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The Electronic Structures and Electronic Spectra of Some Aliphatic Nitroso Compounds

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The electronic structures and electronic spectra of 1-chloro-1-nitrosocyclohexane, nitrosyl chloride, methyl nitrite and dimethylnitrosoamine were studied by making molecular orbital calculations and by measuring the electronic absorption spectra. Concerning 1-chloro-1-nitrosocyclohexane, the $n \to \pi^*$ and $\pi \to \pi^*$ bands were observed at 650 and 160 mμ respectively. The conjugation effect of electron donors such as Cl, OCH_3 and $N(CH_3)_2$ upon the electronic spectrum of the nitroso group was studied. The intramolecular charge-transfer bands characteristic of the donor-acceptor interaction were found at 190, 210 and 230 mμ for nitrosyl chloride, methyl nitrite and *N*, *N*-dimethylnitrosoamine respectively. This shows that the intramolecular charge-transfer bands appear at longer wavelengths in the order of the increasing ability of the electron donors, $Cl < OCH_3 < N(CH_3)_2$. On the other hand, the $n \to \pi^*$ bands shift to shorter wavelengths in the same order.

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In a previous paper which studied the electronic absorption spectra of nitrosobenzene[1] and its derivatives, it was shown that the nitroso group is a strong electron acceptor, and that their ultraviolet absorption spectra are greatly different from that of benzene. Nitrosobenzene exhibits a new band characteristic of the charge-transfer interaction between the benzene ring as an electron donor and the nitroso group as an electron acceptor. Moreover, the maximum wavelength of the band is longer than the corresponding band of nitrobenzene. This seems to mean that the electron affinity of the nitroso group is greater than that of the nitro group. In view of the large electron-accepting ability of the nitroso group, the electronic structures of aliphatic nitroso compounds have been studied in the present paper by combining the experimental data of the absorption spectra with the theoretical results based on the molecular orbital calculations.

The electronic absorption spectra of aliphatic nitroso compounds have been studied by several workers from both experimental[2-7] and theoretical[8,9] points of view. In the present study, the electronic absorption spectrum of 1-chloro-1-nitrosocyclohexane was measured in order to obtain fundamental knowledge about the electronic structure of the nitroso group itself. Then the charge-transfer interaction of the nitroso group with electron donors such as Cl, OCH_3 and $N(CH_3)_2$ has been studied by the aid of the electronic absorption spectra in the vacuum ultraviolet region.

Experimental

Materials.—*Methyl Nitrite.*[2]—A sulfuric acid (12 N) solution was dropped on a mixture of methanol and a 45% aqueous sodium nitrite solution. The crude product was dried over calcium chloride and was purified by repeated low-temperature distillations in vacuo.

N, N-Dimethylnitrosoamine.[10]—A mixture of dimethylamine and sodium nitrite was heated for several hours. The oil layer was separated and the aqueous portion was extracted with benzene. The benzene was removed by distillation and the residue was fractionally distilled under reduced pressure. The nitrosoamine was obtained as a light yellow liquid; b. p. 104°C/ca. 10mmHg.

1-Chloro-1-nitrosocyclohexane.[5]—Cyclohexanone oxime was dissolved in diluted hydrochloric acid and the solution was cooled by ice water.

A fairly rapid stream of chlorine was passed through the solution until no more gas was absorbed. The separated blue oil was extracted with ether and then washed with an aqueous sodium bicarbonate solution and with water. After the extract had been dried with anhydrous sodium sulfate, the ether was removed. The nitroso compound was then distilled under reduced pressure as a purple oil with a very unpleasant smell; (b. p. 58°C/13 mmHg).

Measurements.—The absorption spectra of the

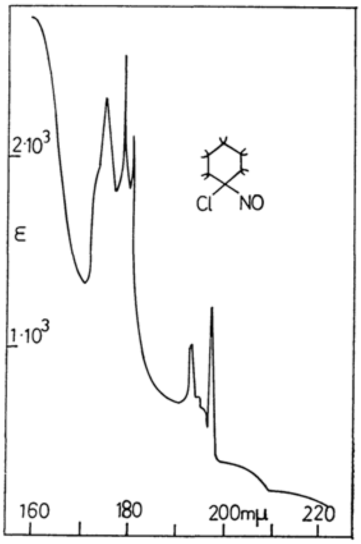

Fig. 1. The ultraviolet absorption spectrum of 1-chloro-1-nitrosocyclohexane.

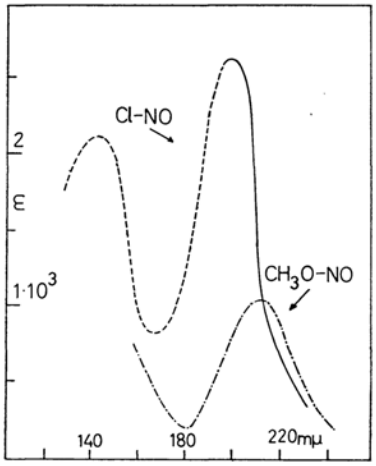

Fig. 2. The ultraviolet absorption spectra of methyl nitrite and nitrosyl chloride.

—— nitrosyl chloride, measured by Goodeve and Katz

---- nitrosyl chloride, measured by Price and Simpson

-·— methyl nitrite, measured by the present authors

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[1] K. Tabei and S. Nagakura, This Bulletin, **38**, 965 (1965).

[2] P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1955).

[3] R. N. Haszeldine and B. J. H. Hattinson, *J. Chem. Soc.*, **1955**, 4172.

[4] J. Mason, ibid., **1957**, 3904.

[5] D. L. Hammick and M. W. Lister, ibid., **1937**, 489.

[6] C. F. Goodeve and S. Katz, *Proc. Roy. Soc.*, **A172**, 437 (1939).

[7] W. C. Price and D. M. Simpson, *Trans. Faraday Soc.*, **37**, 106 (1941).

[8] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 1647 (1957).

[9] K. L. McEwen, *J. Chem. Phys.*, **34**, 546 (1961).

[10] M. Kotake, "Daiyuki Kagaku-Organic Chemistry-III," Asakura, Tokyo (1959), p. 126.

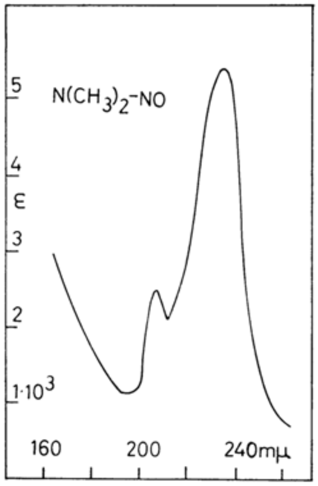

Fig. 3. The ultraviolet absorption spectrum of *N, N*-dimethylnitrosoamine.

above-mentioned samples were measured in the gaseous states. The ultraviolet absorption measurements down to 190 mμ were made with a Cary recording spectrophotometer, model 14 M, a quartz cell 10 cm. long being used. A vacuum ultraviolet spectrophotometer constructed in our laboratory was used for the measurements in the vacuum ultraviolet region. In this case, a gas cell 0.7 cm. long and equipped with lithium fluoride windows was used.

The results are shown in Figs. 1—3, together with the absorption spectrum of nitrosyl chloride, which was measured by Goodeve and Katz[6] down to 190 mμ and by Price and Simpson[7] down to 130 mμ.

The peak wavelengths and molar extinction coefficients are tabulated in Table I.

TABLE I. THE OBSERVED PEAK WAVELENGTHS AND MOLAR EXTINCTION COEFFICIENTS FOR VARIOUS ALIPHATIC NITROSO COMPOUNDS

Sample	λ_{max}, mμ	ε_{max}
1-Chloro-1-nitroso-cyclohexane	(750	0.6)*[5]
	197	1200
	179	2800
	~160	>2600
Nitrosyl chloride[6,7]	(615	0.7)*
	197	2550
	145	2000
Methyl nitrite	(386	10)*
	212	1050
N, N-Dimethyl nitrosoamine	(377	50)*
	227	5200
	205	2350

* These absorptions have vibrational structures. The wavelengths given in this table are those for the longest wavelength bands which may be assigned to the 0—0 band.

Theoretical

The π-electron structures of nitrosyl chloride, methyl nitrite and *N, N*-dimethylnitrosoamine have been studied theoretically on the basis of the geometrical structures shown in Fig. 4. The geometrical structures of nitrosyl chloride and methyl nitrite were studied by Ketelaar and Palmer[11] and by Rogowski[12] respectively. However, the geometrical structure of *N, N*-dimethylnitrosoamine has not yet been studied experimentally. Therefore, we assume its structure to be as is shown in Fig. 4.

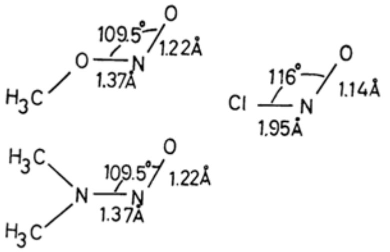

Fig. 4. The geometrical structures of nitrosyl chloride, methyl nitrite and *N, N*-dimethylnitrosoamine.

Calculation of the MO of the Nitroso Group. —First of all, the LCAO SCF MO's ϕ_i of the π-electron system of the nitroso group were evaluated by means of the usual equation[13]:

$$F\phi_i = \varepsilon_i\phi_i, \quad \phi_i = a\chi_{\mathrm{N}} + b\chi_{\mathrm{O}}$$

where χ_{N} and χ_{O} indicate the 2pπ atomic orbitals of the nitrogen and the oxygen atoms of the nitroso group respectively. The details of the calculation will be given in the Appendix.

The resultant molecular orbitals, ϕ_i, and orbital energies, ε_i, are given below:

$$\varepsilon_1 = -17.70 \text{ eV.}, \quad \phi_1 = 0.5963\chi_{\mathrm{N}} + 0.8028\chi_{\mathrm{O}}$$

$$\varepsilon_2 = -0.61 \text{ eV.}, \quad \phi_2 = 0.8028\chi_{\mathrm{N}} - 0.5963\chi_{\mathrm{O}}$$

It is clear from these results that the μ-electron distribution in the ϕ_1 orbital of the nitroso group inclines toward the oxygen atom, and that the electron affinity of the nitroso group, $-\varepsilon_2 = 0.61$ eV., is larger than those of the nitro and carbonyl groups, 0.40 eV.[14] and −1.20 eV.[15] respectively.

The transition energy, $\Delta E(\mathrm{N}\rightarrow\mathrm{V})$, and oscillator strength, *f*, were calculated as follows:

$$\Delta E(\mathrm{N}\rightarrow\mathrm{V}) = 7.96 \text{ eV.}$$

$$f = 0.475$$

For the purpose of checking the theoretical results,

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[11] J. A. Ketelaar and K. J. Palmer, *J. Am. Chem. Soc.*, **59**, 2629 (1937).

[12] F. Rogowski, *Ber.*, **75**, 244 (1942).

[13] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

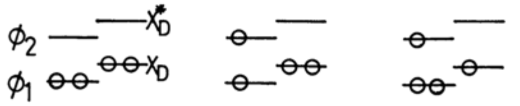
[14] J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 1643 (1957).

[15] S. Nagakura, *Mol. Phys.*, **3**, 105 (1960).

we measured the absorption spectrum of 1-chloro-1-nitrosocyclohexane. As may be seen in Table I, 1-chloro-1-nitrosocyclohexane shows absorption bands at 750, 197, 179 and ~160 mμ. The 750 mμ band may safely be regarded as the $n \rightarrow \pi^*$ transition band. The peak at about 160 mμ (7.75 eV.) may correspond to the N→V ($\pi \rightarrow \pi^*$) transition of the nitroso group, while the other two peaks, at 179 mμ and 197 mμ, seem to correspond to an $n \rightarrow \pi^*$ transition or a band of the Rydberg series.

Configuration Interaction Calculation.—The π-electron energy levels and the wave functions of nitrosyl chloride, methyl nitrite and *N*, *N*-dimethylnitrosoamine were calculated by taking into account the configurational interaction among several electron configurations. The respective molecules were separated into the two components, the electron donor, Cl–, CH_3O– or $(CH_3)_2N$– and the electron acceptor, NO–. The interaction between them was considered by means of the configurational interaction among π electron configurations which were constructed by putting the four π electrons into the appropriate orbitals of the components.

The electron configurations actually taken up in the present calculation are shown in Fig. 5.



ground config. locally excited config. charge-transfer config.

Fig. 5. The electron configurations of the nitroso compounds.

In addition to the ground configuration, G, a charge-transfer configuration, CT, caused by an electron transfer from the electron donor toward the electron acceptor, and a locally excited configuration, LE, were considered. The energy of the ground configuration, H_G, was taken as the standard. The energy of the locally excited configuration, H_{LE}, was set equal to 7.96 eV., the N→V transition energy of the nitroso group as evaluated theoretically by the present authors. The energy of the charge-transfer configuration, H_{CT}, was calculated by the following equation:

$$H_{CT} = I_D - A_{NO} - 0.5963^2(NN/DD) - 0.8028^2(OO/DD)$$

Here the I_D's are the ionization potentials of the electron-donating groups, i. e., Cl–, CH_3O– and $(CH_3)_2N^-$. They were taken to be 12.84, 10.85 and 8.24 eV. for the chloro, methoxy and *N*, *N*-dimethylamino groups respectively from the ionization potentials of hydrochloric acid,[16] methanol[17] and dimethylamine[18]. A_{NO} is the electron affinity of the electron-accepting group, –NO; it was calculated to be 0.61 eV. by the present authors. D indicates the 2pπ or 3pπ atomic orbital for the lone pair electrons of the donor.

Two center Coulomb repulsion integrals like (NN/DD) were evaluated nonempirically, using Slater orbitals except for (NN/ClCl) and (OO/ClCl), which were calculated by Pariser and Parr's method.[19] The energies and wave functions of the configurations used in the present calculations are tabulated in Table II.

Table II. The energies and wave functions of the electron configurations

Energy, eV.	Wave function
$H_G=0$	$\Phi_G=\mid \phi_1\overline{\phi_1}D\overline{D} \mid$
$H_{LE}=7.96$	$\Phi_{LE}=1/\sqrt{2}\{\mid \phi_1\overline{\phi_2}D\overline{D} \mid$ $+\mid \phi_2\overline{\phi_1}D\overline{D} \mid\}$
$H_{CT}=5.77(NOCl)$ $2.58(CH_3ONO)$ $-0.04((CH_3)_2NNO)$	$\Phi_{CT}=1/\sqrt{2}\{\mid \phi_1\overline{\phi_1}\phi_2\overline{D} \mid$ $+\mid \phi_1\overline{\phi_1}D\overline{\phi_2} \mid\}$

Table III. The off-diagonal elements used in the present calculation

$$H_{GLE}=0 \qquad H_{G\,CT}=\sqrt{2}\,b\beta_{ND} \qquad H_{LE\,CT}=-a\beta_{ND}$$

$$\beta_{NCl}=\int \chi_N \boldsymbol{H}^{core}\chi_{Cl}d\tau=-1.40\text{ eV.}$$

$$\beta_{NO}=\int \chi_N \boldsymbol{H}^{core}\chi_{Cl}d\tau=-2.20\text{ eV.}$$

$$\beta_{NN}=\int \chi_N \boldsymbol{H}^{core}\chi_{Cl}d\tau=-2.10\text{ eV.}$$

The off-diagonal matrix elements of the total electronic Hamiltonian, each of which represents the magnitude of the interaction between two different configurations, were evaluated by the aid of the formulations by Pople[20] and by Longuet-Higgins and Murrell.[21] They are given in Table III in terms of the core resonance integrals, β_{NCl}, β_{NO} and β_{NN}. By solving the determinants constructed by the matrix elements given in Tables II and III with an electronic computer, Facom 202, in our Institute, the π electron energy levels and the wave functions for nitrosyl chloride, methyl nitrile and *N*, *N*-dimethylnitrosoamine were evaluated. The results are shown in Table IV. From these results, the dipole moments due to the π electrons in the ground state, the transition energies and the oscillator strengths were calculated for these nitroso compounds. The results are shown Table V, together with the observed results.

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[16] W. C. Price, *Proc. Roy. Soc.*, **A167**, 216 (1938).

[17] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[18] K. Watanabe, ibid., **26**, 1773 (1957).

[19] R. Pariser and R. G. Parr, ibid., **21**, 466, 767 (1953); R. Pariser, ibid., **24**, 250 (1956).

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

[21] H. C. Longuet-Higgins and J. N. Murrell, *Proc. phys. Soc.*, **A68**, 601 (1955).

TABLE IV. THE ENERGY LEVELS AND WAVE FUNCTIONS FINALLY OBTAINED WITH NITROSYL CHLORIDE, METHYL NITRITE AND *N*, *N*-DIMETHYLNITROSOAMINE

	Energy, eV.	Wave function
Nitrosyl chloride	$W_0=-0.41$	$\Psi_0=\ 0.9673\Phi_G-0.0251\Phi_{LE}+0.2522\Phi_{CT}$
	$W_1=\ 5.86$	$\Psi_1=-0.2442\Phi_G-0.3588\Phi_{LE}+0.9009\Phi_{CT}$
	$W_2=\ 8.28$	$\Psi_2=-0.0679\Phi_G+0.9330\Phi_{LE}+0.3533\Phi_{CT}$
Methyl nitrite	$W_0'=-1.57$	$\Psi_0'=\ 0.8441\Phi_G-0.0731\Phi_{LE}+0.5312\Phi_{CT}$
	$W_1'=\ 3.80$	$\Psi_1'=-0.5308\Phi_G-0.2551\Phi_{LE}+0.8082\Phi_{CT}$
	$W_2'=\ 8.30$	$\Psi_2'=-0.7644\Phi_G+0.9641\Phi_{LE}+0.2542\Phi_{CT}$
N, *N*-Dimethyl-nitrosoamine	$W_0''=-2.48$	$\Psi_0''=\ 0.6900\Phi_G-0.0862\Phi_{LE}+0.7187\Phi_{CT}$
	$W_1''=\ 2.23$	$\Psi_1''=\ 0.7222\Phi_G+0.1477\Phi_{LE}-0.6757\Phi_{CT}$
	$W_2''=\ 8.17$	$\Psi_2''=-0.0479\Phi_G+0.9853\Phi_{LE}+0.1642\Phi_{CT}$

TABLE V. THE OBSERVED AND CALCULATED DIPOLE MOMENTS, TRANSITION ENERGIES AND OSCILLATOR STRENGTHS

	Dipole moment in the ground state (DU)		Transition	Transition energy eV.		Oscillator strength	
	Obs.	Calcd.		Obs.	Calcd.	Obs.[a]	Calcd.
Nitrosyl chloride	1.83[22]	1.91	$W_0\rightarrow W_1$	6.28	6.28		0.263
			$W_0\rightarrow W_2$	8.55	8.69		0.263
Methyl nitrite	3.84[23]	3.90	$W_0'\rightarrow W_1'$	5.90	5.38	0.052	0.272
			$W_0'\rightarrow W_2'$	7.5	9.88		0.270
N, *N*-Dimethyl-nitrosoamine	3.98[24]	5.50	$W_0''\rightarrow W_1''$	5.47	4.71	0.150	0.253
			$W_0''\rightarrow W_2''$	7.5	10.65		0.194

a) Observed oscillator strengths are uncertain.

Discussion

Nitrosyl Chloride.—As is shown in Fig. 2 and Table I, nitrosyl chloride shows three absorption bands in the visible and ultraviolet regions. The 615 mμ band may be ascribed to the $n\rightarrow\pi^*$ transition. The 197 mμ band can be assigned to the W_0-W_1 transition. From the wave function, Ψ_1, given in Table IV, it may be seen that the band has the character of the intramolecular charge-transfer band. The band at about 145 mμ is due to the W_0-W_2 transition, which has the property of the local excitation within the nitroso group. Therefore, the 160 mμ band of the nitroso group shifts to 145 mμ by conjugation with the nonbonding electrons of the chlorine atom.

It may be seen from Ψ_0 given in Table IV that the contribution of the charge-transfer configuration in the ground state of this compound is only 6%. The calculated dipole moment due to the π-electrons can explain the observed value satisfactorily (see Table V).

Methyl Nitrite.—Methyl nitrite shows two absorption peaks, at 386 mμ and 212 mμ. In addition, a strong band appears below 160 mμ (see Fig. 2). The 386 mμ band may be assigned to the $n\rightarrow\pi^*$ band of the nitroso group. The 212 mμ band, which corresponds to the $W_0'\rightarrow W_1'$ transition of methyl nitrite, may be regarded as an intramolecular charge-transfer band. This is because, as may be seen from Ψ_1' in Table V, the contribution of the charge-transfer configuration in the W_1' state amounts to 65%. The shorter wavelength band, the maximum of which does not appear until 160 mμ, may be ascribed to the $W_0'\rightarrow W_2'$ transition. This band may be interpreted as the blue-shifted band of the 170 mμ band of the nitroso group. It is known from Ψ_0' given in Table IV that the contribution of the charge-transfer configuration in the ground state is 28%.

***N*, *N*-Dimethylnitrosoamine.** — The absorption spectrum of *N*, *N*-dimethylnitrosoamine is similar to that of methyl nitrite. The 377 mμ band may be regarded as an $n\rightarrow\pi^*$ transition band, as may be the 386 mμ band of methyl nitrite. The strong band at 227 mμ corresponds to the 212mμ band of the methyl nitrite and may be interpreted as an intramolecular charge-transfer band. The absorption tail below 190mμ may be due to the local excitation within the NO group. A similar absorption tail was also observed with methyl nitrite. The peak at 205 mμ may be thought to be an extra band in the sense that the corresponding band was not observed with methyl nitrite. This may be regarded as the $n\rightarrow\pi^*$ transition band of the dimethylamino group.[25]

As may be seen from Table IV, the contribution of the charge-transfer configuration in the ground state

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22) J. A. Ketelaar, *Rect. trav. chim.*, **62**, 289 (1943).

23) T. Chiba, This Bulletin, **28**, 505 (1955).

24) E. G. Cowley and J. R. Rartington, *J. Chem. Soc.*, **1933**, 1255.

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

decreases in the following order; *N, N*-dimethylnitrosoamine$>$methyl nitrite$>$nitrosyl chloride. This means that the electron-donating power of the substituents decreases in the order of $N(CH_3)_2>OCH_3>Cl$.

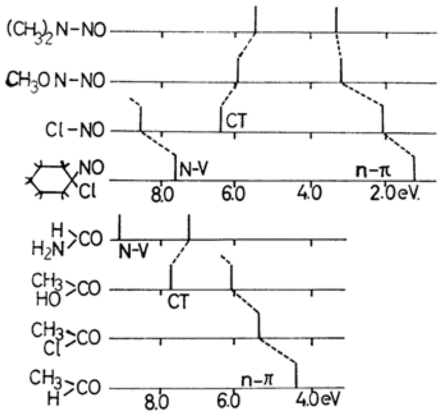

Fig. 6. The relation between the transition energy and the electron-donating ability of Cl, OCH_3 and $N(CH_3)_2$.

The Effect of the Electron-donating Group upon the Absorption Spectrum of the Nitroso Compounds.—The results obtained by the present authors are summarized in Fig. 6. This figure shows that the absorption spectra of XNO change regularly with the electron-donating power of X. That is, with the increasing electron-donating power of X, the $n\rightarrow\pi^*$ band shifts toward the shorter wavelengths, and the charge-transfer band toward the longer wavelengths. As is shown in Fig. 6, the same tendency was observed with the carbonyl compounds, O=CRX. The $n\rightarrow\pi^*$ transition band which appears at 280 mμ for acetaldehyde shifts to 232 mμ and to 205 mμ for acetylchloride and acetic acid respectively[26]. The band of acetamide shifts to a shorter wavelength than 200 mμ. On the other hand, the intramolecular charge-transfer band appears at 171.7 mμ and at 160 mμ for formamide and acetic acid respectively[15,27].

The authors' thanks are due to Dr. Michiya Itoh for his kind advice in preparing 1-chloro-1-nitrosocyclohexane, and also to Mr. Koji Kaya for his kind help in measuring the vacuum ultraviolet absorption spectra.

Appendix

The molecular orbital energies ε_i are solutions of the following secular determinant

$$\begin{vmatrix} F_{NN}-\varepsilon & F_{NO} \\ F_{NO} & F_{OO}-\varepsilon \end{vmatrix}=0$$

By the aid of the Pariser-Parr method,[19] the F_{NN}, F_{OO} and F_{NO} are given in the following

$$F_{NN} = \alpha_N + a^2(NN/NN) + 2b^2(NN/OO)$$
$$F_{OO} = \alpha_O + 2a^2(NN/OO) + b^2(OO/OO)$$
$$F_{NO} = \beta_{NO} - ab(NN/OO)$$

In this expression, one-center Coulomb repulsion integrals (NN/NN) and (OO/OO) are estimated by the aid of Pariser's approximation, namely averaging the I_p—A of the 2pπ electron at various valance states, where I_p is the appropriate valence state ionization potential[28] and A the appropriate valence state electron affinity.[28] The two-center Coulomb repulsion integral was calculated by the use of the Slater orbitals[29] at the bond length $r_{NO}=1.22$ Å. Following the Pariser-Parr theory, the core integral β_{NO} was left as an adjustable parameter, and α_N and α_O were given by the following equations.

$$\alpha_N = -I_p(N) - (NN/OO)$$
$$\alpha_O = -I_p(O) - (NN/OO)$$

The above-mentioned various quantities are presented in Table VI.

TABLE VI. INTEGRALS INVOLVING π-ATOMIC ORBITALS (eV.)

$\alpha_N=-23.15$	$\alpha_O=-28.41$
$I_p(N)=14.51$	$I_p(O)=17.79$
$(NN/NN)=13.38$	$(OO/OO)=14.33$
$(NN/OO)=10.62$	
$\beta_{NO}=-3.10$	

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26) S. Nagakura, ibid., **25**, 164 (1952).

27) S. Nagakura, K. Kaya and H. Tsubomura, *J. Mol. Spect.*, **13**, 1 (1964).

28) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

29) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).