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The Electronic Structure of the Electron Donor-Acceptor Complex in Its Lowest Excited Singlet State. II

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The electronic spectra of some 1,2,4,5-tetracyanobenzene complexes in the lowest excited singlet state at 77 K were obtained by laser photolysis method. The observed spectra can be well reproduced with the superposition of the bands similar to those of acceptor anion as well as donor cation, independent of donors. Comparing the spectra with those of ionic radical salts, it is concluded that the electronic structure of these complexes is quite polar and the fluorescent state is a contact ion-pair. The electronic structures of excited electron donor-acceptor systems have been discussed, on the basis of the interaction between donor cation and acceptor anion. The charge-transfer degree in the excited complexes was found to increase in the following order; 1,2,4,5-tetracyanobenzene-hexamethylbenzene complex in the phosphorescent state < hydrocarbon-amine heteroexcimers < the present complexes in the fluorescent state.

The electronic spectra of excited electron donor-acceptor (EDA) systems such as EDA complexes in the fluorescent as well as phosphorescent states and heteroexcimer have been investigated by laser photolysis method. The excited singlet-singlet ($S_n \leftarrow S_1$) absorption spectra of EDA complexes, which are stable in the ground state, were observed for the first time in the case of 1,2,4,5-tetracyanobenzene (TCNB) and pyromellitic dianhydride (PMDA) complexes with methylsubstituted benzenes.[1-3] The spectra were similar to those of acceptor anion, which indicated the quite polar structure of the lowest excited charge-transfer singlet (^{1}CT) state of EDA complexes. On the other hand, the absorption spectra of intermolecular as well as intramolecular heteroexcimers show numerous bands in the visible region, some of which were found to coincide with those of acceptor anion and donor cation.[4,5] The absorption spectra of the charge-transfer triplet (^{3}CT) state of EDA complex were found to be different from those of acceptor anion and donor cation. The triplet-triplet ($T_n \leftarrow T_1$) absorption spectra of naphthalene, pyrene as well as phenanthrene complexes are similar to those of the donor.[6-8] In the case of the $T_n \leftarrow T_1$ spectra of TCNB complexes with methylsubstituted benzenes, some bands which cannot be ascribed to those of the component triplet state have been reported.[7,9]

In view of the above results, the problems on the electronic structures of the excited EDA systems may be summarized as follows; (1) elucidation of the relation between the electronic spectra and CT degree in these systems, (2) investigation of the difference among the electronic structures of ^{1}CT as well as ^{3}CT states of EDA complexes and heteroexcimer, (3) theoretical study on energies as well as intensities of back CT transitions from acceptor anion to donor cation,[2] (4) investigation of the structural change, which occurs in the course of the relaxation from the excited Franck-Condon (FC) to fluorescent states.[2,10]

We have been studying the electronic spectra of some excited EDA complexes for elucidating the above problems. Although the $S_n \leftarrow S_1$ spectra of TCNB complexes with benzene, toluene and mesitylene were obtained at room temperature, the observation of the $S_n \leftarrow S_1$ spectra of TCNB complexes with α-methylstyrene, durene and hexamethylbenzene (HMB)

1) H. Masuhara and N. Mataga, *Chem. Phys. Lett.*, **6**, 608 (1970).
2) H. Masuhara and N. Mataga, *Z. Phys. Chem. N. F.*, **80**, 113 (1972); Part I of this series.
3) R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970).
4) R. Potashnik, C. R. Goldschmidt, M. Ottolenghi, and A. Weller, *J. Chem. Phys.*, **55**, 5344 (1971).
5) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972).
6) G. Briegleb, H. Schuster, and W. Herre, *ibid.*, **4**, 53 (1969); G. Briegleb and H. Schuster, *Z. Phys. Chem. N. F.*, **77**. 269 (1972).
7) N. Tsujino, H. Masuhara, and N. Mataga, *Chem. Phys. Lett.*, **15**, 360 (1972).
8) Z. Teitelbaum, R. Potashnik, and M. Ottolenghi, *Mol. Photochem.*, **3**, 107 (1971).
9) S. Matsumoto, S. Iwata, J. Nakamura, and S. Nagakura, *Chem. Phys. Lett.*, **13**, 463 (1972).
10) N. Mataga and Y. Murata, *J. Amer. Chem. Soc.*, **91**, 3144 (1969).

donors was difficult because of their short lifetimes of the lowest excited singlet state. However, in rigid solutions the fluorescence lifetimes of the latter complexes become long enough for measurement of the $S_n \leftarrow S_1$ spectra. In the present paper, the $S_n \leftarrow S_1$ spectra of several TCNB complexes in polymethylmethacrylate (PMMA) at room temperature as well as in rigid glass at 77 K will be reported.

Experimental

The fluorescence intensities of the present TCNB complexes are stronger than the monitoring light intensity. Accordingly, the observation of the $S_n \leftarrow S_1$ spectra is difficult. However, we can obtain those spectra by the re-absorption method developed by us.[11] Namely, the $S_n \leftarrow S_1$ spectra have been obtained by comparing fluorescence spectra observed by laser excitation of low intensity (one three hundredth of high intensity) with those observed by laser excitation of high intensity which are partially re-absorbed by the complex in the fluorescent state. Some points should be noted on this method. The first one is the selection of the wave number, at which both fluorescence spectra are normalized. Secondly, it is difficult to obtain the $S_n \leftarrow S_1$ spectra in the wave number regions where the fluorescence intensity is about one tenth of its peak intensity, because in this case the noise of the out-put of photomultiplier is in the same order of magnitude as the signal and a slight fluctuation of fluorescence intensity out-put leads to a large uncertainty of the $S_n \leftarrow S_1$ spectra. Thirdly, it is necessary to remove the contribution of the absorption of ^{3}CT state from the observed spectra since ^{3}CT state of some TCNB complexes is confirmed to be formed from the excited FC state, competing with the formation of ^{1}CT state.[12] The wave number where we have normalized two fluorescence spectra obtained by high and low laser excitations, and the absorbances of the $T_n \leftarrow T_1$ transitions at those wave numbers respectively, are indicated in Table 1. At the longer wavelength regions, we have measured $S_n \leftarrow S_1$ spectra by usual nsec flash photolysis method.[13] The apparatus and the chemicals were the same as used before.[12,13]

Table 1. Normalization conditions of fluorescence spectra of some TCNB complexes, obtained by high and low intensity laser excitations

Donors	Wave number of normalization	Optical density of $T_n \leftarrow T_1$ spectra at the wave number of normalization
Toluene	20 kK	0.1
Mesitylene	24.8	~0 (neglected)
	18.9~19.2	~0 (neglected)
Durene	22.5	~0 (neglected)
HMB	17~18	~0 (neglcctcd)
Naphthalene	18.2	0.1

11) H. Masuhara and N. Mataga, This Bulletin, **45**, 43 (1972).
12) H. Masuhara, N. Tsujino, and N. Mataga, *Chem. Phys. Lett.*, **12**, 481 (1972); N. Tsujino, H. Masuhara, and N. Mataga, *ibid.*, **15**, 357 (1972).
13) H. Masuhara, M. Shimada, N. Tsujino, and N. Mataga, This Bulletin, **44**, 3310 (1971).

Results

Fluorescence spectra obtained by plotting the peak intensity at each wave number and the transient absorption spectra of excited TCNB complexes at 77 K are given in Figs. 1—5. Since we have shown that the intersystem crossing process to the triplet state

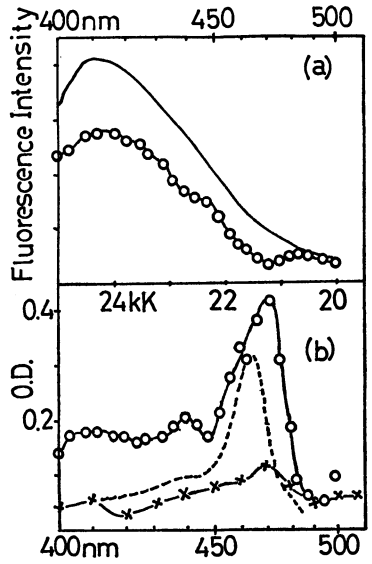

Fig. 1. Flurescence spectra and the transient absorption spectra of TCNB-toluene complex in rigid mixed solvent of *n*-propyl alcohol and isopropyl alcohol (*n*P–*i*P) with volume ratio of 2 : 3 at 77 K.
(a) Flurescence spectra obtained by laser excitation of high intensity (-O-O-) and by laser excitation of low intensity (——).
(b) The obtained transient absorption spectra (-O-O-) and the $T_n \leftarrow T_1$ spectra observed previously[7] (-×-×-). The absorption spectra of TCNB anion taken from literature[14] are included (----).

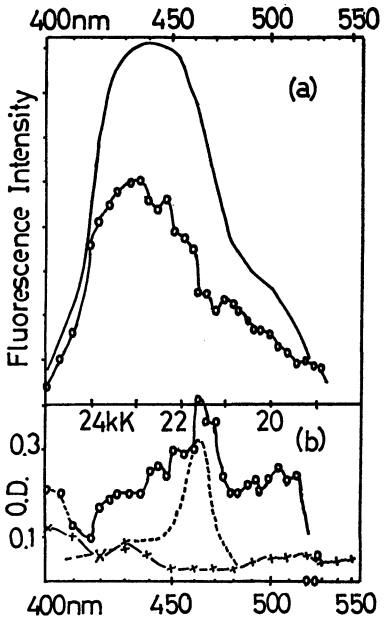

Fig. 2. Flurescence spectra and the transient absorption spectra of TCNB-mesitylene complex in *n*P–*i*P at 77 K. Notations are the same as described in Fig. 1.

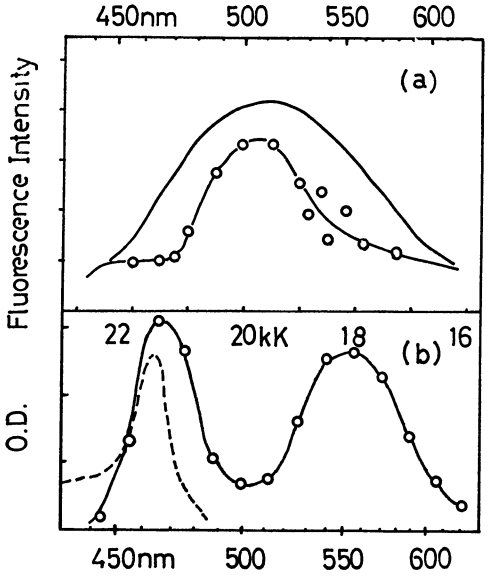

Fig. 3. Fluorescence spectra and the transient absorption spectra of TCNB-durene in PMMA at room temperature. Notations are the same as described in Fig. 1.

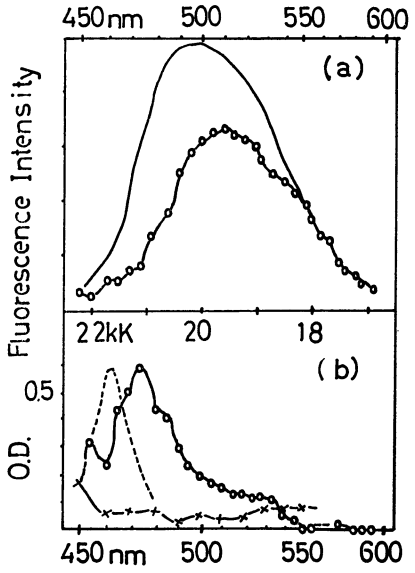

Fig. 4. Fluorescence spectra and the transient absorption spectra of TCNB-HMB complex in *n*P–*i*P at 77 K. Notations are the same as described in Fig. 1.

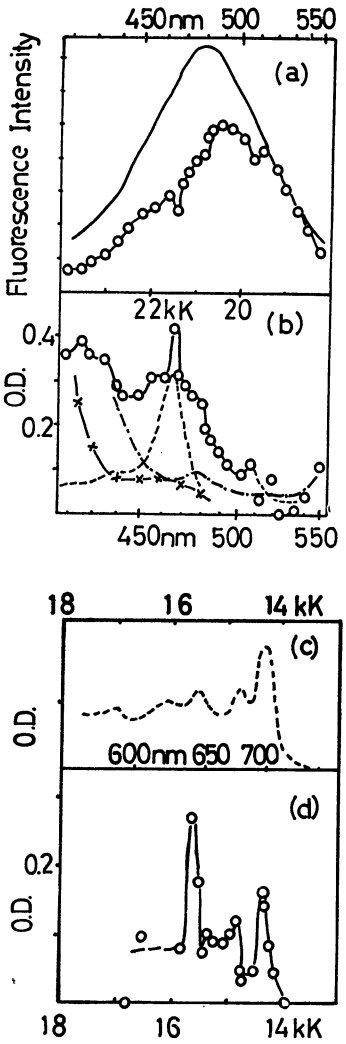

Fig. 5. Fluorescence spectra and the transient absorption spectra of TCNB-naphthalene complex in PMMA at room temperature.
(a) Fluorescence spectra obtained by laser excitation of high intensity (-O-O-) and by laser excitation of low intensity (——).
(b) The transient absorption spectra (-O-O-) and the $T_n \leftarrow T_1$ spectra observed previously[7] (-×-×-). The absorption spectra of TCNB anion[14] (----) as well as naphthalene cation (—·—·—)[16] are included.
(c) The absorption spectra of naphthalene cation at longer wavelengths.[16]
(d) The $S_n \leftarrow S_1$ spectra of TCNB-naphthalene complex observed by nsec flash photolysis method.

occurs from the excited FC state, the contribution of the $T_n \leftarrow T_1$ spectra to the observed transient spectra should be taken into consideration. The transient absorption band with maximum at about 21 kK cannot be ascribed to the TCNB anion produced by laser excitation, but is due to the fluorescent state of TCNB complexes which has a very polar structure, since the fluorescence at this wave number shows a particular nonexponential decay as shown in Fig. 6.

In the case of TCNB-toluene complex, the peak at 21.2 kK is similar to the band of TCNB anion.[14] A slight red shift and broadening of this band, compared to the case of the solution spectra of TCNB anion, can be noted. In the lower wave number region, no information is available by means of the present reabsorption method. In the present $S_n \leftarrow S_1$ spectra, one cannot observe any band which can be ascribed to the toluene cation.

In the transient spectra of TCNB-mesitylene system, the peak at 21.6 kK may be attributed to the TCNB anion-like component in the fluorescent state of the complex. In this case no red shift in comparison with the solution spectra of TCNB anion was observed. The broad band in the region of 22.4~24 kK may be attributed to the $T_n \leftarrow T_1$ transition, while the band at 20 kK may be ascribed to mesitylene cation-like

14) A. Ishitani and S. Nagakura, *Theoret. Chim. Acta (Berl.)*, **4**, 236 (1966).

component in the excited complex, since Badger and Brocklehurst have reported the cation band at 19.2 kK.[15]

Quite similar interpretation of the spectra may be possible also in the case of TCNB-durene-PMMA system. One can recognize a little broadening of 21.5 kK band. The band at about 18 kK may be related to the durene cation-like state in the fluorescent complex as well as the ^{3}CT state.[9]

In the case of TCNB-HMB complex, the bands in high wave number region cannot be obtained by the present re-absorption method. The band, 21.2 kK is similar to that of TCNB anion. The red shift and a little broadening of the latter band are observed. The absorption band in the low wave number region is almost identical with that of HMB cation.[15] The contribution of $T_n \leftarrow T_1$ absorption to the spectra is rather small.

The spectra of TCNB-naphthalene-PMMA system can be well reproduced by a superposition of the $T_n \leftarrow T_1$ spectra and the band similar to those of TCNB anion and naphthalene cation.[16] The peak at 21.4 kK and the shoulder at 20.8 kK are similar to those of TCNB anion and naphthalene cation, respectively. The strong broad band near 23 kK can be attributed to the superposition of the $T_n \leftarrow T_1$ spectra with large intensity and the $S_n \leftarrow S_1$ band similar to those of naphthalene cation. The similarity of the $S_n \leftarrow S_1$ band to the band of naphthalene cation can be observed clearly also in the low wavenumber region, where the spectra were measured by nsec flash photolysis method.[13]

These spectra are the first observations of the $S_n \leftarrow S_1$ spectra of EDA complexes at 77 K. Although the $S_n \leftarrow S_1$ spectra of TCNB complexes with benzene, toluene and mesitylene donors at room temperature have been reported,[1-3] the absorption spectra of TCNB complexes in the fluorescent state with rather strong donors such as durene, HMB and naphthalene are given for the first time in the present work.

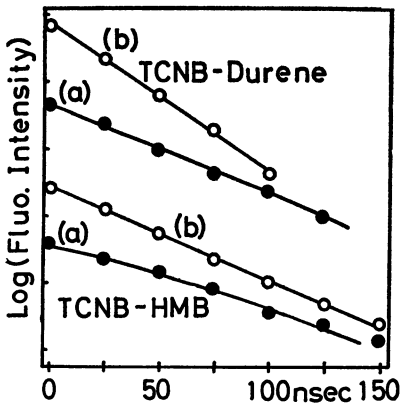

Fig. 6. Fluorescence decay curves of TCNB-durene and TCNB-HMB complexes. (a) 475 nm. (b) 515 nm. In the case of TCNB-mesitylene and TCNB-naphthalene complexes, similar results were obtained but the deviation from the exponential decay is small. The decay curve of TCNB-toluene complex in *n*P–*i*P has been reported in Ref. 12.

Discussion

The $S_n \leftarrow S_1$ spectra of the present TCNB complexes at 77 K can be well reproduced by the superposition of the bands similar to those of TCNB anion as well as donor cation. Although the wave numbers and bandwidths of the ion-like bands in the $S_n \leftarrow S_1$ spectra are a little different from those of the free ions in solution, the electronic structures of the fluorescent states may be concluded to be quite polar in general even at 77 K, irrespectively of the donors. This result is the same as that obtained from some TCNB complexes at room temperature. Since it can be expected theoretically[17] that the CT degree of the excited FC state is not so large as that of the fluorescent state and depends on the strength of the donor, there may exist a relaxation process involving structural changes as well as solvent re-orientation from the excited FC state to the fluorescent state, leading to the quite polar structure.[2]

The $S_n \leftarrow S_1$ spectra of the present complexes may be compared with the spectra of ionic radical salts, since the latter are deemed to be composed of donor cation and acceptor anion. The characteristics of the spectra of some ionic radical salts are summarized as follows.[18-20] (1) The blue shift of the bands associated with component ions is observed to be about 2~4 kK. (2) The absorption bands of the original ions are broadened. (3) The CT transition from acceptor anion to donor cation is observed in the near-infrared region, which is not obtained in solution spectra of both ions. The shift as well as the broadening of the bands of component ions in the present case of the TCNB complexes are rather different from those of the ionic radical salts. On the other hand, Kimura et al. have reported electronic spectra of ion-pair produced by irradiating EDA complexes and those of photoionized molecules in rigid solution and have pointed out a slight red shift of the ion bands in the ion-pair.[21] These comparisons suggest that the component ions in the fluorescent state of TCNB complexes does not interact with each other through the overlap integrals as in the case of ionic radical salts, but are influenced only by electrostatic interaction between both ions. Since fluorescence, which is accompanied with an electron transfer from anion to cation, is observed, it is concluded that the fluorescent state of these complexes at 77 K is not a solvent-shared but a contact ion-pair. However, the latter ion-pair

15) B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **65**, 2582 (1969).
16) B. Badger and B. Brocklehurst, *ibid.*, **65**, 2588 (1969); T. Shida and W. H. Hamill, *J. Chem. Phys.*, **44**, 2375 (1966).
17) S. Iwata, J. Tanaka, S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).
18) T. Amano, H. Kuroda, and H. Akamatu, This Bulletin, **41**, 83 (1968).
19) H. Kuroda, S. Hiroma, and H. Akamatu, *ibid.*, **41**, 2855 (1968).
20) Y. Iida, *ibid.*, **42**, 71 (1969).
21) K. Kimura, S. Katsumata, and K. Sawada, *J. Phys. Chem.*, **76**, 639 (1972); Y. Achiba, S. Katsumata, and K. Kimura, Preprint for the Symposium on EDA Complexes, Sendai, 1971.

may be strongly solvated, which leads to weak interaction. Although the CT band is reported in the case of ionic radical salts, we have observed no back CT transition from TCNB anion to donor cation in the $S_n \leftarrow S_1$ spectra. This result is consistent with the above conclusion.

Now it is interesting to discuss generally the electronic structure of the excited EDA systems such as ^{1}CT as well as ^{3}CT states of EDA complexes and heteroexcimer. In the case of heteroexcimer formed through the quenching of aromatic hydrocarbon by aromatic amines and nitriles, the polar character of the electronic structure has been confirmed by a number of investigations.[22] The direct observation of the electronic spectra of heteroexcimer has been made possible by nsec flash photolysis. Potashnik *et al.* reported the spectra of diethylaniline-aromatic hydrocarbon systems, which seem to be interpretable as originating from the local transitions in aromatic hydrocarbon anion as well as dietylaniline cation and the back CT transition from anion to cation.[4] Similar results have been obtained in the pyrene–dimethylaniline systems in various solvents and also in the case of the intramolecular EDA systems containing the aromatic hydrocarbon and dimethylaniline moieties in the same molecule.[5] In the case of ^{3}CT state of TCNB complexes with methylsubstituted benzene donors, the CT degree was concluded to increase with the decrease of ionization potential of donor.[23] The CT degree of TCNB-HMB complex in the phosphorescent state was calculated to be about 95%. Thus, its electronic structure is quite polar. Therefore, it seems to be appropriate to study on the electronic structure of ^{1}CT state of the present TCNB complexes, ^{3}CT state of TCNB-HMB complex and the above mentioned heteroexcimer, based on the interaction between donor cation and acceptor anion.

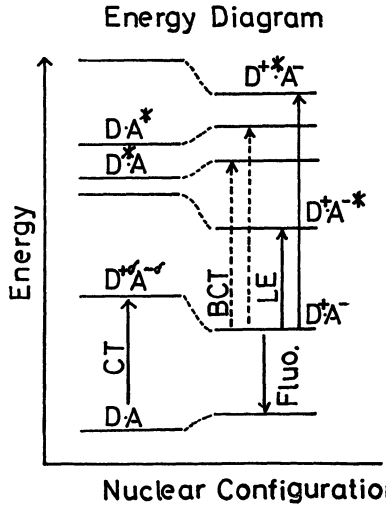

Fig. 7. Energy diagram of ground, CT and locally excited configurations of donor, acceptor as well as component ions. LE; local excitations of donor cation or acceptor anion. BCT; back CT transition from acceptor anion to donor cation.

We made a theoretical study on the fluorescent state by considering the configuration interactions (CI) among the ground, CT, back CT configurations and locally excited configurations of the acceptor anion-donor cation system.[2] This method may be useful also in analyzing ^{3}CT state of TCNB-HMB complex and the fluorescent state of heteroexcimer. The wave functions of several configurations may be given in the same form as in the previous paper.[2] The energies of the locally excited configurations of anion and cation may be taken from the observed values of the ions. It is rather difficult to estimate the energy of back CT transition from acceptor anion to donor cation. We have proposed a semiempirical method for obtaining the latter transition energy in terms of the rearrangement energy.[2] As indicated in Fig. 7, the transition energy can be given as

$$E(\text{back CT}) = E(\text{D*A}) \text{ or } E(\text{DA*}) - h\nu_{\text{f, 0-0}} + E_{\text{rea}}$$

where E(D*A) and E(DA*) represent the energies of locally excited configurations of donor and of acceptor, respectively, and $h\nu_{\text{f,0-0}}$ is the 0–0 band of fluorescence. E_{rea} is the rearrangement energy in question. Two methods for the evaluation of E_{rea} were proposed. In one method, it is assumed that E_{rea} involves the effects of the change of the geometrical structure and the CT degree in the higher excited state of the complex. In the other method, it is assumed that the contribution of the solvation energy to E_{rea} is overwhelming. The latter method is applied in the present work, since the problem of the structural change in the higher excited state is not yet elucidated. Putting E_{rea} as E_{des}, destablization energy in the FC ground state due to the solvent orientation, one can obtain the following equation.

$$\begin{aligned} E(\text{back CT}) &= E(\text{D*A}) \text{ or } E(\text{DA*}) - h\nu_{\text{f, 0-0}} + E_{\text{des}} \\ &= E(\text{D*A}) \text{ or } E(\text{DA*}) - h\nu_{\text{f, max}} \end{aligned}$$

where $h\nu_{\text{f,max}}$ represents the fluorescence maximum energy. The nondiagonal terms of CI secular equation should be evaluated theoretically using open shell MO.

Using the above theoretical treatment, we will now discuss the electronic structures of some excited EDA systems. In the first place, the $S_n \leftarrow S_1$ spectra of the present TCNB complexes and the absorption spectra of heteroeximers will be examined. The spectra of heteroexcimers were assigned to the transition associated with component ions and to the back CT transitions, where the intensities of both transitions are in the same order.[4] This assignment is consistent with theoretical model proposed by us. On the other hand, no large band due to back CT transition was observed

22) N. Mataga, T. Okada and N. Yamamoto, This Bulletin, **39**, 2562 (1966); H. Beens, H. Knibbe and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967); H. Beens and A. Weller, *Acta Phys. Polon.*, **34**, 593 (1968); D. Rehm and A. Weller, *Z. Phys. Chem. N. F.*, **69**, 183 (1970); A. Weller, "Nobel Symposium 5, Fast Reactions and Primary Processes in Chemical Kinetics," ed. by S. Claesson, Almqvist and Wiskell, Stockholm (1967), p. 413; T. Okada, H. Oohari, and N. Mataga, This Bulletin, **43**, 2750 (1970); N. Mataga, T. Okada, and K. Ezumi, *Mol. Phys.*, **10**, 201, 203 (1966).

23) H. Hayashi, S. Iwata, and S. Nagakura, *J. Chem. Phys.*, **50**, 993 (1969).

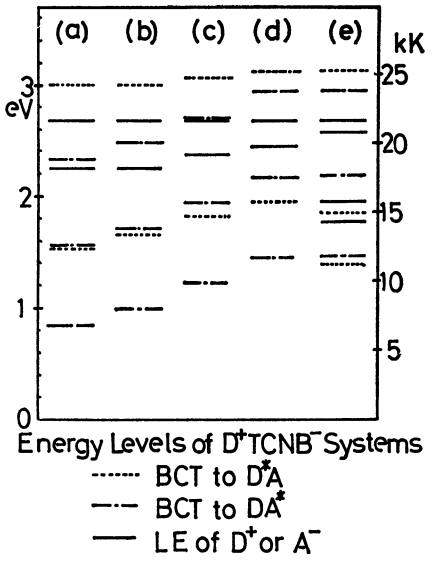

Fig. 8. Estimated energy levels for higher excited states of donor cation-TCNB anion system. The energy of fluorescent state of some TCNB complexes at 77 K was set as the standard. Donors are (a) benzene (b) toluene (c) mesitylene (d) HMB and (e) naphthalene. The energy levels of TCNB-durene complex are omitted since the precise value of higher excited state of durene is not known. However, almost the same values as in the case of TCNB-HMB complex are expected. Each value is estimated, using the data of Refs. 10, 24 and 25.

in the present work, which is the important difference between the ^{1}CT state of EDA complex and heteroexcimer. We have estimated the back CT transition energy using the above theoretical model and obtained the results as shown in Fig. 8. Here only *ungerade* states of locally excited configurations of donor as well as acceptor are included, although notations of *gerade* and *ungerade* are meaningless in the symmetry of the EDA complex. There may be more locally excited configurations, which corresponds to the *gerade* state of component molecules, and more back CT transitions may be expected. However, we have observed no absorption bands other than those due to the transitions associated with component ions. Since back CT transitions are forbidden without CI interaction the mixing of the back CT and locally excited configuration is required for the observation of these transitions. The fact that it is possible to observe the back CT transitions in the case of heteroexcimer means the more extensive mixing of both configurations than in the case of ^{1}CT state of the TCNB complexes. Hence, it may be concluded that ^{1}CT state of TCNB complexes at 77 K is more polar than heteroexcimer.

In the second, the $S_n \leftarrow S_1$ spectra of the present complexes and $T_n \leftarrow T_1$ spectra of TCNB-HMB complex will be discussed. Because the diagonal terms are the same in both cases, there may be nondiagonal matrix element that leads to the different electronic spectra. In the first approximation, the matrix elements between CT and other configurations may be important for elucidating the electronic structure of both of lowest singlet and triplet states. Under the condition of neglecting intermolecular differential overlap integrals, the matrix elements of the triplet state are identical with those of the singlet state and consist of one core attraction term.[7] Assuming the same geometrical structure in the fluorescent and phosphorescent states, it is expected that the $T_n \leftarrow T_1$ spectra are similar to $S_n \leftarrow S_1$ spectra. However, the observed results are different from this expectation and in the $T_n \leftarrow T_1$ spectra[7] we have found no band which coincides with that of TCNB anion. This result may be attributed to the difference of CT degree of the triplet state from that of the singlet state which may have different geometries, contrary to the above treatment.

We have made clear that the observed $S_n \leftarrow S_1$ spectra similar to those of TCNB anion can be explained statisfactorily when donor cation and acceptor anion are completely overlapped each other in C_{2v} symmetry or when both ions are loosely interacting with each other at a longer distance.[2] Moreover the CT degree was determined to be $\sim$100% in the case of these geometrical configurations. Thus, it is concluded that the CT degree in the phosphorescent state of TCNB-HMB complex is lower than that in the fluorescent state and the geometrical configurations of the former state are different from those of the latter. Moreover, the CT degree in the ^{3}CT state of the TCNB-HMB complex may be lower than that of heteroexcimer since any band similar to that of the acceptor anion was not observed in the case of the former system.

Now it is concluded that the CT degree increases in the following order; ^{3}CT state of TCNB-HMB complex < heteroexcimer < ^{1}CT state of some TCNB complexes.

24) T. Kobayashi, K. Yoshihara, and S. Nagakura, This Bulletin, **44**, 2603 (1971).

25) "UV Atlas of Organic Compounds," Butterworth, London (1966).