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ESR and Optical Studies on the EDA Complexes of Di-*t*-butyl-*N*-oxide Radical

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It has been confirmed that di-*t*-butyl-*N*-oxide (DTBNO) forms EDA complexes with various electron acceptors, and the resulting complexes show CT (charge transfer) absorption bands. Wave-numbers of the CT bands agreed satisfactorily with theory. Charge distributions in the EDA complexes of DTBNO, including hydrogen bonded complexes with proton donors, have been investigated by means of ESR. From the effect of the EDA complex formation upon the hyperfine coupling constant of ^{14}N of DTBNO, contribution of electrostatic forces to complex formation has been demonstrated. However, in the case of complexes with strong acceptors such as tetracyanoethylene, the values of the hyperfine coupling constant have indicated a significant contribution of CT interaction to complex formation.

The structures and properties of the EDA complexes have been studied extensively and are being subjected to active investigation. Among organic molecular complexes, there are numerous EDA complexes consisting of molecules with closed shell ground state.[2] However, little investigation has been carried out on the complexes in solution which have unpaired spins in the electronic ground state.

Studies on the ground state of molecular complexes have supported the CT theory,[2] but there are still some questions concerning the extent to which the classical electrostatic forces contribute to the binding energy and dipole moments of EDA complexes, especially in the case of weak complexes.[3-5] For example, Hanna[4] has shown that quadrupole-induced dipole forces may be comparable to CT forces in importance in explaining the stability of benzene-iodine and of similar complexes. Other authors have also insisted that the multipole-multipole and multipole-induced multipole interactions are important for the stability of π–π type EDA complexes.[3] Nevertheless, it seems

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[2] See for example, G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Göttingen, 1961; R. S. Mulliken and W. B. Person, "Molecular Complexes," A Lecture and Reprint Volume, John Wiley and Sons, New York, 1969.

[3] H. O. Hooper, *J. Chem. Phys.*, **41**, 599 (1964); M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron*, *Suppl.*, **7**, 97 (1956).

[4] M. W. Hanna, *J. Amer. Chem. Soc.*, **90**, 285 (1968); M. W. Hanna and D. E. Williams, *ibid.*, **90**, 5358 (1968); J. L. Lippert, M. W. Hanna, and P. J. Trotter, *ibid.*, **91**, 4035 (1969).

[5] R. S. Mulliken and W. B. Person, *ibid.*, **91**, 3409 (1969).

that there is no direct evidence for the predominant contributions of the electrostatic forces to the interactions in the complexes.

Elucidation of the above problem and CT interactions can be achieved by measurement of the ESR spectra of complexes which have unpaired spins in the ground state.

Since almost all radicals with doublet ground state are unstable, ESR studies are possible only for some complexes involving exceptionally stable radicals. We have found that DTBNO forms stable complexes with some electron acceptors, and studied the complexes by means of optical as well as ESR spectral measurements.

Experimental

The absorption spectra were measured with a Cary 15 spectrometer and a Shimadzu MPS-50L spectrophotometer. ESR spectra were recorded by a JES-3BX spectrometer of Japan Electron Optics using X-band.

DTBNO was synthesized according to the method given in literature,[6] and was purified by repeated distillation under reduced pressure. The purified sample was distilled in a vacuum and sealed off in parts. Tetracyanoethylene (TCNE) was recrystallized several times from monochlorobenzene and was sublimed in vacuum. Purified sample of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was kindly supplied by Dr. Y. Sato of this institute. Chloranil was recrystallized twice from benzene. 2,5-Dichloro-*p*-benzoquinone (DQ) and phthalic anhydride (PA) were sublimed under reduced pressure. Phenol was carefully distilled. Pyromellitic dianhydride (PMDA) was recrystallized twice from ethylacetate. *s*-Tetracyanobenzene (TCNB) was the same sample as used before.[7] It was recrystallized several times from ethanol and sublimed in a vacuum before use. Cyclohexane and *n*-hexane were passed through a column of activated silica gel twice, dried over metallic sodium, and distilled. Toluene and benzene were shaken with sulfuric acid, neutralized, and distilled. The distillate was passed through a column of activated silica gel, dried over metallic sodium and distilled. Tetrahydrofurane (THF) was refluxed over metallic sodium fifty hours, and distilled. Other solvents were purified by the methods described in literature.[8]

For ESR measurements, solutions in the sample tube were carefully deaerated by an ordinary procedure with an evacuating system equipped with a rotary and oil diffusion pump.

Results and Discussion

A. Optical Absorption Spectra. The visible absorption spectrum of DTBNO in *n*-hexane is given in Fig. 1. This absorption band can be assigned to the n–π^* transition.[9] When amines which can act as electron donors in the complex formation, are added to the solution of DTBNO, or when they are used as solvents for DTBNO, the absorption spectrum of DTBNO does not change. As will be discussed later in detail, the hyperfine coupling (hfc) constant due to the nitrogen atom of DTBNO dissolved in *N,N*-dimethylaniline (DMA) is almost the same as when it is dissolved in monochlorobenzene. The ionization potential of DMA is much smaller than that of monochlorobenzene while their dipolemoments or static dielectric constants are almost equal. Thus, it seems certain that DTBNO hardly works as an electron acceptor.

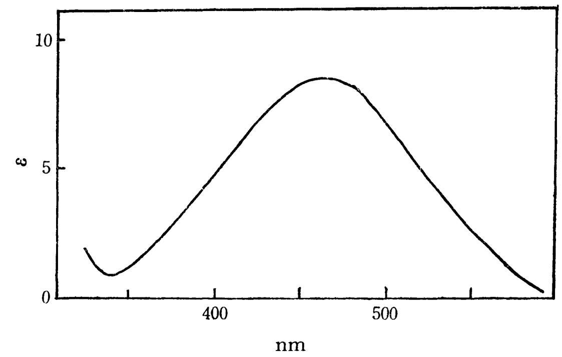

Fig. 1. Visible absorption spectrum of DTBNO in *n*-hexane at room temperature (~23°C).

On the other hand, when a strong electron acceptor such as TCNE or DDQ is added to the DTBNO solution, we can observe a new absorption band as indicated in Fig. 2. In a sufficiently polar solvent such as acetonitrile, we can observe clearly that the DTBNO-TCNE

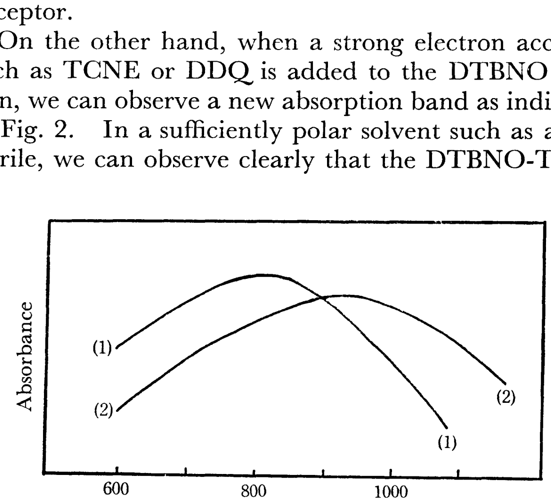

Fig. 2. Absorption spectra of DTBNO complexes in ether solution at room temperature (~23°C). Acceptors: (1) TCNE, (2) DDQ.

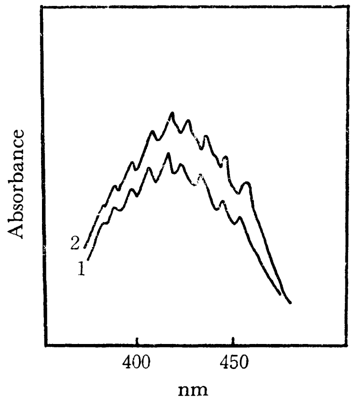

Fig. 3. Absorption band of TCNE anion observed for DTBNO-TCNE-acetonitrile system at room temperature (~23°C).

1. Immediately after mixing of DTBNO and TCNE solutions.
2. 10 min after the mixing.

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[6] A. K. Hoffman, *ibid.*, **86**, 641 (1964).

[7] N. Mataga and Y. Murata, *ibid.*, **91**, 3144 (1969).

[8] A. Weissberger, ed., "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, New York, N. Y. (1955).

[9] T. Kawamura, S. Matsunami, and T. Yonezawa, This Bulletin, **40**, 1111(1967).

system undergoes ionic dissociation and there arises the anion radical of TCNE (Fig. 3). The reaction of ion radical formation is not very rapid, and the produced TCNE anion is fairly stable even in the air.

We have examined the origin of the new absorption band in Fig. 2 by the method frequently used for usual EDA complexes. Application of the Benesi-Hildebrand equation[10] to the three component system, TCNE-DTBNO-diethylether, gives a good linear relation as shown in Fig. 4, from which the equilibrium constant for the complex formation has been evaluated to be 4.0 *l*/mol. Thus it is certain that DTBNO forms 1 : 1 complex with TCNE.

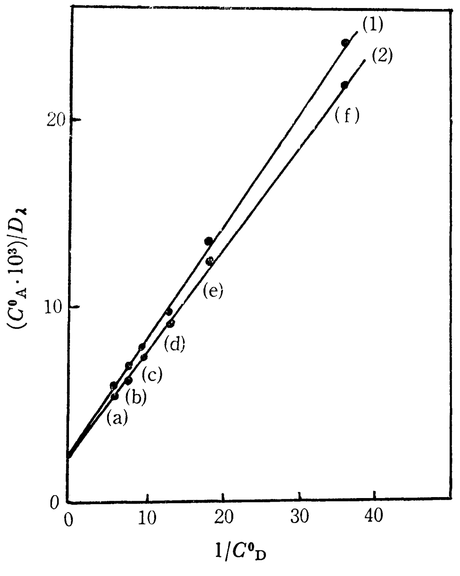

Fig. 4. Benesi-Hildebrand plot for DTBNO-TCNE system in ether at room temperature (~23°C). C^0_A and C^0_D are analytical concentrations of TCNE and DTBNO, respectively.
$C^0_A = 2.57 \times 10^{-3}$ M.
C^0_D: (a) 1.6×10^{-1} M, (b) 1.3×10^{-1} M, (c) 1.0×10^{-1} M, (d) 7.7×10^{-2} M, (e) 5.6×10^{-2} M, (f) 2.8×10^{-2} M.
1. at 850 nm, 2. at 790 nm.

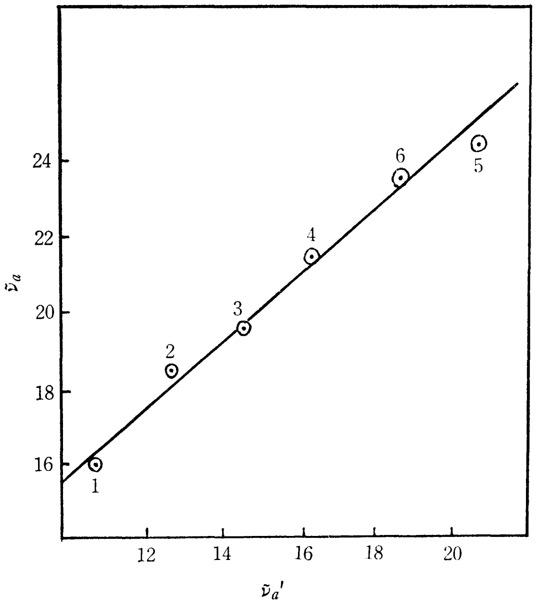

Fig. 5. Relation between the band maxima of the hexamethylbenzene complexes ($\tilde{\nu}_a$) and those of the DTBNO complexes ($\tilde{\nu}'_a$) for the common acceptors. See Table 1 for the numbering of the points in the figure.

The wavelengths of the new absorption bands which appeared when various electron acceptors are added to the solution are listed in Table 1. We see that the larger the electron affinity of the acceptor, the longer the wavelength of the absorption band. Furthermore, we have compared the wavenumbers of the absorption bands of DTBNO-acceptor systems with those of the CT absorption bands of hexamethylbenzene complexes with the same acceptors. As shown in Fig. 5, we have a linear relation which can be written approximately as

$$\tilde{\nu}'_a = \tilde{\nu}_a + \text{Const.} \tag{1}$$

For ordinary EDA complexes, the energy of the CT absorption band is approximately given by

$$h\nu_{CT} = I_D - E_A + C \tag{2}$$

where I_D, E_A, and C are ionization potential of the donor, electron affinity of the acceptor, and the interaction term including the coulomb energy between the ion-pair, respectively. The corresponding equation for the DTBNO complexes may be written as

Table 1. Wavelengths of absorption band maxima of DTBNO complexes with electron acceptors in several solvents (wavelength in nm)

Solvent	Acceptor					
	1. DDQ	1. TCNE	3. Chloranil	4. 2.5-Dichloro-*p*-benzoquinone	5. PMDA	6. TCNB
Ether	925	790	(a)	(a)	(a)	(a)
THF	925	790	685	610	480	—
Acetonitrile	(b)	anion	(a)	605	(a)	530
Electron affinity of acceptor (c)	1.9	1.80	1.3	1.1	0.8	0.4

(a) Because of the small solubilities of the acceptor and the small equilibrium constant of the complex formation, the new absorption band could not be detected.
(b) Immediately after the preparation of the solution, some chemical changes occured and the new absorption band of the complex was not observable.
(c) In units of electron volts. The numerical values were taken from G. Briegleb, Angew. Chem. International Ed., 3, 617 (1964).

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[10] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

TABLE 2. SOLVENT SHIFTS OF ABSORPTION BAND MAXIMA OF DTBNO

	Solvent	n	ε	$\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)$	$\lambda_{\max}$ (nm)
1	*n*-Hexane	1.375	1.89	0.000	466
2	Toluene	1.49413	2.379	0.022	461
3	Monochlorobenzene	1.5248	5.621	0.300	456
4	THF	1.4040	7.6	0.443	457
5	Benzonitrile	1.5282	25.20	0.582	454
6	Acetonitrile	1.3441	38.8	0.715	454
7	Ethanol	1.3614	24.30	0.664	441
8	Acetic acid	1.3716	6.15	0.405	428
9	Water	1.3330	81.0	0.758	421
10	*m*-Cresole	1.5438	11.8	0.467	418

$$h\nu_{\mathrm{CT}}'=I_{\mathrm{D}}'-E_{\mathrm{A}}+C' \qquad (3)$$

where I_{D}' is the ionization potential of DTBNO. Thus we have

$$\tilde{\nu}'_{\mathrm{CT}}\approx\tilde{\nu}_{\mathrm{CT}}+\mathrm{Const.} \qquad (4)$$

From the above arguments, it has been confirmed that DTBNO forms EDA complexes with various electron acceptors and the new absorption band due to the complex can be ascribed to the CT transition.

In connection with the CT interaction, we have examined the hydrogen bonding of DTBNO with several proton donors. The solvent effect upon the wave number of the visible absorption band of DTBNO is indicated in Table 2 and Fig. 6. In Fig. 6, the wave number is plotted against the factor $[(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)]$, where ε and n are the static dielectric constant and the refractive index of the solvent, respectively. The solvent shift of the electronic spectrum, when the short range interactions such as molecular complex formations are absent, can be given as a function of ε and n. As an example, the equation given by McRae[11] is

$$hc\Delta\tilde{\nu}_a\approx(AL_0+B)\frac{(n^2-1)}{(2n^2+1)}+C\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)+D\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right)^2 \qquad (5)$$

The second term on the right hand side of Eq. (5) comes from the permanent dipole-permanent dipole interaction between the solute and solvent molecules. The contribution of this term will be predominant in the present case, since DTBNO has a large dipolement (3.08D) in the ground state. As we see from Fig. 6, $\tilde{\nu}_a$ is approximately linear with respect to $[(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/((n^2+2)]$ when the solvent is not likely to form the hydrogen bond with DTBNO (from this linear relationship, we have estimated the dipolemoment of DTBNO in the lowest excited state to be 2.6D.). In the case of the solvent which seems to form hydrogen bond with DTBNO, the blue shift of the spectrum is large and the deviation from the linear relation is remarkable. The spectral behaviors in the hydrogen bonding solvents are quite similar to those of the *n*–*π** transitions of ordinary closed shell molecules. Of course, the hydrogen bonding interaction may also affect the distribution of the unpaired electron of DTBNO.

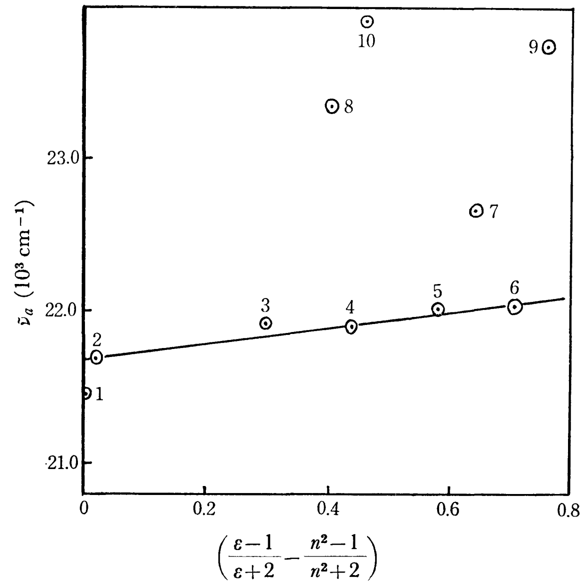

Fig. 6. Solvent shift of the absorption band of DTBNO. See Table 2 for the numbering of the points.

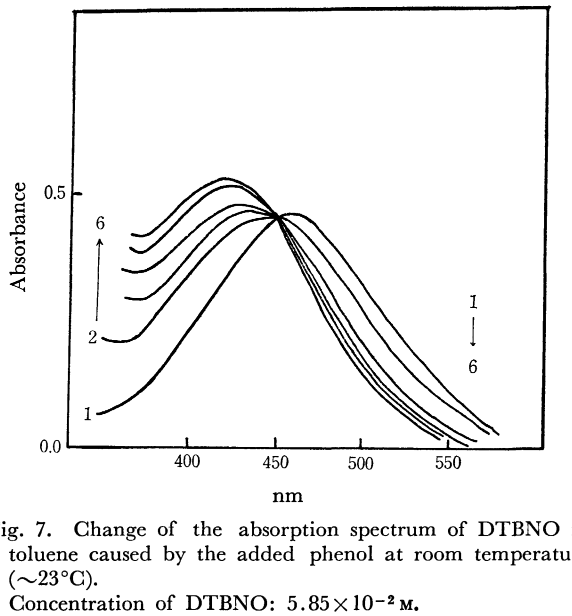

Fig. 7. Change of the absorption spectrum of DTBNO in toluene caused by the added phenol at room temperature (~23°C).
Concentration of DTBNO: 5.85×10^{-2} M.
Concentration of phenol: (1) 0, (2)—(6) 8.5×10^{-2} M—2.02M.

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[11] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

In order to make a more detailed study of the hydrogen bonding effect on the absorption spectrum, we have examined the three component system DTBNO-phenol in toluene. It is evident from Fig. 7 that there arises 1 : 1 hydrogen complex. We have evaluated equilibrium constant to be 6.4 *l*/mol at room temperature.

When trifluoroacetic acid, a strong proton donor, was added to the benzene solution of DTBNO, the visible absorption band of DTBNO vanished completely and a new absorption band with a maximum at *ca.* 700 nm appeared. In contrast to the case of DTBNO-phenol-toluene system, this benzene solution showing the new absorption band does not show any ESR signal. We have observed the absorption band at 700 nm also for the acetic acid solution of DTBNO when a small amount of concd. sulfuric acid is added to the solution. Although the origin of this long wavelength absorption band is not clear, it may be due to some product of unknown reaction occurring in a strongly acidic media.

B. ESR Spectra. The ESR spectrum of DTBNO in toluene solution at room temperature is shown in Fig. 8. It is possible that, in a highly concentrated solution, DTBNO forms a cluster which has a spin multiplicity greater than doublet. However, the ESR spectrum due to triplet or higher multiplet state could not be observed at room temperature. At 77°K the mixtures of DTBNO and cyclohexane (volume ratio 1 : 1 and 1 : 10) showed ESR spectrum due to triplet state ($\Delta m=2$ transition). From the spectrum we can evaluate the dipole-dipole interaction parameter D, which is directly related to the separation between two unpaired electrons. D/hc was found to be 0.0370 *cm.*$^{-1}$ By using the equation[12)]

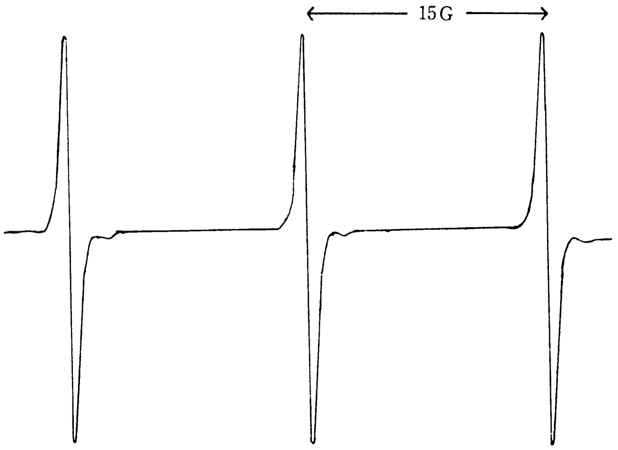

Fig. 8. ESR spectrum of DTBNO in toluene. Concentration of DTBNO: 10^{-4} M.

$$\tilde{r}_{12}=(2|D|/3\,g^2\beta^2)^{1/3} \qquad (6)$$

the average separation $\tilde{r}_{12}$ between two unpaired electrons was evaluated as 4.2 Å.

Hirota[12)] measured D/hc and $\tilde{r}_{12}$ for some ion radical pairs. For the anion radical of hexamethylacetone with lithium cation as gegen ion: $D/hc=0.0210$ *cm*$^{-1}$ and $\tilde{r}_{12}=5.0$ Å. For the same radical with sodium cation: $D/hc=0.0155$ cm^{-1} and $\tilde{r}_{12}=5.6$ Å. Since these radical pairs are ion-pair dimers, *i.e.* the gegen ion is placed between the two radical ions, their $\tilde{r}_{12}$ values are a little larger than that of DTBNO dimer. Though DTBNO molecules have bulky *t*-butyl groups which can more or less hinder the interactions between unpaired electrons, they can approach each other to form a triplet state dimer.

Let us examine the effect of the EDA complex formation on the ESR spectrum.

$$\mathrm{A}+\dot{\mathrm{D}} \rightleftarrows (\mathrm{A}\dot{\mathrm{D}}) \qquad (7)$$

According to Gendell *et al.*,[13)] when the complex formation and dissociation reaction of Eq. (7) is very rapid, the observable hfc constant $\bar{a}$ is given by

$$\bar{a}=\frac{1}{2}(a_{\mathrm{D}}+a_{\mathrm{AD}})+\frac{1}{2}(K[\mathrm{A}]-1)/(K[\mathrm{A}]+1)\,(a_{\mathrm{AD}}-a_{\mathrm{D}}) \qquad (8)$$

where a_{D} and a_{AD} are the coupling constants of $\dot{\mathrm{D}}$ and $\mathrm{A}\dot{\mathrm{D}}$, respectively, and K is the equilibrium constant of complex formation.

Equation (8) can be rewritten as[13)]

$$\bar{a}=a_{\mathrm{AD}}-\left(\frac{1}{K}\right)(\bar{a}-a_{\mathrm{D}})/[\mathrm{A}]. \qquad (9)$$

Validity of Eqs. (8) and (9) for the hydrogen bonded complex formation has been examined by several workers and it has been proved that these equations

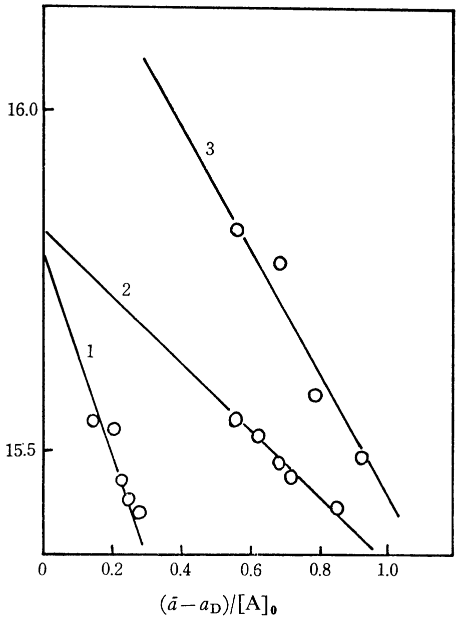

Fig. 9-a. $\bar{a}$ *vs.* $(\bar{a}-a_{\mathrm{D}})/[\mathrm{A}]_{\mathrm{D}}$ relation for DTBNO-electron acceptor systems. ($\bar{a}$ is the observed nitrogen hfc constant of DTBNO.)

	A	Solvent
1	PA	THF
2	TCNE	Toluene
3	PMDA	THF

[12)] N. Hirota, *J. Amer. Chem. Soc.*, **89**, 32 (1967).

[13)] J. Gendell, J. H. Freed, and G. K. Frenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

Table 3. Equilibrium constant of complex formation obtained by optical and ESR measurements and the values of nitrogen hfc constant of DTBNO complexes

	Optical spectra			ESR spectra		
	λ_{max} (nm)	K(M^{-1})	Solvent	$a_N(G)$	K(M^{-1})	Solvent
TCNE	790	4.0	Ether	15.82	5.0	Toluene
PMDA	480	—	THF	16.34	1.1	THF
PA	—	—	—	15.80	0.6	THF
Benzonitrile	—	—	—	15.9	0.1	Toluene
Acetonitrile	—	—	—	15.9	0.1	Toluene
Phenol	423	6.4	Toluene	16.80	6.7	Toluene

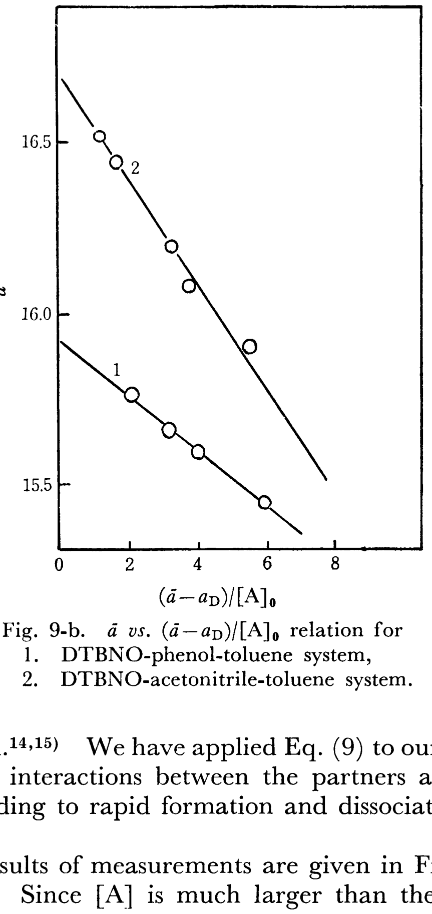

Fig. 9-b. $\bar{a}$ *vs.* $(\bar{a}-a_D)/[A]_0$ relation for
1. DTBNO-phenol-toluene system,
2. DTBNO-acetonitrile-toluene system.

are useful.[14,15] We have applied Eq. (9) to our systems, since the interactions between the partners are rather weak leading to rapid formation and dissociation reactions.

The results of measurements are given in Fig. 9 and Table 3. Since [A] is much larger than the concentration of DTBNO in our present systems, we can use the analytical concentration $[A]_0$ instead of [A], and we can evaluate K and a_{AD} from the plot of $\bar{a}$ against $(\bar{a}-a_D)/[A]_0$. As can be seen from Table 3, agreement between the K value obtained by optical spectral measurement and that estimated by ESR measurement is satisfactory. For some systems where optical measurement was not possible, K values were determined by means of ESR.

The interactions between the halves in the EDA complexes, which seem to affect the ESR spectra, will be the CT interaction and the electrostatic one, because both can affect the spin densities on DTBNO. According to the theory of Karplus and Frenkel,[16] the hfc constant of DTBNO nitrogen can be written as

$$a_N = Q_1\rho_N + Q_2\rho_o \qquad (10)$$

in terms of the spin densities on nitrogen and oxygen. As an example, Ayscough and Sargent[17] show that, for diphenyl-*N*-oxide, $a_N = 36.65\rho_N + 1.38\rho_O$ when Hückel MO was used for the spin density calculation, and $a_N = 35.61\rho_N - 0.93\rho_O$ if the McLachlan spin densities were used. Furthermore, Vasserman and Buchechenko[18] have used the formula $a_N = Q\rho_N$ for some nitric oxide derivatives. According to the SCF calculation by Kikuchi[19] with CNDO/2 approximation, the unpaired electron is almost completely localized on the $2p\pi$ AO's of nitrogen and oxygen of nitric oxide derivatives.

In the case of CT interaction with an electron acceptor, both of ρ_N and ρ_O of DTBNO will decrease. Since $|Q_1| \gg |Q_2|$ and $Q_1 > 0$ in Eq. (10), the CT interaction may cause the decrease of a_N.

The electrostatic interaction seems to polarize the charge distribution on the NO group, thus affecting the densities. Namely, when DTBNO is put in a polar environment or if some polar group approaches the NO group, the polarization in the sense $\rangle N^{+\delta}\text{–}O^{-\delta}$ will occur, leading to the enhancement of the spin density on nitrogen. We assume that the spin densities change respectively to $\rho_N + \delta\rho_N$ and $\rho_O - \delta\rho_O$ by electrostatic interaction. Thus, the change of a_N can be written as $\Delta a_N = Q_1\delta\rho_N + Q_2\delta\rho_O$. As $\delta\rho_N - \delta\rho_O = 0$ (no intermolecular charge transfer), $\Delta a_N = (Q_1 - Q_2)\delta\rho_N = (Q_2 - Q_1)\delta\rho_O$. Since $\delta\rho_N > 0$ and $Q_1 \gg Q_2$ as mentioned above, a_N may increase by electrostatic interaction.

In the case of the hydrogen bonding interaction with proton donors such as ethanol and phenol, the σ-type lone pair electrons on oxygen of DTBNO will be mainly concerned with the bonding. Owing to the short range interaction, the electrostatic polarization $\rangle N^{+\delta}\text{–}O^{-\delta}$ will be more extensive in the hydrogen bonding interaction than in the case of the non-hydro-

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[14] T. Kubota, Y. Oishi, K. Nishikida, and H. Miyazaki, This Bulletin, **43**, 1622 (1970).

[15] A. H. Maki and E. W. Stone, *J. Amer. Chem. Soc.*, **87**, 454 (1965).

[16] M. Karplus and G. K. Frenkel, *J. Chem. Phys.*, **35**, 1312 (1961).

[17] P. B. Ayscough and F. P. Sargent, *J. Chem. Soc.*, *B*, **1966**, 907.

[18] A. M. Vasserman and A. L. Buchechenko, *J. Struct. Chem., USSR*, **7**, 633 (1966).

[19] O. Kikuchi, This Bulletin, **42**, 1187 (1969).

gen-bonding electrostatic interaction. Moreover, the electron delocalization in the hydrogen bond as indicated by $\rangle N^{+}\text{–}O\text{–}H\cdots O^{-}\text{–}$ will contribute to the enhancement of the spin density on nitrogen. Thus, the hydrogen bonding interaction will increase a_N a great deal.

Summarizing the above arguments, the hfc constant of nitrogen decreases by the charge transfer from the highest occupied π-orbital of DTBNO in the EDA complex formation, while it increases by the non-hydrogen-bonding electrostatic interaction as well as by the hydrogen bonding interaction.

Deguchi[20] pointed out that the increase of the hfc constant of some stable radicals in non-hydrogen-bonding polar solvents was approximately proportional to the dipole moment μ of the solvent molecule. The solvent effects on the hfc constant of DTBNO nitrogen is shown in Fig. 10 and Table 4. We see from Fig. 10, that there is an approximately linear relation between the a_N value of DTBNO and the μ value of the non-hydrogen-bonding solvent. The relation between a_N and μ values might be ascribed to the fact that the ESR spectra reflect the short range molecular interactions more sensitively than the optical spectra.

TABLE 4. SOLVENT EFFECT ON THE ^{14}N hfc CONSTANT OF DTBNO

	Solvent	ε	$\lvert\mu\rvert$	$a_N(G)$
1	Cyclohexane	2.023	0	15.15
2	Benzene	2.284	0	15.41
3	Mesitylene	2.27	0	15.31
4	Toluene	2.379	0.39	15.36
5	Monochlorobenzene	5.621	1.56	15.49
6	DMA	5.29	1.61	15.49
7	*o*-Dichlorobenzene	9.93	2.26	15.51
8	Nitrobenzene	34.82	3.99	15.62
9	Benzonitrile	25.20	4.05	15.65

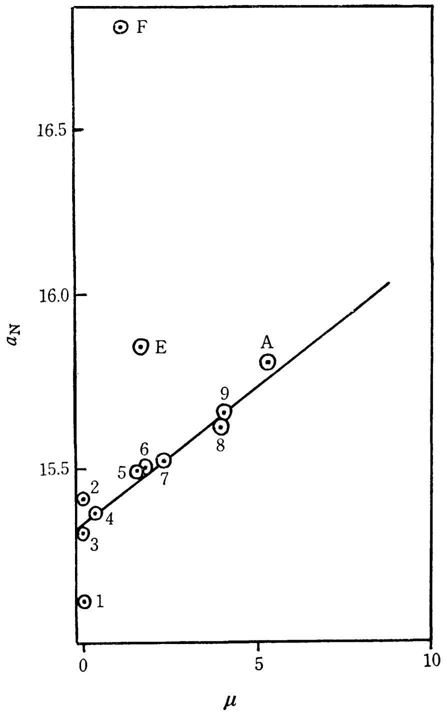

Fig. 10. The relation between the nitrogen hfc constant of DTBNO and the dipole moment of the solvent. See Table 4 for numberings 1—9 in the figure.
A: the value for DTBNO-PA complex in toluene.
E: the a_N value in ethanol solution.
F: the a_N value of DTBNO-phenol complex in toluene.

The a_N value of the DTBNO-phenol hydrogen bonded complex in toluene and that of DTBNO in ethanol are given in Fig. 10. The a_N values are much larger than those expected from the $a_N \sim \mu$ linear relation in the non-hydrogen-bonding solvents. This is in accordance with the above argument.

It can be seen from Tables 3 and 4 that the EDA complex formation of DTBNO with electron acceptors such as TCNE, PMDA, and PA leads to the increase of a_N. Several workers argued that electrostatic interaction between the partners in the EDA complex seems to make an important contribution to the stability of the complex, particularly in the case of weak π-π complexes. Our results indicate that the electrostatic forces play important roles also in the case of π-π complexes of DTBNO. Although TCNE as well as PMDA molecules do not have dipole moment as a whole, they have large local dipole moment. The local electric moment seems to cause the increase of a_N in the molecular complex formation. However, we cannot conclude even for these weak π-π complexes that the electrostatic interaction is predominant (or exclusive) in the ground state. If the electrostatic interaction is predominant, we can expect that the a_N value of TCNE-DTBNO complex is larger than or at least nearly equal to that of PMDA-DTBNO complex, since TCNE seems to have larger local dipole moments than those of PMDA. Contrary to this, the observed a_N value of the former complex is significantly smaller than the value of the latter. Thus, in the case of the TCNE-DTBNO complex, the CT interaction seems to play an important role. This is in accordance with the ordinary CT concept in view of the fact that the electron affinity of TCNE is 1.8 eV compared with 0.8 eV of PMDA.

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