Effects of External Pressure on the Light Absorption and Fluorescence of *s*-Tetracyanobenzene Complexes

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The effects of high pressure on the charge-transfer (CT) absorption and fluorescence spectra of tetracyanobenzene (TCNB) complexes at room temperature have been examined. The pressure-induced change in the absorption intensity indicated the reduction of the distance between donor and acceptor in the complex and the increase in the overlap between their electron clouds. The pressure-induced red shifts of the absorption and fluorescence spectra were almost equal to each other in the case of the TCNB-toluene system, but the former shift was larger than the latter shift in the case of the TCNB-mesitylene system. These results were interpreted in terms of the reduction of the donor-acceptor distance in the complex as well as in terms of electrical solute-solvent interactions. It has been confirmed that the fluorescence quantum yield and the decay time of the complex decrease with the increase in the pressure, and that the rate of the decrease of the former is much larger than that of the latter, in the case of TCNB-toluene system. These results have been interpreted as being due to the pressure-induced increase in the quenching process at the Franck-Condon excited state as well as in the course of the relaxation process from the excited Franck-Condon state to the equilibrium fluorescent state.

It is well-known from recent experimental results that, on going from vapor to the condensed phase, optical-absorption spectra of weak EDA (electron donor-acceptor) complexes undergo quite remark able changes.[2–5] That is, the CT absorption bands of such complexes as tetracyanoethylene-aromatic and iodine-aromatic systems show red shifts of 1000—4000 cm^{-1} and an intensity enhancement of 200—800% upon this phase change. Furthermore, these effects can be facilitated by an external high pressure added to the condensed phase.[5,6]

It should be noted that the above spectral changes are much larger in the case of weak complexes than in the case of strong complexes or free molecules. It has been argued[4,5,7–9] that these spectral changes in the weak EDA complexes may be related to the reduction in the distance between the component molecules in the complex, which is itself caused by the internal compressional force of the solvent or the host and also by the external pressure. For example, Trotter[7] has pointed out on the basis of statistical mechanical calculations, that liquids exert an internal mechanical pressure of the order of 10^3—10^4 atm on dissolved molecules, and this pressure causes a very large vapor-to-liquid change in the spectra of weak complexes.

It seems that it would be interesting and important to study the effect of high pressure not only on the absorption spectra but also on the fluorescence spectra of EDA complexes. Offen and his co-workers[8,9] have examined the high pressure effect on the absorption and fluorescence spectra of some EDA complexes contained in high polymer matrices. According to their results, *e.g.*, in the case of the TCPA (tetrachlorophthalic anhydride) complexes with aromatic hydrocarbons in a polymethylmethacrylate matrix, the fluorescence spectra showed a much smaller pressure-induced red shift than the absorption spectra. This difference was explained in terms of the potential energy curves for the ground and excited states characterizing the molecular complex. Moreover, the absorption intensity increased, while the fluorescence intensity decreased, as the pressure was increased. The extent of the decrease in the fluorescence intensity was larger than that of the enhancement of the absorption intensity. At any rate, this fact appears to indicate an increase in the quenching process due to the external pressure, though its mechanism is not clear.

As far as we know, there has been no quantitative study of the EDA complex in a liquid solution in which the pressure effects upon both fluorescence and absorption spectral shifts, and upon the fluorescence quantum yields and decay times are investigated. We have, therefore, undertaken a systematic study concerning the high pressure effects on the EDA interactions in the electronic ground state as well as in the excited state, including the weak EDA complex formation, the contact CT interactions, and the exciplex formation in solution. In the present report, we shall describe the results of our study of the TCNB-toluene system, the fluorescence behavior of which has been studied previously in some detail under 1 atom,[10] and also the results of some studies of the TCNB-mesitylene system.

Experimental

The TCNB was the same sample as was used before.[10]

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[4] J. Prochorow and A. Tramer, *J. Chem. Phys.*, **44**, 4545 (1966).

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The toluene was purified by the method described in the literature.[11] The mesitylene was distilled carefully under reduced pressure. The fluorescence spectra were measured with an Aminco-Bowman spectrophotofluorometer which had been calibrated to obtain the correct fluorescence quantum spectrum, while the absorption spectra were measured by means of a Cary 15 spectrometer. The fluorescence spectra were excited exclusively at the wavelength of the first CT absorption band. The fluorescence decay times were measured with a giant pulse ruby laser which has an output powder of 1.5 J and a 15—20 nsec pulse width, or with a pulsed nitrogen gas laser. The exciting light pulse from the ruby laser was produced by an ADP frequency doubler which converted *ca.* 8 per cent of the energy of the 694 nm beam to that of the 347 nm beam. The light pulse of the nitrogen gas laser had an output power of 10 kW and a duration of 3 nsec. Its repetition rate was *ca.* 50 Hz. The fluorescence emission was observed with a travelling wave-pulsed photomultiplier. The outputs from the photomultiplier with a delay line were displayed on an X-Y recorder.

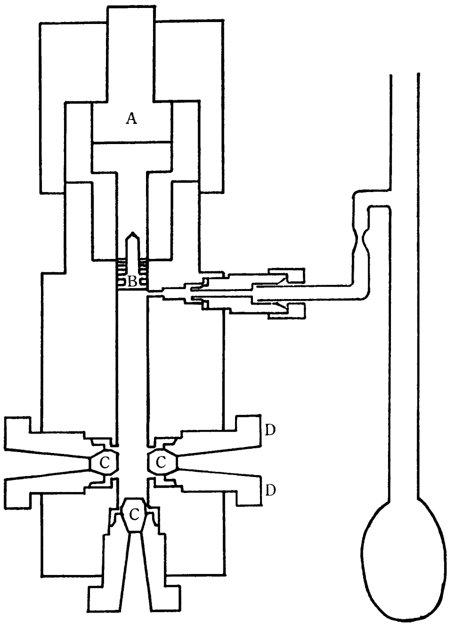

Fig. 1. High pressure optical cell.
A. Low pressure piston, B. High pressure piston
C. Sapphier window, D. Window plug.

Figure 1 shows a cross section of the high-pressure optical cell, the cell is reasonably small, is portable, and can be introduced into various spectrometers and other optical setups. All the metallic parts of the cell, including the pistons and window plugs, are made of copper-beryllium alloy. In order to prevent the leakage of solutions through gaps in the regions of the sapphire-metal contact and metal-metal contacts at the windows and piston parts, various packings, such as teflon, lead, and Viton A of du Pont, were used. The deaeration of the solution was conducted as follows. The solution in an ampoule, which was connected with the high-pressure cell, was deaerated by freeze-pump-thaw cycles. The deaerated solution was then transferred to the high-pressure cell and the transfer glass tube was sealed off. The highest pressure which could be applied to the solution in our high-pressure optical cell was *ca.* 8000 atm.

Results and Discussion

The absorption and fluorescence spectra of the TCNB-toluene system under various external pressures are indicated in Fig. 2. The first absorption band of the TCNB-toluene complex appears only as a shoulder at *ca.* 29000 cm^{-1}; one cannot observe any distinct peak, even under 7000 atom. However, as is shown in Fig. 3, the rate of the pressure-induced increase in its absorbance is much larger than that of the density of the solvent. Moreover, the rate of the absorbance increase is much larger at longer wavelengths than at shorter wavelengths. The latter fact indicates that the pressure-induced red shift of the first absorption band occurs. We have estimated the wave numbers of the first absorption maximum at various external pressures by subtracting the contributions of the strong second band from the spectra. The results are shown in Fig. 4, where a similar spectral shift of the fluorescence band is also indicated.

We have also carried out quite similar studies of the spectra of the TCNB-mesitylene two-component system. The TCNB-mesitylene complex is stronger than the TCNB-toluene complex and shows a distinct CT

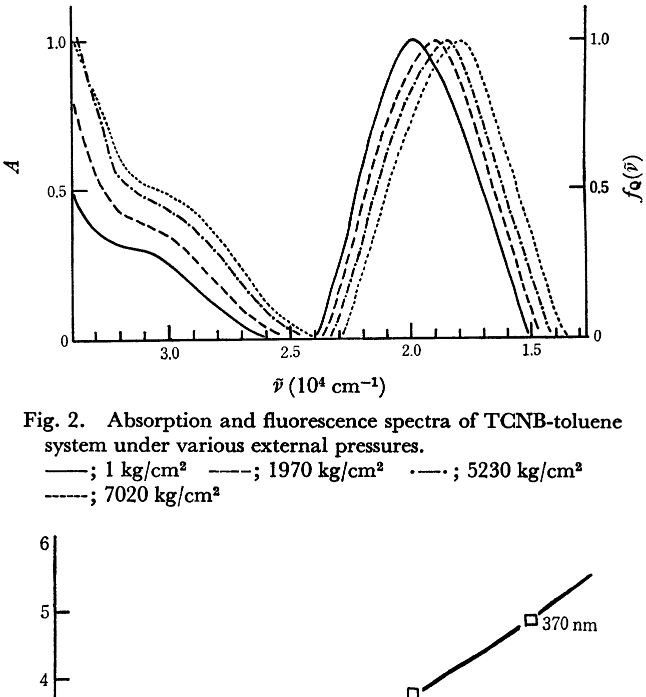

Fig. 2. Absorption and fluorescence spectra of TCNB-toluene system under various external pressures.
——; 1 kg/cm^2 – – –; 1970 kg/cm^2 ·—·; 5230 kg/cm^2
······; 7020 kg/cm^2

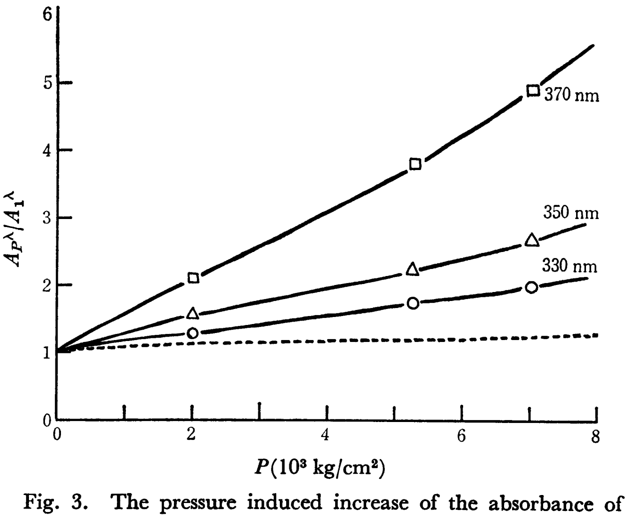

Fig. 3. The pressure induced increase of the absorbance of TCNB-toluene system in comparison with that of the density of toluene. A_P^{λ} represents the absorbance under pressure P (at λ nm). ------density of toluene.

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[11] A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, New York, N. Y. (1955). p. 318

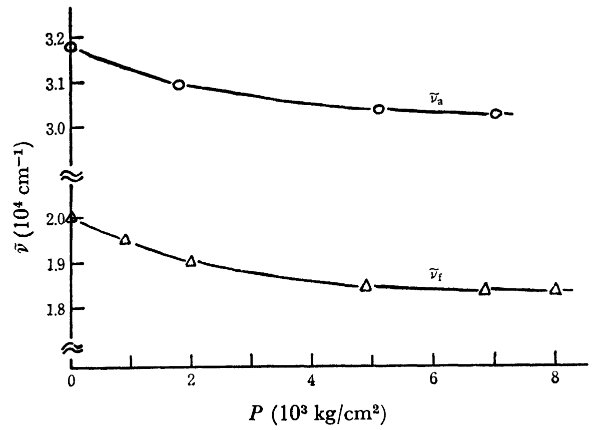

Fig. 4. Dependence of the wave numbers of absorption ($\tilde{\nu}_a$) and fluorescence ($\tilde{\nu}_f$) band maxima of TCNB-toluene system on the external pressure.

absorption maximum at *ca.* 28200 cm^{-1}. The effects of the external high pressures (at most, ~3000 atm, since the solidification of mesitylene occurs at higher pressures) are indicated in Figs. 5 and 6. One may see that the results are rather different from those in the TCNB-toluene system.

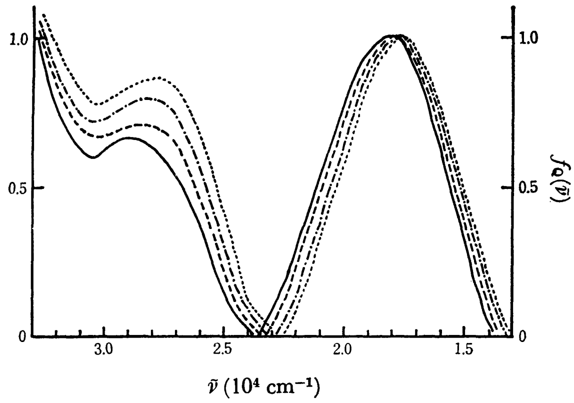

Fig. 5. Absorption and fluorescence spectra of TCNB-mesitylene system under various external pressures.
——; 1 kg/cm^2 ——; 790 kg/cm^2 —·—·; 2100 kg/cm^2
------; 2990 kg/cm^2

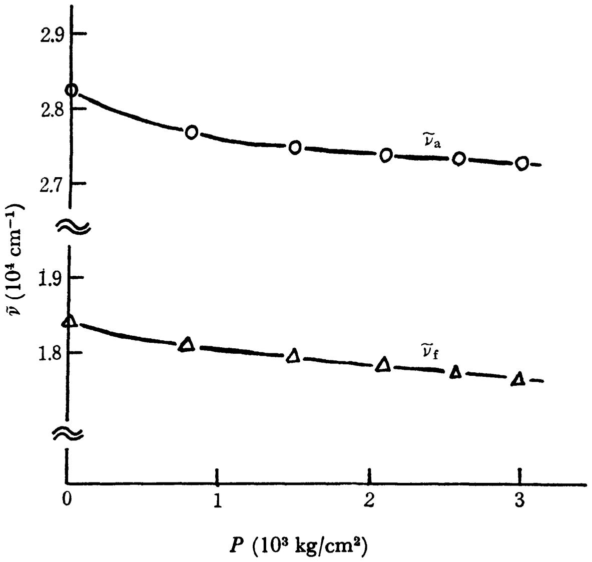

Fig. 6. Dependence of $\tilde{\nu}_a$ and $\tilde{\nu}_f$ values of TCNB-mesitylene system on the external pressure.

The pressure-induced change in the absorbance corrected for the volume contraction might be attributed to the increase in the solvent refractive index, n, at high pressures. Although n values of mesitylene[12] have been observed under various external pressures, we have no such values for toluene. We have estimated the n values for toluene by means of the Debye equation as well as by means of the Onsager equation for dielectric polarization,[13] using the observed values of density and the dielectric constant of toluene under various external pressures.[14,15] The two equations gave practically the same values. By employing these n values, we have made a rough estimation of the pressure-induced absorbance change according to Chako's simplified equation;[16]

$$A \propto f(n) \equiv \left(\frac{n^2+2}{3}\right)^2 / n$$

Table 1. Comparison of the integrated absoption intensity (A) with Chako's function $f(n)$

P(kg/cm^2)	A_P/A_1	$f_P(n)/f_1(n)$
	TCNB-toluene system	
1970	1.09	1.04
5230	1.13	1.08
7020	1.19	1.11
	TCNB-mesitylene system	
790	1.03	1.02
1480	1.06	1.03
2100	1.07	1.04
2580	1.08	1.05
2990	1.12	1.06

A_P: integrated absorbance under pressure P.
$f_P(n)$: Chako's function under pressure P.

One can see from Table 1 that the pressure-induced absorbance increases as corrected for the change in the refractive index, are rather small. However, the corrected increase for the TCNB-mesitylene system appears a little larger than that of the TCNB-toluene system.

One should note here that there are opposing effects of the external pressure upon the intensity of the CT absorption band of TCNB complexes. That is, there occurs a reduction in the donor-acceptor distance in the complex; this reduction, on the one hand, increases the orbital overlap between the partners in the complex, causing the enhancement of the CT absorption intensity. On the other hand, the decrease in the donor-acceptor distance in the complex presumably makes the excited state more ionic, thus reducing the con-

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[12] D. W. Langer and R. A. Montalvo, *J. Chem. Phys.*, **49**, 1836 (1968).

[13] H. Fröhlich, "Theory of Dielectrics," Oxford at the Clarendon Press (1949), p. 33; S. Oka, "Theory of Dielectrics" (in Japanese), Iwanamishoten, Tokyo (1954), p. 135.

[14] J. F. Skinner, E. L. Cussler, and R. M. Fuoss, *J. Phys. Chem.*, **72**, 1057 (1968): W. E. Danforth, Jr., *Phys. Rev.*, **38**, 1224 (1931).

[15] Z. T. Chang, *Chinese J. Phys.*, **1**. 1 (1933).

[16] N. Chako, *J. Phys. Chem.*, **2**, 644 (1934).

tribution from the locally-excited configuration, which in turn decreases the absorption intensity because of the decrease in the intensity borrowing from the locally-excited state of TCNB. Moreover, if a pressure-induced change in the geometrical structure of the complex from an unsymmetrical structure to a symmetrical overlapping one occurs, the CT transition probability is decreased.[17,18] Becasuse these effects cancel each other out, the appearent increase in the absorption intensity may be rather small. Therefore, one should not exclude the possibility of the pressure-induced reduction of the donor-acceptor distance in the complex in interpreting the other spectral behavior of these complexes, even if the pressure-induced net increase in the absorbance is small.

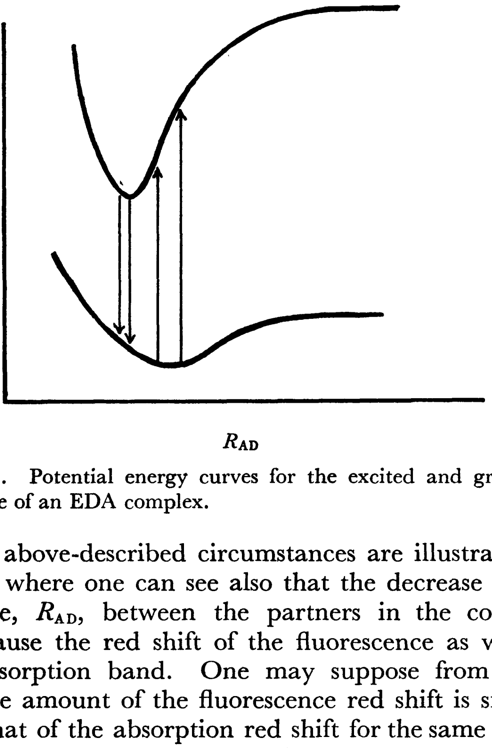

Fig. 7. Potential energy curves for the excited and ground state of an EDA complex.

The above-described circumstances are illustrated in Fig. 7, where one can see also that the decrease in the distance, R_{AD}, between the partners in the complex may cause the red shift of the fluorescence as well as the absorption band. One may suppose from Fig. 7 that the amount of the fluorescence red shift is smaller than that of the absorption red shift for the same added external pressure, as a result of the difference between the potential energy curves for the excited and ground states of the complex. Such an example was actually observed, as we have previously described, in the case of TCPA complexes in high polymer matrices.[8,9) In the case of a liquid solution, however, dielectric polarization interactions between the surrounding solvent molecules and the complex in the fluorecent state may be larger than in the case of solid solution, leading to a stronger fluorescence red shift. Nevertheless, the extent of the fluorescence red shift is considerably smaller than that of the absorption in the case of the TCNB-mesitylene system (Fig. 6). The solute-solvent dielectric interaction seems to be larger in the case of the TCNB-toluene system than in the case of the TCNB-mesitylene system. Thus, for the former system, the magnitude of the pressure-induced red shift of the fluorescence spectrum is almost the same as that of the absorption spectrum. On the other hand, the fact that both the absorption and fluorescence spectral shifts became almost saturated at about 6500 atm in the case of the TCNB-toluene does not seem to be interpreted satisfactorily by the ordinary theory of the solvent shift of spectra, since the solvent refractive index and the dielectric constant do not show such a strong saturation effect at pressures of 6000—7000 atm. We can also observe, in the case of the TCNB-mesitylene system (Fig. 6), a tendency for the spectral shifts to become saturated, even at 3000 atm. These results can be explained, at least qualitatively, as due to the structure change in the complex caused by the external pressure. That is, when R_{AD} becames smaller, the complex becomes stronger, and the pressure effect on the spectral shift becomes smaller, because of the enhanced blue-shift contribution from the resonance interaction between the no-bond and CT structure, as has been suggested by Kadhim and Offen.[9] Thus, the pressure-induced spectral shift in our present system may be ascribed to combined effects due to CT forces and potential energy curves appropriate for weak complexes as well as to dielectric polarization interactions between the complex and surrounding solvent molecules.

TABLE 2. FLUORESCENCE QUANTUM YIELDS (η_F) AND DECAY TIMES (τ_F) AT VARIOUS PRESSURES

P(kg/cm^2)	η_F[a]	τ_F(nsec)
	TCNB-toluene system	
1	1.00(0.080)	109
2070	0.54(0.035)	82
5010	0.13(0.010)	44
6920	0.07(0.006)	35
	TCNB-mesitylene system	
1	1.00(0.010)	45
790	0.84(0.0084)	41
1480	0.69(0.0069)	34
2100	0.65(0.0065)	30
2590	0.60(0.0060)	28
2990	0.596(0.0059)	25

a) The values in parenthesis are absolute quantum yield. The values of the absolute quantum yield at 1 atm were taken from: T. Kobayashi, Y. Yoshihara, and S. Nagakura, The Symposium on EDA Complex (Osaka), 1970, Preprint.

For a closer examination of the behavior of the excited complex, it is necessary to measure the fluorescence quantum yields and decay times under various external pressures. The results of our measurements are indicated in Table 2. One can see from Table 2 that both the relative fluorescence quantum yield and the fluorescence decay time decrease with the increase in the external pressure. In the case of the TCNB-toluene system, where the fluorescence decay time was measured by means of the giant pulse laser, the rate of decrease in the quantum yield is considerably larger than that of the decay time. Therefore according to the $K_F=\eta_F/\tau_F$ equation, the radiative transition probability decreases with the pressure increase. However, it should be noted here that the above statement is valid only if the quenching process at the excited

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17) S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).

18) H. Masuhara and N. Mataga, *ibid.*, to be published.

Franck-Condon (F.C.) state as well as in the course of the relaxation from the excited F.C. state to the equilibrium (e.q.) fluorescent state is not affected by the added pressure.

On the other hand, as has been elucidated in previous works,[10,19,20] the energy and the electronic structure of the excited F.C. state of the TCNB-toluene system are very different from those of the e.q. excited state. It has been confirmed that the observed fluorescence decay time is much longer than the radiative lifetime calculated from the intensity of the absorption band, and there must occur a change in the electronic structure in the course of the relaxation from the excited F.C. state to the e.q. state. It was assumed that the anomalously long fluorescence decay time was due to the very polar structure of the excited e.q. state.[10] This assumption has been proved to be correct by measuring the absorption spectra of the complex in the fluorescent state, using the nanosecond laser photolysis method.[18,19,21] The relaxation from the excited F.C. state to the e.q. state is accompanied by a change in the geometrical structure of the complex from an asymmetrical structure to a symmetrical overlapping sandwich one as well as by a rearrangement of the surrounding solvent molecules, leading to stronger solvation, which in turn makers the probability of radiative transition smaller. Since the dielectric constant of the solvent increases with the pressure, it seems that the fluorescent state of the complex will become more strongly solvated under higher external pressure, leading to a decrease in the probability of radiative transition. However, this statement is not wholly valid, since the pressure-induced red shifts of the spectra cannot be interpreted satisfactorily in terms of the pressure-induced change in the macroscopic dielectric constant and the refractive index of the solvent, as has been discussed already.

According to the interpretation indicated in Fig. 7, the probability of radiative transition for the fluorescence will be enhanced by an increase in the external pressure, as a result of the increase in the orbital overlap between donor and acceptor. Then, it seems to be necessary to assume that the inner quenching processes at the excited F.C. state as well as in the course of the F.C.→ e.q. relaxation are enhanced by the external pressure.

According to the measurement of the time-resolved fluorescence spectra of the TCNB-toluene system under 1 atm,[20] the excited F.C.→ e.q. relaxation is very rapid (relaxation time $<10^{-9}$ sec) and the fluorescence can be regarded as being emitted exclusively from the e.q. state at room temperature. The time-resolved fluorescence spectrum becomes measurable only in a quite viscous, almost rigid solution at 147°K, by means of an apparatus with nanosecond time-resolving power.[20] Since the external pressure enhances the viscosity of the solution, the F.C.→ e.q. relaxation process might be slowed under high pressure. However, the fluorescence decay times of the TCNB-toluene system measured under 7500 atm at different wavelengths of the fluorescence band agreed with each other. Moreover, although we have tried to measure the time-resolved fluorescence spectrum of the TCNB-toluene system under 7500 atm by exciting the solution with nitrogen-gas laser, the spectra observed at various delay times from exciting pulse were not essentially different from each other. Thus, the F.C.→ e.q. relaxation under the high pressures applied here occurs rather rapidly during times smaller than nanosecond. Therefore, the pressure-induced inner quenching process at the F.C. state, and that in the course of the F.C.→ e.q. relaxation process, may occur far more rapidly than that at the e.q. state, which has a lifetime of 10^{-7}—10^{-8} sec.

Contrary to the case of the TCNB-toluene system, the rate of the decrease in the fluorescence quantum yield and that of the decay time caused by the external pressure are not very different from each other in the case of the TCNB-mesitylene system, where the decay time is measured by means of the nitrogen-gas laser. Therefore, the pressure-induced fluorescence quenching of the TCNB-mesitylene system may be said to occur mainly at the excited e.q. state.

Although the explanation for the different behavior of the TCNB-toluene and TCNB-mesitylene systems with respect to the pressure-induced fluorescence quenching is not clear at the present stage of investigation, the difference in the quenching process might be ascribed to the essential difference in electronic structures between the two system. That is, the energy difference and the difference in electronic structure between the excited F.C. and e.q. states are much greater in the case of the TCNB-toluene system than in the case of the TCNB-mesitylene system.

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21) R. Potashnik and M. Ottolenghi, *ibid.*, **6**, 525 (1970).