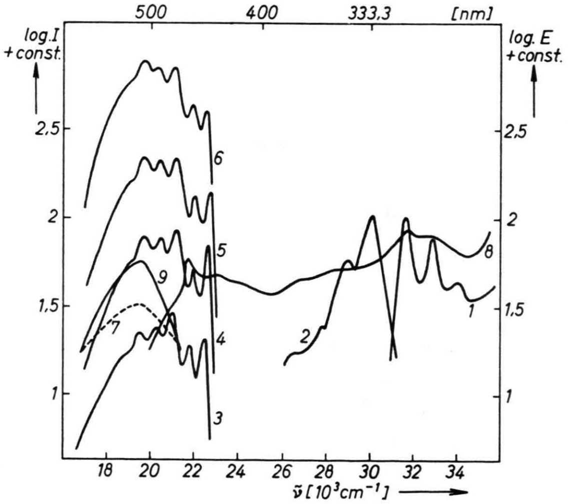

Fig. 1. (1) Absorption spectrum; (2) normal fluorescence spectrum; (3) phosphorescence spectrum of TCNB in glassy nPE-solution at $T = 100$ °K, $c_{\text{TCNB}} = 1.1 \times 10^{-4}$ mol/l; (4), (5), (6) phosphorescence spectra after irradiation for several minutes; (7) the mean difference spectrum of (4), (5), (6) and (3). All possible difference spectra between (4), (5), (6) and (3) have in the mean a frequency maximum at 19,600 cm^{-1}; (8) absorption spectrum after formation of X; (9) emission spectrum of X by excitation in the long wave peak at 21,600 cm^{-1}.

Simultaneously, a new *absorption* spectrum appears [Fig. 1 (8)] with two characteristic regions at about 22,000 cm^{-1} and 26,000 cm^{-1}. The absorption intensity increases with increasing irradiation time. The new molecular species causing the new absorption spectrum shall be abbreviated hereafter by X.

By subtracting the phosphorescence spectrum [Fig. 1 (3)] of TCNB, yielded after exciting the TCNB-solution within the absorption peak at 31,600 cm^{-1} for only a short time, from the phosphorescence spectrum of solutions irradiated somewhat longer, we obtained in the mean a broad long-lived emission band with a maximum at about 19,600 cm^{-1} [Fig. 1 (7)]. *The position and the shape of this long-lived emission corresponds to a prompt emission band which may be observed on excitation in the long-wave region of the X-absorption at 21,600 cm*$^{-1}$ [Fig. 1 (9)].

On the basis of these experimental results, we assume that the broad long-lived, long-wave emission band [Fig. 1 (7)] with a maximum at 19,600 cm^{-1} may be interpreted as a delayed emission of X, caused by an energy transfer from the excited triplet state of TCNB [5].

As the long-lived emission of X and the TCNB-phosphorescence are superimposed, it is not possible to measure the lifetimes separately. In glassy nPE solutions at 100 °K, we have measured $\tau = 2.7$ sec ($c_{\text{TCNB}} = 1.1 \times 10^{-4}$ mol/l). But after an irradiation within 31,000 – 36,000 cm^{-1} for such a long time that X increases, e. g. 10 minutes, τ decreases: $\tau = 2.3$ sec (for further details, see a following publication).

It has to be emphasized that the long-lived, long-wave emission band which may be observed by exciting rigid glassy solutions of TCNB or *crystalline TCNB within the* $S_0 \rightarrow S_1$ *absorption peak of TCNB at 31,600 cm*$^{-1}$ *is the same emission band as has been observed from rigid solutions of the TCNB-EDA-complexes under consideration here when the complexes are excited in the CT-absorption band* (see below). There are only slight differences be-

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[5] For an interpretation of the observed ESR spectra [2b, c] after irradiating the glassy solutions of the complexes under discussion at $T = 77$ °K, it seems that further studies involving some new points of view arising from our investigations are needed.

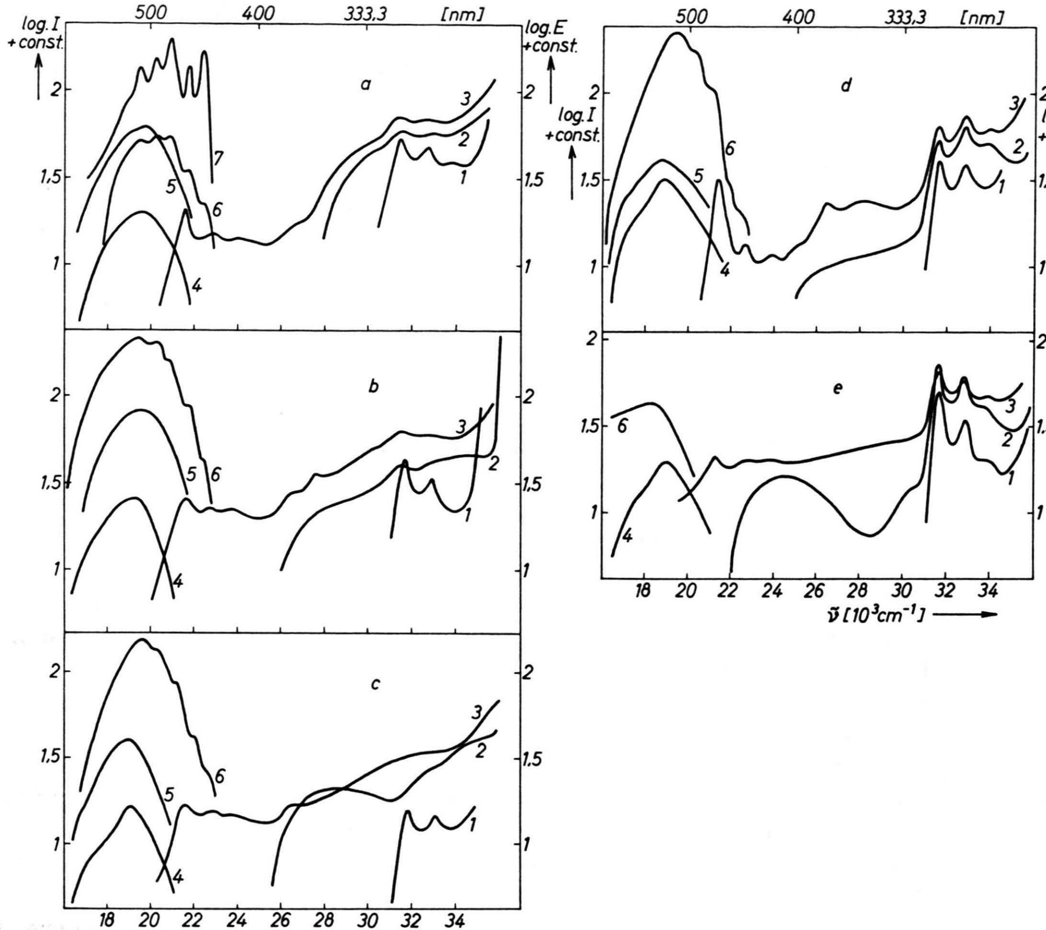

Fig. 2. Absorption- and emission-spectra of the EDA-complexes with a) To, b) Xy, c) Me, d) Du and e) HMB in nPE. (curves 1) absorption spectra at $T=293$ °K; (curves 2) absorption spectra of the EDA-complexes in glassy solutions at $T=100$ °K involving the CT-absorption band; (curves 3) absorption spectra at $T=100$ °K after 15 minutes irradiation within the CT-absorption band; (curves 4) emission spectra by excitation within the longest wave peak of the long-wave absorption band of X at about 21,000 – 22,000 cm^{-1}; (curves 5) long-lived emission by excitation within the CT-band at *high* donor/acceptor ratios $q=c_D/c_A$: $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{To}=1.1$ mol/l; $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{Xy}=3.9\times10^{-1}$ mol/l; $c_{TCNB}=1.37\times10^{-4}$ mol/l, $c_{Me}=5.1\times10^{-1}$ mol/l; $c_{TCNB}=1.46\times10^{-4}$ mol/l, $c_{Du}=4.2\times10^{-2}$ mol/l; (curves 6) long-lived emission by excitation within the CT-band at relatively *low* donor/acceptor ratios $q=c_D/c_A$: $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{To}=2.8\times10^{-3}$ mol/l; $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{Xy}=7.2\times10^{-3}$ mol/l; $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{Me}=8.5\times10^{-3}$ mol/l; $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{Du}=4.4\times10^{-4}$ mol/l; $c_{TCNB}=1.1\times10^{-4}$ mol/l, $c_{HMB}=1.2\times10^{-5}$ mol/l; (curve 7) phosphorescence spectrum of TCNB at 100 °K, $c_{TCNB}=1.1\times10^{-4}$ mol/l.

tween the frequency maxima of the long-lived emission band in the case of single TCNB and of complexed TCNB in the frequency range of about 17,800 – 19,800 cm^{-1} [see Fig. 1 (7) and curve 5 of Fig. 2 a – 2 d].

Furthermore, also in the case of the complexes, the formation of X after excitation in the CT-absorption band may be observed and, moreover, X yields a prompt emission band which corresponds in position and shape to the long-lived, long-wave emission band emitted when the complex is excited in the CT-absorption band. *Hence, it does not seem to be unequivocal that the long-lived broad emission bands of the TCNB-complexes, emitted after excitation in the CT-band, originate from a charge transfer triplet state.*

In the complexes of TCNB with To, Xy, Me, Du and HMB, and also in the complexes of tetrachlorophthalic-anhydride (TCPA) or pyromellitic-dianhydride (PMDA) with the same donors, the acceptor-triplet results from a *complex* singlet excited state $|\dot{D}^+\dot{A}^-|_S^*$ when the complexes are excited in the CT-absorption band. In all the complexes under discussion here, the complex singlet state lies energetically higher than the triplet state of the acceptor, but lower than the singlet state of the complexed acceptor: $E_{|\dot{D}^+\dot{A}^-|_S^*} > E_{|D\ldots A_T^*|}$. Only when this necessary condition is met may the X-formation be observed. In such complexes in which the singlet state of the complex lies energetically lower than the *triplet energy of the acceptor*, any X-formation cannot be observed, e. g. tetramethyl-p-phenylene-diamine-TCNB. In such cases, $E_{|\dot{D}^+\dot{A}^-|_S^*} < E_{|D\ldots A_T^*|}$ so that A_T^* may not be formed. Obviously, it seems that in the case of TCNB itself as well as in the *complexes* of TCNB under discussion here, X is formed via the *triplet* excited state of TCNB. This results from a $S_1 \rightarrow T_1$ intersystem crossing energy transfer after excitation within the $S_0 \rightarrow S_1$ absorption band of TCNB and within the CT-absorption bands of the complexes, respectively.

It might be supposed that the decisive step of X-formation is a charge transfer either from A to A_T^* or from A_T^* to A_T^*[6], taking account that in the triplet excited state of the acceptor, the electron affinity is increased and the ionization energy is decreased by the triplet excitation energy. (For further details see a forthcoming publication.)

HIN[2b, c] have observed the ESR spectra of $TCNB^-$ in glassy ethanol solutions of TCNB-*complexes* under consideration here at $T = 77$ °K by irradiation in the CT-absorption band.

Proof of the positive radical ion $TCNB^+$ seems to be lacking. It might be posible that $TCNB^+$ undergoes a resonance spin exchange or a subsequent chemical reaction with either TCNB or, in solutions, possibly also with the solvent molecules. The interpretation of the detailed mechanism of $TCNB^-$-formation starting from the triplet excited state of TCNB needs further investigations. We will report soon about results of investigations on the kinetics and the mechanism of X-formation.

A steady state concentration of X during irradiation in glassy nPE ($T = 100$ °K) could not be observed, but the concentration of X is continuously increasing during the irradiation time. In rigid glassy solutions, and *also in crystals at* $T = 100$ °K or lower, X is perfectly stable after incident light is shut off. At higher temperatures when the nPE-glass becomes viscous or in fluid solutions, the steady concentration of X becomes too small for identification by absorption spectra and only the characteristic emission of X may be observed and the ESR spectrum as well, but only in suitable solvents.

3. TCNB–EDA-Complexes with HMB, Du, Me, Xy and To

Figure 2 shows the absorption spectra of TCNB with the donors HMB, Du, Me, Xy and To at 293 °K (curves 1) and at 100 °K (curves 2) in rigid glassy nPE solutions. The spectra indicate the appearance of a CT-absorption band.

It is highly important for the question under discussion that, in the case of the complexes of TCNB with To, Xy, Me and Du, the characteristic features of the long-lived emission spectra emitted by exciting the complexes in the CT-band (curves 5 and 6 of Fig. 2) are decidedly dependent upon the donor concentration[7].

At relatively *low* donor concentrations [see $q = c_D/c_A$ in Table 1 (12)], the long-lived emission spectra of the complexes (curves 6 of Fig. 2), yielded by excitation in the CT-band, are virtually similar to the phosphorescence spectra of the non-complexed TCNB [Fig. 1 (3) to 1 (6)]. The frequencies of the individual vibration bands of the long-lived emission bands (curves 6 of Fig. 2) are approximately unchanged compared with the peaks of the phosphorescence spectrum of TCNB itself [$\tilde{\nu}(10^3\ \mathrm{cm}^{-1}) = 22.6$, 21.9, 21.1, 20.4 and 19.6]. However, the bands in the long-lived emision spectra of the complexes are considerably broadened. Furthermore, in the case of the TCNB-complexes with Xy, Me and Du, the intensity maximum of the vibration bands is at $19{,}200 - 19{,}600\ \mathrm{cm}^{-1}$ while

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[6] M. SOFUE and S. NAGAKURA, Bull. Chem. Soc. Japan **38**, 1048 [1965] have measured the absorption spectrum of $TCNB^-$ in solution of acetonitrile after flash irradiation in accordance with the spectrum Fig. 1 (8) of TCNB in glassy nPE-solution at $T = 100$ °K after formation of X.

[7] An interpretation of the influence of the donor concentration on this feature and the maximum frequencies of the ll-emission spectra will be given soon in a later publication on the basis of the kinetics of X-formation.

the phosphorescence spectra of TCNB itself and of TCNB-toluene have a maximum at 21,100 cm^{-1} [see also Table 1 (13) and 1 (14)].

It is difficult to explain unambiguously the red shift of the intensity maximum in the case of the TCNB-Xy, -Me and -Du complexes compared with TCNB itself and with TCNB-To. The red shift may be caused by intermolecular interaction effects or by superposition of the delayed emission of X (see further below).

In the case of TCNB-HMB, the structured phosphorescence of TCNB may not be observed when excited in the CT-absorption band at 24,600 cm^{-1}, even at low donor concentrations; only the broad unstructured long-lived emission band in the "green" frequency region appears [Fig. 2 e (6)].

By *gradually increasing* the donor concentrations [see the *q* in Table 1 (8)], the long-lived emission spectra of the complexes TCNB-To, -Xy, -Me and -Du yielded by excitation in the complex CT-absorption band are obviously altered[7]. The long-lived emission spectra at higher donor concentrations are unstructured with intensity maxima shifted to lower frequencies [curves 5 of Fig. 2 and Table 1 (9) and 1 (10)].

In the case of the Du- and Me-complexes, ITN[2a] did not observe the structured phosphorescence spectra which we observed at *small* donor concentrations [Fig. 2 c (6) and 2 d (6)], but they only found the unstructured long-lived, long-wave emission spectra which we measured solely at *large* donor concentrations [Fig. 2 c (5) and 2 d (5), and Table 1 (8) to 1 (10)]. ITN gave no information about concentrations and assigned the long-wave, long-lived emission bands, in the case of TCNB-Me, -Du and -HMB, to emission from a *complex triplet state* $|\overset{\uparrow}{D}{}^{+}\,\overset{\uparrow}{A}{}^{-}|$ [see also x[2b] in Table 1 (11)].

However, on the other hand, in the case of TCNB-To- and -Xy-complexes, ITN[2a] did not note the unstructured long-lived, long-wave emission bands [Fig. 2 a (5) and 2 b (5), and Table 1 (9)] which we observed at large donor/acceptor ratios *q* [Table

Acceptor TCNB	$\tilde{\nu}_{\text{CT}}^{\text{Abs}}$ $10^3\,\text{cm}^{-1}$		$\tilde{\nu}_{\text{CT}}^{\text{Fluoresc.}}$ $10^3\,\text{cm}^{-1}$			$\tilde{\nu}_{\text{X}'}^{\text{Abs}}$ $\tilde{\nu}_{\text{X}'}^{\text{Em}}$ $10^3\,\text{cm}^{-1}$		q	$\tilde{\nu}^{11\ \text{Em}}$ $10^3\,\text{cm}^{-1}$		x	q	$(\tilde{\nu}_{\text{TCNB}}^{\text{P}})_{\max}$ $10^3\,\text{cm}^{-1}$	
Donors	a		maxima			k	l	m	n		r	s	t	u
Benzene	32.5[b]	—	26.3[h, i]	25[j′]	20.3[g′, j]	—	—	—	—	—	0.02	—	—	20.7
Toluene	31.8[b]	—	24,7[h, i]	23,8[j′]	20.0[g′, j]	21.7	19.7	10^4	19.8	20.5[p]	0.04	25	21.1	20.5
p-Xylene	—	28—30[e, f]	22.2[i]	—	—	21.6	19.3	4.10^3	19.5	—	0.13	65	19.6	—
Mesitylene	28.3[c]	28.2[e]	22.5[h]	22.1[i]	—	21.4	18.9	$\approx 10^2$	18.9	19.8[o]	0.16	77	19.5	—
Durene	25[d]	25.6[g]	21.5[h]	20.2[i]	17.9[g, g′]	21.2	18.7	$\approx 10^2$	18.8	19.5[o]	0,44	4	19.2	—
Hexamethyl-benzene	23.5[d]	24.6[e] 23.6[g]	20[h]	19.3[i] 16.8[g, g′]	19.4[e]	21.1	19.1	≈ 10	18.3	18.3[o]	0,8	—	v	—
1	2	3	4		5	6	7	8	9	10	11	12	13	14

Table 1. Experimental data. [a] Long-wave CT-absorption maxima reported by ITN[8]. In some cases, a second short-wave CT-absorption band may also be observed at $T=298\ ^\circ\text{K}$. [b] Soluted in benzene and toluene, respectively. [c] Single crystal. [d] Soluted in CH_2Cl_2. [e] This work, $T=100\ ^\circ\text{K}$ in glassy nPE-solutions. [f] No separate CT-absorption maximum. [g] MATAGA and MURATA[3], 293 °K, soluted in benzene. [g′] Further studies are needed to interpret, in the case of TCNB-benzene, -toluene, -durene and -HMB, the great difference between the CT-fluorescence maxima at 295 °K[3] in benzene or toluene solutions, and at low temperatures (77° or 100 °K), in glassy solutions in ethylether-isopentane or nPE ([h, i, j,] and [e]). [h] ITN[2a], $T=77\ ^\circ\text{K}$, ethylether-isopentane (1 : 1). [i] HIN[2b], $T=77\ ^\circ\text{K}$, ethanol. [j] MATAGA and MURATA[3], $T=295\ ^\circ\text{K}$, TCNB soluted in benzene and toluene, respectively, $c_{\text{TCNB}}=2.0\times10^{-4}$ mol/l. [j′] $T=77\ ^\circ\text{K}$[3]. [k] Peak of the longest wave absorption band of X′. [l] Maximum of X′-emission band, when excited within the long-wave peak of the X′-absorption band (column 6). [m] $q=c_{\text{D}}/c_{\text{A}}$ is related to the measured $\tilde{\nu}^{\text{llEm}}$ recorded in column 9. [n] This work: long-lived, long-wave emission bands after excitation within the CT-absorption band maxima are recorded in columns 2 and 3. For the concentrations c_{TCNB} and c_{donors}, see Figi. 2 and the values of *q* in column 8. [o] ITN[2a]. Excitation within the CT-absorption band in glassy solutions in ethylether-isopentane (1 : 1) at 77 °K. ITN give no information about concentrations of either the donors or TCNB. [p] MATAGA and MURATA[3], $T=79\ ^\circ\text{K}$, TCNB soluted in toluene, $c_{\text{TCNB}}=2.0\times10^{-4}$ mol/l. [r] x is the CT-character of the phosphorescence state given by HIN[2b], based on the interpretation of $\tilde{\nu}^{\text{llEm}}$ as a CT-phosphorescence by ITN[2b]. x is evaluated by means of ESR spectra[2b, c]. [s] $q=c_{\text{D}}/c_{\text{A}}$ is related to column 13, $c_{\text{A}}=1.1\times10^{-4}$ mol/l. [t] Maxima of the most intense peak of the long-lived structured emission spectra, when excited in the CT-absorption band with low irradiation intensities at relative low D concentrations (see the *q* in column 12). [u] ITN[2a] (no information about concentrations). [v] May not be observed even at low concentrations of HMB.

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[8] S. IWATA, I. TANAKA, and S. NAKAKURA, J. Amer. Chem. Soc. **88,** 894 [1966].

1 (8)]. ITN [2a] observed at unspecified concentrations, in the case of TCNB-To and -Xy, only the structured phosphorescence spectra similar to TCNB itself which we have also measured [Fig. 2 a (6) and 2 b (6)], but at *small* donor/acceptor ratios q [Table 1 (12)]. Because of the appearance of the *structured phosphorescence*, ITN [2a] and HIN [2b] assume that the CT-character of the phosphorescence state of the TCNB-To- and -Xy-complexes is nearly zero [see the x in Table 1 (11)].

To summarize, we emphasize that – when exciting in the CT-absorption band – we have found, in the *case* of the complexes of TCNB with To, Xy, Me and Du, *either the long-wave, long-lived emission* (curves 5 of Fig. 2) or the structured *phosphorescence band* (curves 6 of Fig. 2) *similar* to TCNB itself according to whether the donor concentration is large or small. In the case of TCNB-HMB, only the unstructured long-lived, long-wave emission may be observed.

In the EDA complexes of TCNB with To, Xy, Me and Du, the triplet energy level of the complexed acceptor TCNB lies below the energy of the CT-singlet energy level. Therefore, excitation of the CT-singlet state by absorption in the CT-band of the soluted complexes results from an intersystem crossing process in a population of triplet-excited complexed TCNB molecules.

The question as to whether DA_T^* dissociates immediately after intersystem crossing cannot be decided unequivocally. It has to take into consideration that, immediately after the intersystem crossing energy transfer via the CT-singlet state $|\mathrm{D}^+\mathrm{A}^-|_\mathrm{S}^*$, the complex DA_T^* is first in a Franck-Condon state. Therefore, we may write $|\mathrm{DA}_\mathrm{T}^*|_\mathrm{FC}$. The FC-state, involving solvation, will be gradually converted in the glassy matrix into a stable state:

$$|\mathrm{DA}_\mathrm{T}^*|_\mathrm{FC} \rightarrow \mathrm{DA} \quad \text{or} \quad |\mathrm{D}\ldots\mathrm{A}_\mathrm{T}^*|,$$

depending on whether the bond between A_T^* and D is more or less strong or loose. The influence of the solvation and of the structure of the matrix has to be taken into consideration. Henceforth, we will write $|\mathrm{D}\ldots\mathrm{A}_\mathrm{T}^*|$ to express the experimental result that the phosphorescence spectrum of the locally excited triplet state of the complexed TCNB is somewhat different from the phosphorescence spectrum of the free TCNB.

In the case of TCNB-HMB, it is not *possible* to measure the 0-0-CT transition with sufficient accuracy. Furthermore, an excitation in the CT-absorption band of the TCNB-HMB-complex in solutions in nPE glass does not result in an emission of the structured phosphorescence even under conditions where, in the case of the complexes of TCNB with To, Xy, Me and Du, the structured phosphorescence may be observed. Obviously, the question $E_{|\dot{\mathrm{D}}^+\dot{\mathrm{A}}^-|_\mathrm{S}^*} \gtreqless E_{|\mathrm{DA}_\mathrm{T}^*|_\mathrm{FC}}$ cannot be decided directly.

However, measurements of the absorption after a flash excitation in *the CT-absorption band* of the complex TCNB-HMB in solutions in nPE at $T = 100$ °K yield a $T_1 \rightarrow T_2$ absorption of the triplet excited TCNB [9].

Furthermore, an excitation in the CT-absorption band of the TCNB-HMB-complex soluted in nPE glass at $T = 100$ °K results in an accumulation of the species X (see further below), but X may only be formed by the *triplet* excited TCNB.

Based on the conclusion from the results of CT-absorption measurements and of X-formation, we may assume also in the case of TCNB-HMB that the energy $E_{|\dot{\mathrm{D}}^+\dot{\mathrm{A}}^-|_\mathrm{S}^*}$ will be higher than the energy $E_{|\mathrm{D}\ldots\mathrm{A}|_\mathrm{T}^*}$ of the locally excited TCNB-triplet state.

As in the case of the non-complexed TCNB, irradiation within the CT-absorption band produces a new *absorption spectrum* (curves 3 of Fig. 2). The new absorption spectrum has two characteristic absorption regions at about $\tilde{\nu} = 22{,}000\ \mathrm{cm}^{-1}$ [Table 1 (6)] and $\tilde{\nu} = 26{,}000\ \mathrm{cm}^{-1}$, due to a new molecule species X′ formed by a reaction of the triplet excited complexed TCNB.

Similar to the species X, formed by irradiation of TCNB itself, X′ also yields an immediate unstructured emission spectrum [curves 4 of Fig. 2 and Table 1 (7)] by excitation within the long-wave absorption band of X′ at about 21,000 cm^{-1} to 22,000 cm^{-1}. This prompt X′ emission spectrum has a maximum at the same frequencies as the maxima of the delayed emission bands [curves 5 of Fig. 2 and Table 1 (9) and 1 (10)] [10] yielded by

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[9] G. Briegleb and G. Betz, unpublished.

[10] In the case of TCNB-HMB, the 19,100 cm^{-1} maximum of the prompt X′ emission is in the neighbourhood of the CT-*fluorescence* maximum at 19,400 cm^{-1} yielded by excitation in the 24,600 cm^{-1} CT-absorption band of the TCNB-HMB complex soluted in nPE glass at $T = 100$ °K. ITN and HIN [2a, b] noted the CT-fluorescence at $T = 77$ °K in ethylether-isopentane (1 : 1) at 20,000 cm^{-1} and in ethanol at 19,300 cm^{-1}. In the range of about 21,000–23,000 cm^{-1}, the X′-band and the long wave range of the CT-absorption band are superimposed. Therefore, when the excitation is in the CT-absorption band, a partial superposition of CT-fluorescence with the prompt X′-emission cannot be excluded, but also when the excitation is in the long-wave peak of the X′-absorption band, the prompt

excitation of the complexes in the CT-absorption band at the adequate donor concentrations[11] [Table 1 (8)].

Therefore, we assume that the long-lived unstructured emission of the CT-excited complexes of TCNB with To, Xy, Me, Du and HMB is a delayed emission of X′ due to an energy transfer from the triplet excited complexed TCNB to X′.

It has to be emphasized that the maxima of the long-wave *absorption* bands of X′ [Table 1 (6)] and, similarly, the maxima of the immediate emission spectra of X′ [Table 1 (7)][10] and the long-lived unstructured CT-excited complex emission bands [Table 1 (9) and 1 (10)] *shift to longer waves in the order* $\lambda_{\max}$ of TCNB-HMB > -Du > -Me > -Xy > -To in parallel with a decreasing order of donor strengths or an increasing ionization potential of the donors. In accordance with this correlation of the frequencies of the maxima of the absorption and emission bands of X′ with the donor strength, we asume that X′ may be X interacting with excess $D : X' = D \ldots X$.

ITN[2a] noted that the long-wave shift of the maxima of the long-lived emision of the TCNB-complexes with increasing donor ability (i. e. with decreasing ionization energy of the donor) in parallel with the CT-fluorescence maxima may be considered as essential evidence that the long-lived, long-wave emission bands are due to a charge transfer phosphorescence. However, the shift $\Delta\tilde{\nu}_{\mathrm{To}\to\mathrm{HMB}} = 2000\ \mathrm{cm}^{-1}$ of the long-lived emission band maxima in the order TCNB-To, < -Xy, < -Me, < -Du, < -HMB (see Table 1 – 9) is smal compared to the shift of the CT-*fluorescence:*

$$\Delta\tilde{\nu}_{\mathrm{FCT\ To}\to\mathrm{HMB}} = 5000 - 6000\ \mathrm{cm}^{-1}$$

(see Tables 1 – 4 and 1 – 5).

Immediately after flash, we measured a non-exponential decay of the emission intensity but, after about 5 sec, the decay is exponential in the case of TCNB-Du, -Me, -Xy and -To with a life time $\tau = 2.7$ sec corresponding to the phosphorescence decay time of TCNB itself[12].

From the non-exponential range of the decay curves, one can calculate a shorter decay time which may be expected due to the X′-formation and X′-excitation via the triplet excited TCNB. *Quantitative* calculations of τ from the non-exponential region of the decay curves seem to be somewhat arbitrary.

For a detailed description of the experimental method of absorption, fluorescence, phosphorescence and decay time measurements of glassy solutions at low temperatures, see a recent publication[13].

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emission of X′ may be superimposed by a small amount of CT-fluorescence. Consequently, the prompt X′-emission and the CT-fluorescence cannot be unequivocally separated. Therefore, in the case of TCNB-HMB, the prompt emission band of X′ when excited in the 21,000 – 23,000 cm^{-1} absorption region of X′ will be somewhat shifted to longer waves by superposition with a small amount of CT-fluorescence.

[11] In the case of TCNB-HMB, the lw, ll emission maximum shifts drastically to longer waves. Further details and discussions about this phenomenon will be reported later.

[12] In the case of TCNB-HMB, the intensity of the phosphorescence after flash decays so rapidly due to the shortened triplet life time that we have not been able to measure the life time in the time range > 5 sec. Therefore, an approximation to $\tau = 2.7$ sec could not be determined.

[13] G. Briegleb, W. Herre, W. Jung, and H. Schuster, Z. Physik. Chem. N. F. **38**, 253 [1963]; **45**, 229 [1965].