Near and Vacuum Ultraviolet Absorption Spectra and Electronic Structures of Nitrosobenzene and Its Derivatives

By Katsumi TABEI* and Saburo NAGAKURA

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The electronic absorption spectra of nitrosobenzene and its derivatives are interesting subjects from both experimental and theoretical points of view. Nitrosobenzene is colorless in its crystal form but turns green when it is melted or dissolved in some solvents. This phenomenon has been studied spectroscopically and thermochemically by several investigators.[1] It has been found from these studies that the monomer shows a weak $n\rightarrow\pi^*$ transition band at about 750 mμ; this band, which is responsible for the green color, disappears in the colorless dimer.

The $n\rightarrow\pi^*$ transition band of nitrosobenzene has been studied in detail in connection with the above-mentioned color change. Concerning the ultraviolet absorption spectrum of nitrosobenzene, however, only a few experimental and theoretical studies have hitherto been carried out.[2] This might be because nitrosobenzene and some of its derivatives are rather unstable and because, moreover, their ultraviolet absorption spectra are too complicated to be understood by analogy with that of benzene.

Under these circumstances, we have undertaken to study in more detail the absorption spectra of nitrosobenzene and its derivatives from both experimental and theoretical points of view, in order to bring about a better understanding of their electronic structures and clarify the characteristics of the nitroso group as a chromophoric or electron-accepting group.

Experimental

Materials.—Nitrosobenzene and the following *p*-substituted nitrosobenzenes are studied in the present work : nitrosobenzene, *p*-nitrosotoluene, *p*-nitrosochlorobenzene, *p*-nitrosobromobenzene, *p*-nitrosoanisole, *p*-nitrosophenetole, *p*-nitrosophenol, *p*-nitrosoaniline, *p*-nitroso-*N*, *N*-dimethylaniline, *p*-nitroso-*N*, *N*-diethylaniline, *p*-nitroso-*N*-ethyl-*N*-benzylaniline and *p*-nitrosodiphenylamine.

Nitrosobenzene, *p*-nitrosotoluene, *p*-nitrosochlorobenzene, *p*-nitrosobromobenzene, *p*-nitrosoanisole and *p*-nitrosophenetole were derived from the corresponding nitro compounds via. hydroxylamino compounds by the method of Bamberger et al.[3] The products were separated by steam distillation and were purified by repeated recrystallizations from an ethanol-water mixture.

Commercial G.R. grade *p*-nitrosophenol, *p*-nitroso-*N*, *N*-dimethylaniline and *p*-nitrosodiphenylamine were purified by recrystallization with a ligroin-benzene mixture. *p*-Nitrosoaniline was prepared from *p*-nitrosophenol, ammonium acetate and ammonium chloride following the directions of Fischer and Hepp.[4] *p*-Nitroso-*N*, *N*-diethylaniline and *p*-nitroso-*N*-ethyl-*N*-benzylaniline were prepared from the corresponding anilines by a usual nitrosation with sodium nitrite and hydrochloric acid.[5] The products were recrystallized from ligroin. The melting points of the compounds used in the present study are listed in Table I.

n-Heptane used as a solvent was shaken with concentrated sulfuric acid and washed with aqueous sodium hydroxide and thereafter with water repeatedly. After being kept standing over calcium chloride for a day or so, it was fractionally distilled over sodium metal.

Commercial ethanol, chloroform, dioxane, ethyl ether and acetonitrile of a G.P. grade were purified by distillation.

Measurement.—A Cary recording spectrophotometer model 14-M was used for measuring the visible and near ultraviolet absorption spectra of the solutions with concentrations of the respective nitroso compounds of 10^{-5}—10^{-3} mol./l. The measurements were made at room temperature by using silica cells with light paths 1 cm. and 0.1 cm. long.

The vacuum ultraviolet absorption spectrum of nitrosobenzene in a *n*-heptane solution was measured by using handmade vacuum ultraviolet spectrophotometer.[6]

* Present address: Tokyo College of Pharmacy, 600, Kashiwagi 4-chome, Shinjiku-ku, Tokyo.

1) E. Bamberger and A. Rising, *Ber.*, **34**, 3878 (1901); C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **125**, 173 (1924); D. L. Hammick and W. S. Illingworth, ibid., **1930**, 2358; D. L. Hammick, R. G. A. New and L. E. Sutton, ibid., **1932**, 742; P. Tarte, *Bull. soc. chim. Belges*, **63**, 525 (1954); W. Lüttke, *Z. Electrochem.*, **61**, 302, 976 (1957); **63**, 614 (1959).

2) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956); Y. Tsuzuki, T. Uemura and N. Hirasawa, *Ber.*, **74**, 616 (1941); H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **46**, 1314 (1963).

3) E. Bamberger, *Ber.*, **28**, 1222 (1895), **42**, 3581 (1909); B. Bennett, "Organic Syntheses," Coll. Vol. III, 668 (1955); Y. Tsuzuki, T. Uemura and N. Hirasawa, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **61**, 1063 (1940); **62**, 85 (1941).

4) O. Fischer and E. Hepp, *Ber.*, **20**, 2475 (1887); **21**, 648 (1888).

5) B. Bennett, "Organic Syntheses," Coll. Vol. II, 223 (1943).

6) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, **37**, 417 (1964).

TABLE I. THE MAXIMUM WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS OF THE NITROSO COMPOUNDS

Compound	M. p., °C	Maximum wavelengths (mμ) and molar extinction coefficients (in parentheses)	Solvent
Nitrosobenzene	67	760(44), 301.4(5200), 280.5(10330), 272*(8200), 222*(5000), 218(6480), 194(11890), 174(~45000)	*n*-Heptane
p-Nitrosotoluene	48	755(42), 310.8(8825), 285.8(9856), 229*(5877), 224(6769)	*n*-Heptane
p-Nitrosochlorobenzene	72	750(40), 317*(8000), 310(9230), 288.2(10630), 278*(7500), 231(5910), 226(6810)	*n*-Heptane
p-Nitrosobromobenzene	94	745(42), 318*(9670), 311.4(10420), 291.8(10860), 232.6(5460), 227(6060), 222*(5400)	*n*-Heptane
p-Nitrosoanisole	32	738(47), 333(14270), 320(14860), 298*(6920), 242.5(5430), 236(6400), 228*(5360)	*n*-Heptane
p-Nitrosophenetole	34.5	744(47), 335(15400), 327.5(15870), 298*(6600), 243.5(6380), 237(7300), 231.5*(5000)	*n*-Heptane
p-Nitrosophenol	133	730(74), 295(16000), 242(2950)	5% EtOH - *n*-Heptane
p-Nitrosoaniline	174	690(41), 369(16700), 260(4200)	5% EtOH - *n*-Heptane
p-Nitroso-*N*, *N*-dimethylaniline	92	735(62), 393.5(28990), 381.5(26400), 313(1474), 303(1580), 295*(1300), 270.3(5181), 262(5940), 238(4960)	*n*-Heptane
p-Nitroso-*N*, *N*-diethylaniline	83	730(48), 399(26300), 386(23540), 315(1700), 305(1656), 273(4626), 264(5177), 237(5050)	*n*-Heptane
p-Nitroso-*N*-ethyl-*N*-benzylaniline	61	742(55), 395.8(33400), 383(29100), 314(1670), 304(1739), 295*(1500), 272(5928), 264(6162), 232(5520)	*n*-Heptane
p-Nitrosodiphenylamine	145	704(35), 400(11200), 261(5600), 259(4600)	5% EtOH - *n*-Heptane

* represents absorption shoulders.

Experimental Results

A weak absorption band ($\varepsilon=40$—70) was observed in the 680—760 mμ wavelength region for all the compounds given in Table I. It has been assigned to the $n\rightarrow\pi^*$ transition band.[7]

The ultraviolet absorption spectra of nitrosobenzene in the gaseous state and in *n*-heptane and ethanol solutions are given in Fig. 1. The peak wavelengths and molar extinction coefficients observed with the *n*-heptane solution are tabulated in Table I. Nitrosobenzene exhibits in the ultraviolet region five absorption maxima, at 301.4 mμ ($\varepsilon=5200$), 280.5 mμ ($\varepsilon=10330$), 218 mμ ($\varepsilon=6480$), 194 mμ ($\varepsilon=11890$), and 174 mμ ($\varepsilon=\sim45000$), and two shoulders at 272 mμ and 222 mμ. The absorption spectra of *p*-nitrosotoluene, *p*-nitrosochlorobenzene and *p*-nitrosobromobenzene shown in Fig. 2 are similar to that of nitrosobenzene.

On the other hand, *p*-nitrosophenol, *p*-nitrosoanisole, *p*-nitrosophenetole, *p*-nitrosoaniline and its *N*-substituted derivatives have more intense absorption bands at a longer wavelength region than nitrosobenzene does. The spectra of some of these compounds are shown in Figs. 2 and 3.

As is revealed by Fig. 1, the 300 mμ band of nitrosobenzene is sensitive to solvents.[8]

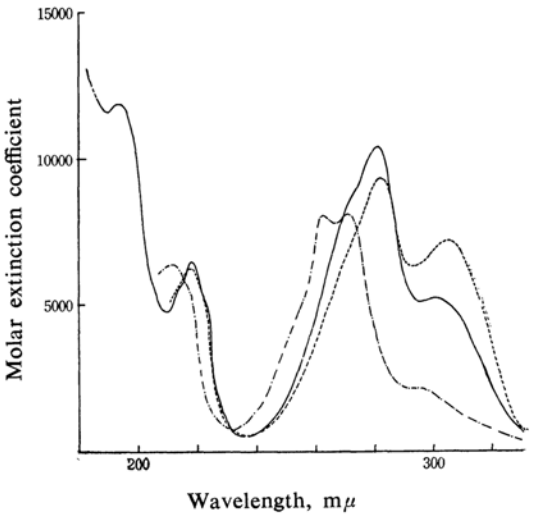

Fig. 1. The ultraviolet absorption spectra of nitrosobenzene in gaseous state, *n*-heptane solution and ethanol solution.
—·—·—·— in gaseous state
———— in *n*-heptane solution
- - - - - - - - - in ethanol solution

The band shows a small red shift and a great increase in intensity with the polarity of the solvent; i. e., the 294 mμ band of nitrosobenzene in the gaseous state shifts to 301.4 mμ

7) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

8) T. Uemura and N. Hirasawa, *Bull. Tokyo Inst. Tech.*, **1943**, 70.

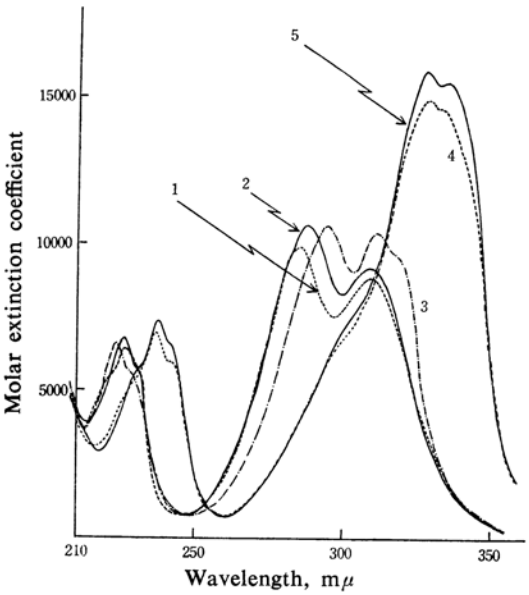

Fig. 2. The ultraviolet absorption spectra of some *p*-substituted nitrosobenzenes in *n*-heptane solution.

(1) ····· *p*-nitrosotoluene
(2) ····· *p*-nitrosochlorobenzene
(3) ····· *p*-nitrosobromobenzene
(4) ····· *p*-nitrosoanisole
(5) ····· *p*-nitrosophenetole

in the *n*-heptane solution and to 304 mμ in the ethanol solution, while the absorption intensity increases from 5200 in the *n*-heptane solution to 7200 in the ethanol solution.

In order to clarify the nature of this solvent effect, we measured the spectrum of nitrosobenzene in ethanol - *n*-heptane mixed solvents. The results are shown in Fig. 4. The 300 mμ and 280 mμ bands respectively increase and decrease in intensity with the concentration of ethanol. This suggests that the following equilibrium might exist between the free nitrosobenzene molecule and the hydrogen-bonded one:

and that the formation of the hydrogen-bonded molecule might be the reason for the change in the above-mentioned absorption spectrum of nitrosobenzene. In order to check this point, we have measured the absorption spectrum of nitrosobenzene in various kinds of solvents with different dielectric constants. The observed maximum wavelengths and molar extinction coefficients are given in Table II.

From the results given in Table II, it is clear that dioxane, chloroform and acetonitrile, in spite of their lack of a proton-donating ability, have an effect on the 300 mμ and 280 mμ bands of nitrosobenzene similar to that of

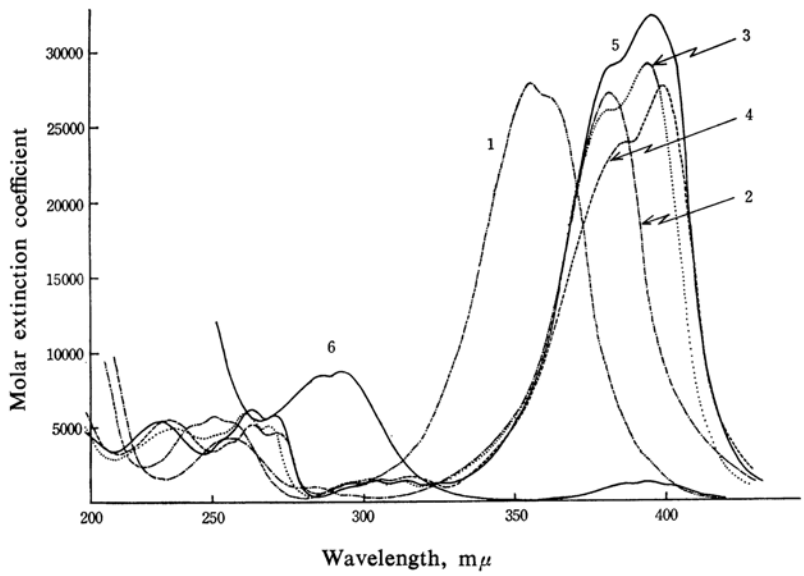

Fig. 3. The ultraviolet absorption spectra of nitrosoaniline and its *N*-substituted derivatives in *n*-heptane solution.

(1) ····· *p*-nitrosoaniline
(2) ····· *p*-nitrosodiphenylamine
(3) ····· *p*-nitroso-*N*, *N*-dimethylaniline
(4) ····· *p*-nitroso-*N*, *N*-diethylaniline
(5) ····· *p*-nitroso-*N*-ethyl-*N*-benzylaniline
(6) ····· *N*-nitrosodiphenylamine

TABLE II. THE SOLVENT EFFECT ON THE 280—300 mμ BAND OF NITROSOBENZENE

Solvent	Dielectric constant (at 20°C)	Absorption maxima and molar extinction coefficients	
n-Heptane	1.95	301.4 mμ (5200)	280.5 mμ (10330)
Ethyl ether	4.33	304 mμ (6070)	281 mμ (9720)
Ethanol	25	304 mμ (7200)	281 mμ (9320)
Dioxane	2.21	305.5 mμ (7060)	283 mμ (9120)
Chloroform	5.05	306 mμ (7890)	283 mμ (9200)
Acetonitrile	38.8	306 mμ (7940)	283.5 mμ (9140)

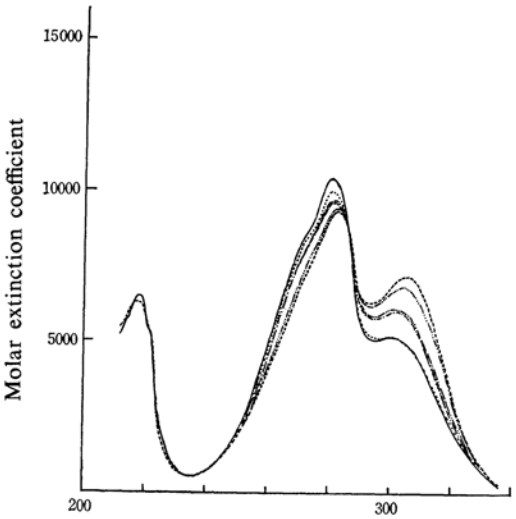

Fig. 4. The dependence of the 300—280 mμ bands of nitrosobenzene upon the ethanol content in the ethanol-*n*-heptane mixed solvents.

EtOH content
0 %
5 %
20 %
40 %
80 %
100 %

ethanol. Therefore, we can safely disregard the possibility that the above-mentioned solvent effect upon the absorption band of nitrosobenzene might be caused by hydrogen bonding. At least, it may be said that hydrogen bonding is not an important factor in the solvent effect. Furthermore, this solvent effect can not be due to the dimer formation because the $n\rightarrow\pi^*$ transition band at 760 mμ does not change in intensity when ethanol is added to the *n*-heptane solution. Therefore, it may be said that the change in the 300 mμ and 280 mμ bands of nitrosobenzene may be regarded as a general solvent effect caused by the polarity of the solvents.*

* In this case the polarity of the solvents has a wide meaning. Besides the average polarity represented by the dielectric constant or refractive index, the local polarity may take part in the solvent effect.

In this connection, it is noteworthy that the electron-donating group at the para position has the same effect upon the intensity of the 300 mμ band of nitrosobenzene. For instance, the corresponding band of *p*-nitrosotoluene, which appears at 310.8 mμ, has the molar extinction coefficient of 8800. This value is apparently larger than that of nitrosobenzene ($\varepsilon=5200$). This means that the methyl substitution brings about the red shift and intensity increment of the 300 mμ band of nitrosobenzene, as the polar solvents do. The above-mentioned solvent and substituent effects may be explained in terms of the stabilization of the charge-transfer structure which is caused by an electron transfer from the benzene ring to the nitroso group. This point will be discussed in detail below.

Theoretical

The electronic structure of nitrosobenzene has been studied by taking eight π-electrons into account. First, the molecule was divided into two components; the benzene ring and the nitroso group. The molecular orbitals of these components were determined. Then the interaction between the two components was considered by means of the configurational interaction among such electron configurations as the ground, locally excited and charge-transfer configurations.[9] The eight electron configurations taken up in the present study are given in Table III. A similar calculation was made by Tanaka,[10] but he disregarded the locally excited configuration within the nitroso group.

First of all, let us evaluate the energy of each configuration, taking the energy of the ground configuration as the standard; $H_G=0$. The energies of the four locally excited configurations of benzene, $H_{E_{1u}}$, $H_{E_{1u'}}$, $H_{B_{1u}}$, and $H_{B_{2u}}$, were taken from the observed transition energies of the corresponding absorption bands of benzene.[11] Their values are shown in Table

9) H. G. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 601 (1955); J. N. Murrell, ibid., **A68**, 969 (1955).
10) J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1647 (1956); **79**, 1114 (1957).
11) K. Kimura and S. Nagakura, *Mol. Phys.*, to be published.

TABLE III. THE ENERGIES AND WAVE FUNCTIONS OF THE EIGHT ELECTRON CONFIGURATIONS

Configuration*	Energy, eV.	Wave function
G	$H_G = 0$	$\Psi_G = \lvert 1\bar{1}2\bar{2}3\bar{3}s\bar{s}\rvert$**
LE*	$H_{E1u} = 6.98$	$\Psi_{E1u} = 1/2\{\lvert 1\bar{1}2\bar{2}3\bar{5}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{2}5\bar{3}s\bar{s}\rvert - \lvert 1\bar{1}2\bar{4}3\bar{3}s\bar{s}\rvert + \lvert 1\bar{1}4\bar{2}3\bar{3}s\bar{s}\rvert\}$
	$H_{E1u'} = 6.98$	$\Psi_{E1u'} = -1/2\{\lvert 1\bar{1}2\bar{2}3\bar{4}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{2}4\bar{3}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{5}3\bar{3}s\bar{s}\rvert + \lvert 1\bar{1}5\bar{2}3\bar{3}s\bar{s}\rvert\}$
	$H_{B1u} = 6.17$	$\Psi_{B1u} = -1/2\{\lvert 1\bar{1}2\bar{2}3\bar{4}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{2}4\bar{3}s\bar{s}\rvert - \lvert 1\bar{1}2\bar{5}3\bar{3}s\bar{s}\rvert - \lvert 1\bar{1}5\bar{2}3\bar{3}s\bar{s}\rvert\}$
	$H_{B2u} = 4.89$	$\Psi_{B2u} = 1/2\{\lvert 1\bar{1}2\bar{2}3\bar{5}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{2}5\bar{3}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{4}3\bar{3}s\bar{s}\rvert + \lvert 1\bar{1}4\bar{2}3\bar{3}s\bar{s}\rvert\}$
LE	$H_{LE} = 8.00$	$\Psi_{LE} = (1/2)^{1/2}\{\lvert 1\bar{1}2\bar{2}3\bar{3}s\bar{w}\rvert + \lvert 1\bar{1}2\bar{2}3\bar{3}w\bar{s}\rvert\}$
CT	$H_{CT} = 4.10$	$\Psi_{CT} = (1/2)^{1/2}\{\lvert 1\bar{1}2\bar{w}3\bar{3}s\bar{s}\rvert + \lvert 1\bar{1}w\bar{2}3\bar{3}s\bar{s}\rvert\}$
	$H_{CT'} = 4.52$	$\Psi_{CT'} = (1/2)^{1/2}\{\lvert 1\bar{1}2\bar{2}3\bar{w}s\bar{s}\rvert + \lvert 1\bar{1}2\bar{2}w\bar{3}s\bar{s}\rvert\}$

* G; ground configuration, LE*; locally (in benzene) excited configurations, LE; locally (in the nitroso group) excited configuration, CT; charge-transfer configurations.

** The precise form is as follows:

$$\Psi_G = (1/8!)^{1/2}\sum(-1)^p P\begin{Bmatrix}\phi_1(1)\phi_1(2)\phi_2(3)\phi_2(4)\phi_3(5)\phi_3(6)\phi_s(7)\phi_s(8)\\ \alpha(1)\ \beta(2)\ \alpha(3)\ \beta(4)\ \alpha(5)\ \beta(6)\ \alpha(7)\ \beta(8)\end{Bmatrix}$$

The molecular orbitals of benzene; ϕ_1, ϕ_2, ϕ_3, ϕ_4, and ϕ_5 are given as follows:

$$\phi_1 = (1/6)^{1/2}(\chi_1+\chi_2+\chi_3+\chi_4+\chi_5+\chi_6)$$
$$\phi_2 = (1/12)^{1/2}(2\chi_1+\chi_2-\chi_3-2\chi_4-\chi_5+\chi_6)$$
$$\phi_3 = 1/2(\chi_2+\chi_3-\chi_5-\chi_6)$$
$$\phi_4 = 1/2(\chi_2-\chi_3+\chi_5-\chi_6)$$
$$\phi_5 = (1/12)^{1/2}(2\chi_1-\chi_2-\chi_3+2\chi_4-\chi_5-\chi_6)$$

The molecular orbitals of the nitroso group, ϕ_s, ϕ_w are as follows[10]:

$$\phi_s = 0.6000\chi_N + 0.8000\chi_O$$
$$\phi_w = 0.8000\chi_N - 0.6000\chi_O$$

where χ_N and χ_O are the $2p\pi$ atomic orbitals of nitrogen and oxygen of the nitroso group respectively.

III. Furthermore, we assumed the energy of the locally excited configuration of the nitroso group, H_{LE}, as 8.00 eV. on the basis of the energy of the $\pi\rightarrow\pi^*$ transition band of chloronitrosocyclohexane. This compound exhibits a $\pi\rightarrow\pi^*$ transition band at about 160 mμ together with an $n\rightarrow\pi^*$ band at 650 mμ.[12]

The energies of two charge-transfer configurations, H_{CT} and $H_{CT'}$, which are caused by an electron transfer from the benzene ring to the nitroso group, are evaluated by the following equations:

$$H_{CT} = I_B - A_N - \Delta_{CT}$$
$$H_{CT'} = I_B - A_N - \Delta_{CT'}$$

where I_B and A_N are the ionization potential of benzene and the electron affinity of the nitroso group respectively, and where Δ_{CT} and $\Delta_{CT'}$ are the electrostatic interaction energies between the positive and negative charges caused by the electron transfer. The value of I_B is set at 9.24 eV., a value which was determined by Watanabe[13] from a photoionization experiment. The electron affinity of the nitroso group was assumed to be 0.55 eV. The values of Δ_{CT} and $\Delta_{CT'}$ were calculated as 4.59 and 4.17 eV. respectively. The two-center

TABLE IV. THE OFF-DIAGONAL MATRIX ELEMENTS*

$$H_{CT\cdot G} = (2/3)^{1/2}\cdot 0.8000\cdot(\beta+\beta') - (1/6)^{1/2}\cdot 0.6000\cdot(\beta''+\beta''')$$
$$H_{CT\cdot LE} = -(1/3)^{1/2}\cdot 0.6000\cdot(\beta+\beta') - (1/12)^{1/2}\cdot 0.8000\cdot(2\beta''+\beta''')$$
$$H_{CT\cdot E1u} = (1/8)^{1/2}\cdot 0.6000\beta'''$$
$$H_{CT\cdot E1u'} = -(1/6)^{1/2}\cdot 0.8000\cdot(\beta-\beta') + (1/24)^{1/2}\cdot 0.6000\cdot(2\beta''-\beta''')$$
$$H_{CT\cdot B1u} = (1/6)^{1/2}\cdot 0.8000\cdot(\beta-\beta') - (1/24)^{1/2}\cdot 0.6000\cdot(2\beta''-\beta''')$$
$$H_{CT\cdot B2u} = -(1/8)^{1/2}\cdot 0.6000\beta'''$$
$$H_{CT'\cdot G} = -(1/2)^{1/2}\cdot 0.6000\beta'''$$
$$H_{CT'\cdot LE} = -(1/2)0.8000\beta'''$$
$$H_{CT'\cdot E1u} = (1/6)^{1/2}\cdot 0.8000(\beta-\beta') - (1/24)^{1/2}\cdot(2\beta''-\beta''')$$
$$H_{CT'\cdot E1u'} = (1/8)^{1/2}\cdot 0.6000\beta'''$$
$$H_{CT'\cdot B1u} = (1/8)^{1/2}\cdot 0.6000\beta'''$$
$$H_{CT'\cdot B2u} = (1/6)^{1/2}\cdot 0.8000\cdot(\beta-\beta') - (1/24)^{1/2}\cdot 0.6000\cdot(2\beta''-\beta''')$$
$$H_{LE\cdot E1u} = (1/2)^{1/2}\{(sw|35) - (sw|24)\}^{**}$$
$$H_{LE\cdot E1u'} = -(1/2)^{1/2}\{(sw|34) + (sw|25)\}^{**}$$
$$H_{LE\cdot B1u} = -(1/2)^{1/2}\{(sw|34) - (sw|25)\}^{**}$$
$$H_{LE\cdot B2u} = (1/2)^{1/2}\{(sw|35) + (sw|24)\}^{**}$$

* β, β', β'', and β''' are the core resonance integrals for C_1—N, C_2—N, C_1—O and C_2—O bonds (see Fig. 5); they are -2.00 eV., -0.208 eV., -0.208 eV. and -0.062 eV. respectively.

** $(sw|mn) = \int \phi_s(1)\phi_w(1)\frac{e^2}{r_{12}}\phi_m(2)\phi_n(2)\,d\tau$

12) M. Tanaka and S. Nagakura, unpublished result.
13) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

TABLE V. ENERGY LEVELS AND WAVE FUNCTIONS OF NITROSOBENZENE

Energy eV.	Coefficients of electron configurations in the wave function of each level							
	Ψ_G	Ψ_{CT}	$\Psi_{CT'}$	Ψ_{LE}	$\Psi_{B_{2u}}$	$\Psi_{B_{1u}}$	$\Psi_{E_{1u}}$	$\Psi_{E_{1u}'}$
$W_0=-0.434$	0.9528	0.3003	−0.0023	−0.0315	0.0006	0.0239	0.0018	−0.0208
$W_1=4.079$	−0.1501	0.4521	0.7120	−0.1204	0.4588	0.1228	0.1416	−0.0766
$W_2=4.140$	0.2551	−0.7633	0.4271	0.1719	0.2784	−0.2005	0.0541	0.1402
$W_3=5.205$	−0.0041	0.0101	−0.5164	0.0190	0.8422	−0.0044	−0.1529	−0.0070
$W_4=6.283$	0.0446	−0.2035	−0.0017	0.0407	0.0027	0.9653	−0.0240	0.1502
$W_5=6.994$	−0.0020	0.0081	−0.1852	−0.2598	0.0452	−0.0397	0.8228	0.4663
$W_6=7.089$	−0.0353	0.1829	0.0939	−0.0001	−0.0231	−0.1038	−0.4675	0.8524
$W_7=8.283$	−0.0363	0.2182	−0.0276	0.9409	0.0033	0.0005	0.2395	0.0863

TABLE VI. CALCULATED AND OBSERVED TRANSITION ENERGIES AND OSCILLATOR STRENGTHS FOR THE ABSORPTION SPECTRUM OF NITROSOBENZENE

Transition	Transition energy, eV.		Oscillator strength	
	Calcd.	Obs.[a]	Calcd.	Obs.[a]
$W_0 \rightarrow W_1$	4.51	4.10 (301.4 mμ)	0.099	0.084
$W_0 \rightarrow W_2$	4.57	4.43 (281 mμ) 4.58 (272* mμ)	0.258	0.202
$W_0 \rightarrow W_3$	5.64	5.57 (222* mμ) 5.68 (218 mμ)	0.002	0.087
$W_0 \rightarrow W_4$	6.71	6.36 (194 mμ)	0.058	0.256
$W_0 \rightarrow W_5$	7.43	7.09 (174 mμ)	1.058	0.831
$W_0 \rightarrow W_6$	7.52		1.115	
$W_0 \rightarrow W_7$	8.72	—	0.629	—

a) The values observed with the *n*-heptane solution. * Vibrational structure

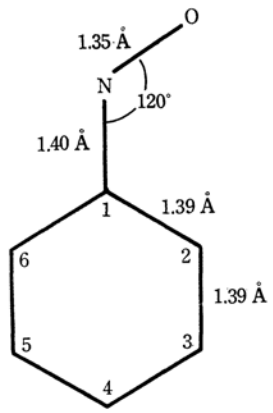

Fig. 5. The geometrical structure of nitrosobenzene.

Coulomb integrals of the (CC|NN) and (CC|OO) types necessary for the evaluation of Δ_{CT} and $\Delta_{CT'}$ were calculated by the aid of the quadratic equation of an atomic distance derived by Pariser and Parr's method.[14] For the actual calculations, the geometrical structure of nitrosobenzene was reasonably assumed to be as shown in Fig. 5, by making use of the X-ray crystal analysis data of the *p*-bromonitrosobenzene dimer.[15] Thus, the energies of the two charge-transfer configurations, H_{CT} and $H_{CT'}$ were determined to be 4.10 eV. and 4.52 eV. respectively.

The off-diagonal matrix elements of the Hamiltonian of the total electrons were calculated following the procedure developed by Pople[16] and by Longuet-Higgins and Murrell[17]. The results are shown in Table IV, where β's are the core resonance integrals; they were estimated on the assumption of the proportionality of the core resonance integrals to the overlap integrals.

The integrals (sw|35) in Table IV can be reduced to two center Coulomb integrals concerning appropriate atomic orbitals, which can be evaluated by the Pariser-Parr method mentioned above.

The energy levels and the wave functions finally evaluated by the aid of a FACOM 202 electronic computer are shown in Table V.

The oscillator strength, *f*, was calculated by means of the usual equation: [18]

$$f_{calc.}=1.085\times10^{-5}\times\nu Q^2$$

where Q and ν are the transition moment (in

14) R. Pariser and R. G. Parr, ibid., **21**, 466, 767 (1953); **23**, 711 (1955).

15) C. Darwin and D. C. Hodgkin, *Nature*, **166**, 827 (1950).

16) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).

17) H. C. Longuet-Higgins and J. N. Murrell, ibid., **A68**, 601 (1955).

18) R. S. Mulliken, *J. Chem. Phys.*, **7**, 34, (1939); J. R. Platt and H. B. Klevens, *Rev. Modern Phys.*, **16**, 183 (1944).

TABLE VII. DEPENDENCE OF TRANSITION ENERGIES AND OSCILLATOR STRENGTHS UPON THE ENERGIES OF THE CHARGE-TRANSFER CONFIGURATIONS

	Case	1	2	3	4
	H_{CT} =	4.30 eV.	4.10 eV.	3.90 eV.	3.70 eV.
	$H_{CT'}$ =	4.72 eV.	4.52 eV.	4.32 eV.	4.12 eV.
$W_0 \rightarrow W_1$	Energy =	4.63 eV.	4.51 eV.	4.38 eV.	4.25 eV.
	f value=	0.061	0.099	0.134	0.137
$W_0 \rightarrow W_2$	Energy =	4.71 eV.	4.57 eV.	4.44 eV.	4.30 eV.
	f value=	0.288	0.258	0.234	0.231
$W_0 \rightarrow W_3$	Energy =	5.68 eV.	5.64 eV.	5.61 eV.	5.59 eV.
	f value=	0.003	0.002	0.002	0.001

units of Å) and the evaluated transition energy (in units of cm^{-1}) respectively. The evaluated oscillator strength values are, in Table VI, compared with the observed ones obtained by the following equation:

$$f_{obs.} = 4.32 \times 10^{-9} \times \int \varepsilon(\nu) d\nu$$

where ε is the molar extinction coefficient.

Theoretical Results and Discussion

When the calculated transition energy and the oscillator strength are compared with the observed values, the 174 mμ band, which was newly found by the present authors, can safely be assigned to the superposed $W_0 \rightarrow W_5$ and $W_0 \rightarrow W_6$ transitions, and the 194 mμ band, to the $W_0 \rightarrow W_4$ transition. Judging from the wave functions of the W_4, W_5 and W_6 levels, the former may be regarded as the shifted band of the $A_{1g} \rightarrow E_{1u}$ transition band of benzene, and the latter, as that of the $A_{1g} \rightarrow B_{1u}$ transition band of benzene.

The 218 mμ band corresponding to the $W_0 \rightarrow W_3$ transition may be said to have the nature of the $A_{1g} \rightarrow B_{2u}$ transition band of benzene, but the contribution from one of the charge-transfer configurations ($\phi_3^{-1}\phi_w$) amounts to 25%.

The 280.5 mμ band can be ascribed to the $W_0 \rightarrow W_2$ transition. The contributions of the charge-transfer configurations to the W_2 level amount to 62% (CT) and 17% (CT') respectively. Therefore, the 280.5 mμ band may safely be regarded as the charge-transfer absorption band, although there are small contributions of such other components as local excitations in the nitroso and benzene groups.

The 301.4 mμ band corresponding to the $W_0 \rightarrow W_1$ transition may be thought to have a character mixing locally excitation within the benzene ring (B_{2u}) and the charge-transfer excitation, since the contributions of the charge-transfer and B_{2u} locally excited configurations are 49% (CT'), 18% (CT) and 20% (B_{2u}) respectively.

As was previously stated, the 280 mμ and 300 mμ bands are sensitive to the polarity of the solvent. In polar solvents, the absorption bands have a tendency to become similar to those of the *p*-nitrosotoluene and other simple *p*-substituted nitrosobenzene derivatives, as is shown in Fig. 4.

In order to explain the polar solvent effect, we calculated the energy levels and wave functions, changing the energy values of the two charge-transfer configurations, H_{CT} and $H_{CT'}$. The results are tabulated in Table VII. It can be seen that the decrease in the energies of the two charge-transfer configurations brings about a decrease in the transition energies for the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ and $W_0 \rightarrow W_3$ transitions and causes an increase in the oscillator strength for the $W_0 \rightarrow W_1$ transition. On the other hand, in the $W_0 \rightarrow W_2$ transition which corresponds to the 280 mμ band of nitrosobenzene, the oscillator strength very slightly decreases in the order of cases 1, 2, 3, and 4.

The above-mentioned theoretical results seem to explain the effects of solvents and of *p*-substituted electron-donating groups. That is to say, the wavelength shifts and intensity changes of the 300 mμ and 280 mμ bands may be thought to be caused by the fact that the energies of the charge-transfer configurations change with the polarity of solvents or when an electron-donating group is substituted for the hydrogen atom at the para position.

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The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo