The Electronic Absorption Spectra and Electronic Structures of Aromatic Azides, Nitrenes, and Diazonium Ions

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Electronic spectra were measured for azidobenzene, 1-azidopyrene, benzenediazonium ion, and 1-pyrenediazonium ion at room temperature, and also for nitrenobenzene and 1-nitrenopyrene at liquid nitrogen temperature. The π-electron structures of these compounds were calculated by the Pariser-Parr-Pople LCAO SCF MO CI method for the closed-shell systems and by the restricted open-shell SCF MO CI method for the open-shell systems. The calculated transition energies and oscillator strengths could satisfactorily explain the observed spectra. It was shown that the π-electron structures of azidobenzene and nitrenobenzene are similar to those of dimethylaniline and the benzyl or anilino radical, respectively.

Aromatic azides, nitrenes, and diazonium ions are interesting research subjects from both physicochemical and photochemical points of view. Reiser *et al.*[1] and also Tsunoda *et al.*[2] observed the electronic absorption spectra of azidobenzene and its derivatives. Theoretical studies of the electronic structure of azidobenzene have been made by several authors with the aid of the Hückel type MO method.[1-4] The more improved LCAO MO SCF CI calculation, however, has not yet been reported on azidobenzene.

The electronic absorption spectra of aromatic diazonium ions were measured by several authors.[5-11] The Hückel type MO studies of their electronic structures have been carried out by Evleth and Cox,[6] Schuster and Polansky,[9] Kikuchi *et al.*,[10] and Bochvar *et al.*[11] The more improved theoretical treatment based on the Pariser-Parr-Pople SCF MO method[12,13] has been made by Sukigara and Kikuchi[7] and also by Yoshida and Kobayashi.[14]

Reiser *et al.*[1,15,16] measured the electronic absorption spectra of several aromatic nitrenes at 77°K and interpreted the observed bands of nitrenobenzene from its similarity to that of the benzyl radical.[1] However, no detailed theoretical study with the aid of the MO method, was made on their electronic spectra.

We have measured the electronic absorption spectra of azidobenzene, nitrenobenzene, and benzenediazonium ion over a wider wavelength region than before and also measured the spectra of some new compounds; 1-azidopyrene, 1-nitrenopyrene, and 1-pyrenediazonium ion. In order to assign the observed spectra, we have theoretically studied the electronic structures of the compounds under consideration by the Pariser-Parr-Pople SCF MO CI method[12,13] and also by the restricted open-shell SCF MO CI method.[17]

Experimental

Materials. Azidobenzene and 1-azidopyrene were prepared by treating 10% hydrochloric acid solution of the corresponding amino-compounds with aqueous sodium nitrite solution and thereafter with aqueous sodium azide solution below 5°C. The precipitate of 1-azidopyrene separated by filtration of the solution was purified by means of column chromatography with active alumina. Azidobenzene was separated from the solution by centrifuging, washed with water, and finally distilled under reduced pressure.

Nitrenes were prepared by illuminating the rigid benzene and ethanol solutions of parent azides with a 500 W mercury lamp at 77 K.

Benzenediazonium fluoroborate and 1-pyrenediazonium fluoroborate were prepared by treating the corresponding amino-compounds with sodium nitrite in 10% hydrochloric acid below 5°C. The precipitates of benzenediazonium fluoroborate and 1-pyrenediazonium fluoroborate were obtained by adding excess 40% fluoroboric acid to the solutions and purified by repeated recrystallizations from methanol.

Ethanol and benzene used as solvents were purified by the methods described previously.[18,19]

Measurements. The electronic spectra of the ethanol solutions of azides and diazonium ions were measured at room temperature with a Cary spectrophotometer Model 14 R. Concerning the benzene and ethanol solutions of nitrenes, spectrophotometric measurements were made at

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[1] A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966).

[2] T. Tsunoda, T. Yamaoka, and K. Ikari, *Kogyo Kagaku Zasshi*, **72**, 156 (1969).

[3] A. Reiser and R. Marley, *Trans. Faraday Soc.*, **64**, 1806 (1968).

[4] G. Favini, *Gazz. Chim. Ital.*, **91**, 270 (1961).

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[6] E. M. Evleth and R. J. Cox, *J. Phys. Chem.*, **71**, 4082 (1967).

[7] M. Sukigara and S. Kikuchi, This Bulletin, **40**, 461 (1967).

[8] L. A. Kazitsyna, N. B. Dzegilenko, A. V. Upadysheba, V. V. Mischenko, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1967**, 1925.

[9] P. Schuster and O. E. Polansky, *Monatsh. Chem.*, **96**, 396 (1965).

[10] S. Kikuchi, K. Honda, and M. Sukigara, *Seisan Kenkyu*, **19**, 161 (1967).

[11] D. A. Bochvar, N. P. Gambaryan, V. V. Mischenko, and L. A. Kazitsyna, *Dokl. Akad. Nauk SSSR*, **175**, 839 (1967).

[12] P. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

[13] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[14] Z. Yoshida and T. Kobayashi, This Bulletin, **45**, 742 (1972).

[15] A. Reiser, H. M. Wagner, and G. Bowes, *Tetrahedron Lett.* **23**, 2635 (1966).

[16] A. Reiser, H. M. Wagner, R. Marley, and G. Bowes, *Trans. Faraday Soc.*, **63**, 2403 (1967).

[17] H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc., Ser. A*, **68**, 591 (1955).

[18] T. Yamaoka, H. Kashiwagi, and S. Nagakura, This Bulletin, **45**, 361 (1972).

[19] H. Kashiwagi, T. Yamaoka, and S. Nagakura, *ibid.*, to be published.

77 K with a Shimadzu MPS type spectrophotometer at the Institute of Physical and Chemical Research.

The concentrations of the solutions used for the spectrophotometric measurements were in the range 10^{-4}—10^{-5} M.

Theoretical

For the calculation of the closed-shell systems, we adopted the Pariser-Parr-Pople SCF MO method.[12,13,20] The configuration interactions were considered by taking all the singly excited configurations for the benzene derivatives and by taking the lowest 40 singly excited configurations for each symmetry in the case of the pyrene derivatives. For the open-shell molecules, the restricted SCF MO CI procedure presented by Longuet-Higgins and Pople[17] was adopted. In this case the lowest 40 singly and doubly excited configurations were taken for each symmetry. The penetration integrals were neglected for both closed- and open-shell systems. The core reasonance integrals (β) were taken to be proportional to the corresponding overlap integrals, the value of β, -2.39 eV, for the C–C bond of the benzene ring being taken as the standard. Two-center Coulomb repulsion integrals were estimated by means of the Nishimoto-Mataga approximation.[21] One-center integrals were determined by taking the effect of charge densities according to the method presented by Iwata and Shida.[22]

The molecular structure of azidobenzene was first estimated on the basis of the well-known structures of benzene and CH_3N_3 determined by the electron diffraction experiment,[23] and finally taken by the standard bond order-bond length relation as shown in Fig. 1 (a).[24] The molecular structure of the benzenediazonium ion[25] shown in Fig. 1(b), was determined by the X-ray diffraction technique on the chloride crystal and was taken for calculation. The molecular structure of nitrenobenzene was taken by using the standard bond order-bond length relation as shown in Fig. 1(c). For the pyrene dirivatives, we adopted the results of the X-ray diffraction experiment of pyrene crystal[26] assuming all the angles to be 120° and the C–N and N–N bond lengths equal to those of the benzene derivatives.

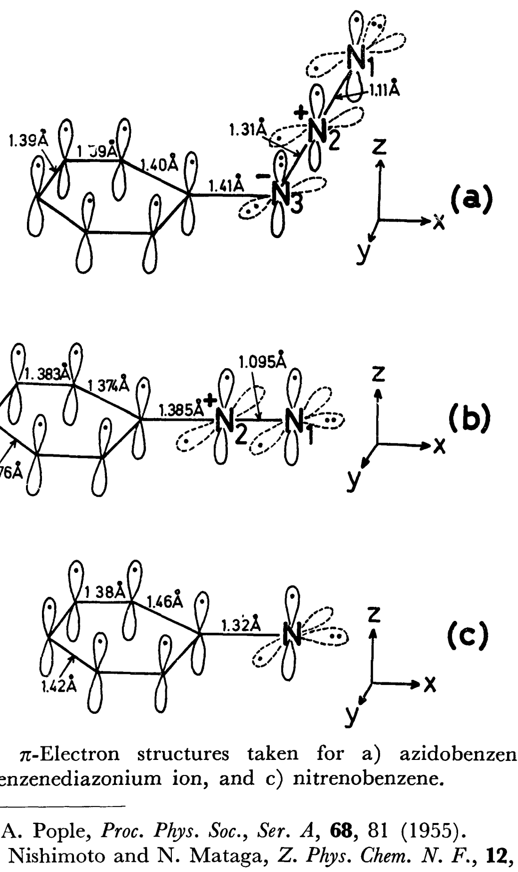

Fig. 1. π-Electron structures taken for a) azidobenzene, b) benzenediazonium ion, and c) nitrenobenzene.

The only out-of-plain (z axis) π-electron orbital on each atom taken in the calculation is shown in Figs. 1(a), (b), and (c) for azidobenzene, benzenediazonium ion, and nitrenobenzene, respectively. The ESR study[27,28] shows that the ground state of nitrenobenzene is the nπ type triplet in which one π-electron occupies the half filled orbital mostly localized on the nitrogen atom. Thus, the ground state of nitrenes under consideration may be regarded as odd π-electron systems.

The calculation was performed with a Facom 270—30 electronic computer at the Institute of Physical and Chemical Research.

Results and Discussion

Electronic Spectrum of Azidobenzene. Figure 2 shows the absorption spectrum of the ethanol solution of azidobenzene at room temperature. In addition to the bands below 45000 cm^{-1} reported by the previous

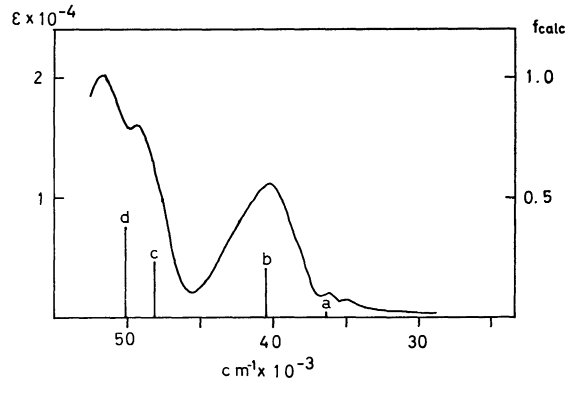

Fig. 2. The absorption spectrum of azidobenzene in ethanol at room temperature. The vertical lines represent the calculated transition energies and oscillator strengths (f_{calc}).

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[20] J. A. Pople, *Proc. Phys. Soc., Ser. A*, **68**, 81 (1955).

[21] K. Nishimoto and N. Mataga, *Z. Phys. Chem. N. F.*, **12**, 335 (1957).

[22] Details of the method will be published by S. Iwata and T. Shida.

[23] C. N. R. Rao, *Dissertation Abstr.*, **19**, 968 (1959).

[24] The following equations are used for the evaluation of the bond length from the bond order:

$l_{pq}=1.514-0.176\,P_{pq}$ for the C–C bond

$l_{pq}=1.472-0.207\,P_{pq}$ for the C–N bond

where l_{pq} and P_{pq} are bond length and bond order, respectively, between p and q atoms

[25] C. Römming, *Acta Chem. Scand.*, **17**, 1444 (1963).

[26] J. M. Robertson, *Proc. Roy. Soc., Ser. A*, **207**, 101 (1951).

[27] J. A. R. Coope, J. B. Farmer, C. L. Gardner, C. A. McDowell, *J. Chem. Phys.*, **42**, 54 (1965).

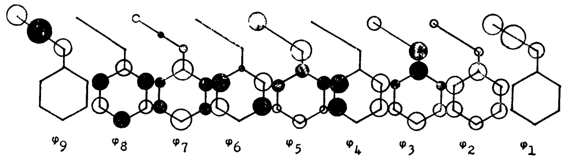
[28] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

Table 1. Calculated and observed transition energies ΔE's (in the units of 10^3 cm^{-1}), and oscillator strengths, f's, of azidobenzene

	Calcd.					Obsd.	
	ΔE	Polarization[a]	f	Character[b]		ΔE	f
				1) Transitions concerning singlet excited states			
a	36.6	y>x	0.026	0.70(5→6) −0.49(4→7) +0.51(3→6)	CT$_1$+LE(B$_{2u}$)	35.0	0.018
b	40.3	x>y	0.205	0.89(5→7) +0.42(4→6)	CT$_2$	40.2	0.27
c	48.1	y	0.245	0.67(5→6) +0.62(4→7) −0.41(3→6)	CT$_1$+LE(B$_{2u}$)+LE(B$_{1u}$)	49.3	0.22
d	50.2	x	0.379	−0.38(5→7) +0.31(3→7) +0.84(4→6)	LE(B$_{1u}$)+LE(E'$_{1u}$)	51.7	0.39
e	55.3	y	0.681	0.59(4→7) +0.75(3→6)	LE(E$_{1u}$)+LE(B$_{2u}$)		
f	55.5	x	0.344	0.92(3→7) −0.33(4→6)	LE(E'$_{1u}$)+LE(B$_{2u}$)		
				2) Transitions concerning triplet excited states			
a'	23.7			0.62(4→6) +0.63(5→7) +0.42(3→7)			
b'	30.9			−0.34(4→6) +0.77(5→6) +0.38(3→6)			
c'	31.7			0.68(4→6) −0.53(5→7) +0.33(5→6)			

a) Axes x and y are taken as shown in Fig. 1.

b) This column shows coefficients of main electron configurations the contribution of which exceeds 9%. (i→j) indicates the electron configuration corresponding to the one electron excitation from the i-th MO (φ_i) to the j-th MO (φ_j). The MO's used in the CI calculation are schematically shown in the following diagram.



authors[1,2] new bands were newly observed at 49300 and 51700 cm^{-1}.

As is clearly seen in Table 1 in which the calculated transition energies and oscillator strengths are given together with the observed values, there is a good agreement between the calculated and observed ones. We show the nature of each transition by giving the coefficients of electron configurations mainly contributed to the corresponding excited state. The bands at 35000, 40200, 49300, and 51700 cm^{-1} can be interpreted as a shifted α band of benzene, an intramolecular charge-transfer (CT) band, a band with mixed characters of CT and local excitation (LE) corresponding to the α band of benzene, and a mixing band of the α and β bands of benzene, respectively. The shifted β bands of benzene may be expected to appear at higher frequencies than the observed wave number region. The present assignment of the absorption spectrum of azidobenzene is similar to that of dimethylaniline.[29] This means that the π-electrons of the azido group give an effect similar to those of the dimethylamino group to the absorption spectrum of benzene.

The π-electron densities and bond orders calculated for azidobenzene are listed in Table 2, which shows that the π-electron migrates from the azido group to the benzene ring by 0.05e. This means that the azido group is an electron donating one like the dimethylamino group.

Finally we found the nπ^* type transition at 30900 cm^{-1} (ε~100) for the concentrated solution of azidobenzene.

Table 2. Calculated π-electron densities and bond orders of azidobenzene and benzenediazonium ion

1) Azidobenzene

π-Electron densities

Atoms[a]	Ground state	S$_1$ state	S$_2$ state	T$_1$ state
N$_1$	1.37	1.20	1.16	1.26
N$_2$	1.04	1.04	1.04	1.04
N$_3$	1.54	1.31	1.20	1.36

Bond orders

Bonds	Ground state	S$_1$ state	S$_2$ state	T$_1$ state
N$_1$-N$_2$	0.776	0.759	0.749	0.762
N$_2$-N$_3$	0.627	0.613	0.602	0.621
N$_3$-C	0.518	0.587	0.625	0.509

2) Benzenediazonium ion

π-Electron densities

Atoms[a]	Ground state	S$_1$ state	S$_2$ state	T$_1$ state
N$_1$	0.86	1.19	1.14	1.23
N$_2$	1.26	1.43	1.42	1.43

Bond orders

Bonds	Ground state	S$_1$ state	S$_2$ state	T$_1$ state
N$_1$-N$_2$	0.891	0.664	0.639	0.649
N$_2$-C	0.364	0.437	0.433	0.428

a) N$_1$, N$_2$, and N$_3$ are taken as shown in Fig. 1.

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[29] K. Kimura and S. Nagakura, *Mol. Phys.*, **9**, 117 (1965).

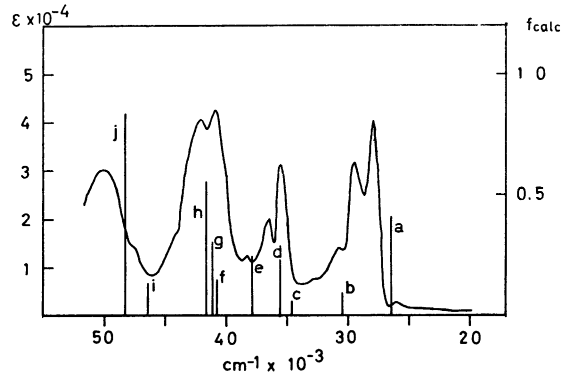


Fig. 3. The electronic absorption spectrum of 1-azidopyrene in ethanol at room temperature. The vertical lines represent the calculated transition energies and oscillator strengths (f_{calc}).

Electronic Spectrum of 1-Azidopyrene. Figure 3 shows the electronic absorption spectrum of 1-azidopyrene in the ethanol solution at room temperature. The calculated and observed peak wave numbers and oscillator strengths for various transitions with lower energies are given in Table 3. Although many transitions are expected in the region $(20 \simeq 50) \times 10^3$ cm^{-1}, those with an oscillator strength greater than 0.05 are shown, except for the lowest energy transition at 26000 cm^{-1}. In the case of 1-azidopyrene, transitions cannot be characterized by three or four dominant electron configurations, except for the lowest two or three transitions. The characters of the transitions are therefore not shown in Table 3. The weak band at 26000 cm^{-1} may be regarded as a shifted α band of pyrene. Band a in Table 3 is assigned to LE (~50 %)+CT (~50%), and bands b and d are characterized by CT. In spite of the existence of the CT bands, the spectral shape is similar to that of pyrene. This is because the absorption intensities of the main bands pertinent to the parent hydrocarbon are very strong and the CT bands are covered by them. Most of the observed peaks are attributed to the superposition of several transitions. The peak positions of the 1-azidopyrene spectrum are shifted toward longer wavelengths compared with those of the pyrene spectrum and are similar to those of the 1-aminopyrene spectrum.

TABLE 3. CALCULATED AND OBSERVED TRANSITION ENERGIES, ΔE'S (IN THE UNITS OF 10^3 cm^{-1}) AND OSCILLATOR STRENGTHS (f) OF 1-AZIDOPYRENE[a]

	Calcd.			Obsd.	
	ΔE	Polarization[b]	f	ΔE	f
	24.8	x>y	0.0029	26.0	0.0042
a	26.4	y>x	0.41	27.9	0.52
b	30.4	y>x	0.09		
c	34.6	x~y	0.06		
d	35.6	x~y	0.23	35.5	0.31
e	37.9	x>y	0.25		
f	40.7	y	0.16		
g	41.1	y>x	0.31		
h	41.6	y	0.57	40.9	0.88
i	46.4	y>x	0.14		
j	48.2	y	0.84	50.0	0.47

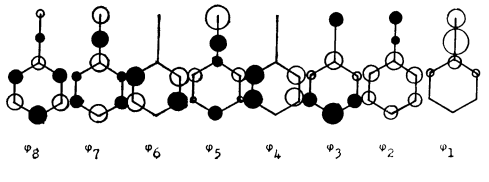
a) We are concerned with only singlet excited states.
b) Axes x and y are taken to be parallel to the short and long molecular axes of pyrene, respectively.

Electronic Spectrum of the Benzenediazonium Ion.

TABLE 4. CALCULATED AND OBSERVED TRANSITION ENERGIES, ΔE'S (IN THE UNITS OF 10^3 cm^{-1}) AND OSCILLATOR STRENGTHS, f'S OF BENZENEDIAZONIUM ION

	Calcd.					Obsd.	
	ΔE	Polarization[a]	f	Character[b]		ΔE	f
				1) Transitions concerning singlet excited state			
a	33.4	y	0.078	$0.63(4\to5)+0.53(3\to6)-0.52(4\to7)$	$CT_1+LE(B_{2u})$	33.9	0.085
b	38.8	x	0.32	$0.91(3\to5)+0.34(4\to6)$	CT_2	38.6	0.22
c	48.8	y	0.15	$0.65(4\to5)-0.63(3\to6)+0.41(4\to7)$	$CT_1+LE(B_{2u})+LE(E_{1u})$	49.4	0.18
d	52.1	x	0.61	$-0.34(3\to5)+0.86(4\to6)+0.32(3\to7)$	$LE(B_{1u})+LE(E'_{1u})$	51.9	0.32
e	60.1	y	0.78	$0.35(4\to5)+0.54(3\to6)+0.73(4\to7)$	$CT_1+LE(E_{1u})+LE(B_{2u})$		
f	60.6	x	0.30	$-0.33(4\to6)+0.92(3\to7)$	$LE(E'_{1u})+LE(B_{1u})$		
				2) Transitions concerning triplet excited states			
a'	27.2			$0.93(4\to5)$		20.7[7]	
b'	31.7			$0.87(3\to5)+0.34(4\to6)$			
c'	39.6			$0.91(3\to6)$			

a) Axes x and y are taken as shown in Fig. 1.
b) See footnote b), Table 1.
The MO's used in the CI calculation are schematically shown in the following diagram.



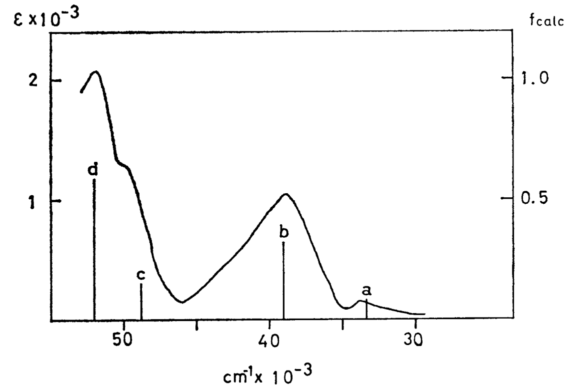


Fig. 4. The electronic absorption spectrum of benzenediazonium fluoroborate in ethanol at room temperature. The vertical lines represent the calculated transition energies and oscillator strengths ($f_{\rm calc}$).

Figure 4 shows the electronic absorption spectrum of benzenediazonium fluoroborate in the ethanol solution. The bands below 40000 cm^{-1} are coincident in their positions and intensities with those given by Sukigara and Kikuchi.[7] The calculated transition energies and oscillator strengths are given in Table 4, together with the observed values. We can find a good agreement between the observed and calculated values both for the transition energies and for the oscillator strenghts. The nature of each transition is also shown in this table by giving the coefficient of the electron configuration mainly contributed to the corresponding excited state.

The observed absorption spectrum of the benzenediazonium ion is similar to that of azidobenzene. The characters of the bands are also similar to each other for both compounds. However, the directions of electron transfer between the substituent group and the benzene ring are reverse to each other for both compounds, *viz.*, in the case of the benzenediazonium ion, the substituent group acts as an electron acceptor. This is clear from the π-electron density given in Table 2.

The nπ^* type transition was observed at 30800 cm^{-1} ($\varepsilon\sim$120) for the concentrated solution.

Electronic Spectrum of the 1-Pyrenediazonium Ion. Figure 5 shows the electronic absorption spectrum of the 1-pyrenediazonium ion in the ethanol solution at room temperature. The transition energies and oscillator strengths are given in Table 5 for several transitions of lower energies and with oscillator strengths greater than 0.05. Band a in this table is assigned to LE ($\sim$60%)+CT ($\sim$40%), and band b to pure CT. Each of the observed peaks shown in Fig. 6 is the superposition of several bands.

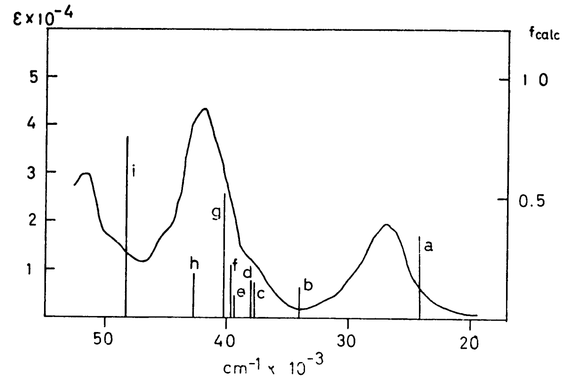


Fig. 5. The electronic absorption spectrum of 1-pyrenediazonium ion in ethanol at room temperature. The vertical line represent the calculated transition energies and oscillator strengths ($f_{\rm calc}$).

Table 5. Calculated and observed transition energies, ΔE's (in the units of 10^3 cm^{-1}) and oscillator strengths, f's, of 1-pyrenediazonium ion[a)]

	Calcd.			Obsd.	
	ΔE	Polarization[b)]	f	ΔE	f
a	24.2	y>x	0.35	26.8	0.43
b	34.0	y$\sim$x	0.14		
c	37.7	x$\sim$y	0.15		
d	38.1	x>y	0.16		
e	39.2	y	0.10		
f	39.6	y>x	0.21		
g	40.2	y	0.52	41.9	0.82
h	42.7	y>x	0.19		
i	48.3	y	0.75	51.7	

a) We are concerned with only siglet excited states.
b) Axes x and y are taken to be parallel to the short and long molecular axes of pyrene, respectively.

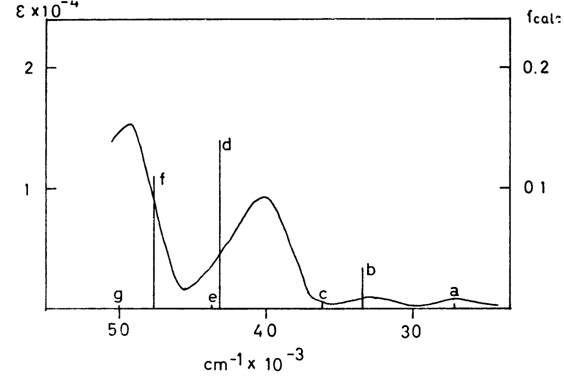


Fig. 6. The electronic absorption spectrum of nitrenobenzene in ethanol at 77°K. The vertical lines represent the calculated transition energies and oscillator strengths ($f_{\rm calc}$)

Electronic Spectrum of Nitrenobenzene. Figure 6 shows the electronic absorption spectrum of nitrenobenzene in the ethanol solution. The bands at higher frequencies than 40000 cm^{-1} were newly found by the present authors. The observed transition energies and oscillator strengths are given in Fig. 6 together with the calculated values. There is a good agreement between the observed and calculated values both for transition energies and oscillator strengths. The nature of each transition is also shown in Table 6.

The electronic spectrum of nitrenobenzene resembles very much that of the benzyl, anilino, or phenoxyl radical. The two lower bands, a and b, can be assigned to the $\phi_0\rightarrow\phi_+$ and $\phi_0\rightarrow\phi_-$ transitions in the Dewar and Longuet-Higgins notation.[30] The strong bands

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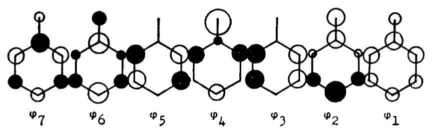
[30] M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc., Ser. A*, **67**, 795 (1954).

TABLE 6. CALCULATED AND OBSERVED TRANSITION ENERGIES, ΔE's (IN THE UNITS OF 10^3 cm^{-1}) AND OSCILLALOR STRENGTH, f's, OF NITRENOBENZENE

	Calcd.					Obsd.	
	ΔE	Polarization[a]	f	Character[b]		ΔE	f
a	22.7	y	0.003	$0.77(3\to4)+0.43(4\to5)+0.30(2\to5)$	CT, B_1	27.2	0.0006
b	33.4	y	0.037	$0.45(3\to4)-0.73(4\to5)-0.33(2\to5)$	CT, B_1	33.0	0.01
c	36.2	x	0.005	$0.71(3\to5)-0.43(3\to5)'$	LE, A_1		
d	43.2	x	0.14	$0.42(2\to4)+0.42(4\to6)+0.48(1\to4)+0.30(4\to7)$	CT, A_1	41.5	0.18
e	43.8	y	0.003	$0.70(3\to6)+0.51(2\to5)+0.33(2\to5)'$	LE, B_1		
f	47.5	x	0.11	$0.39(2\to4)-0.49(4\to6)+0.41(1\to4)-0.35(4\to7)$	CT, A_1	48.9	0.14

a) Axes x and y are taken as shown in Fig. 1.

b) See footnote b), Table 1. $(k\to m)'$ is the abbreviated representation of an excited electron configuration: $(k\to m)'=1/\sqrt{6}\,[-2|k\bar{l}m|+|\bar{k}lm|+|kl\bar{m}|]$. The MO's used in the CI calculation are schematically shown in the following diagram.



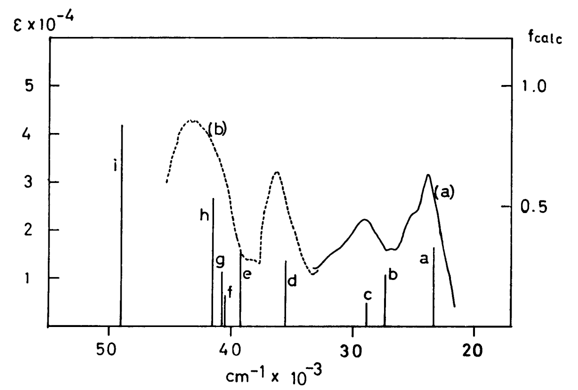


Fig. 7. The electronic absorption spectra of 1-nitrenopyrene in benzene and ethanol at 77 K. The vertical lines represent the calculated transition energies and oscillator strengths (f_{calc}).
a) in benzene, b) in ethanol.

of d and f are represented by the superposition of CT and back CT components, which are also transitions characteristic of open-shell systems. The weak bands of c and e are covered by the strong bands, d and f.

Electronic Spectrum of 1-Nitrenopyrene. Curves (a) and (b) in Fig. 7 show the electronic absorption spectra of 1-nitrenopyrene in the benzene and ethanol solutions at 77 K, respectively. The calculated and observed results for the transitions with higher oscillator strengths than 0.05 are given in Table 7.

TABLE 7. CALCULATED AND OBSERVED TRANSITION ENERGIES, ΔE's (IN THE UNITS OF 10^3 cm^{-1}) AND OSCILLATOR STRENGTHS, f's OF 1-NITRENOPYRENE

	Calcd.			Obsd.	
	ΔE	Polarization[a]	f	ΔE	f
a	23.3	y>x	0.33	23.8	0.58
b	27.4	y	0.21	29.0	0.48
c	28.9	x∼y	0.10		
d	35.5	y>x	0.28	36.4	0.39
e	39.2	x	0.32		
f	40.5	x>y	0.13		
g	40.8	x	0.23		
h	41.1	x	0.54	43.3	1.1
i	49.0	y	0.89		

a) Axes x and y are taken to be paralled to the short and long molecular axes, respectively.

In this case, the two lower absorption bands at 23800 and 29000 cm^{-1} represented by a and b, respectively, are assigned to $\phi_0\to\phi_+$ and $\phi_0\to\phi_-$ transitions in the Dewar and Longuet-Higgins notation.[30] Band c is assigned to the LE transition of pyrene. Since other transitions cannot be characterized by three or four dominant electron configurations, we do not show the characters of transitions in Table 7.

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