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Electronic Spectra and Electronic Structures of Benzonitrile *N*-Oxide and Its Derivatives

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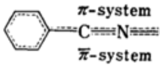
The electronic spectra of 2,6-dimethylbenzonitrile *N*-oxide and its some derivatives were recorded in *n*-heptane and were compared with those of benzonitrile and phenylacetylene. The analyses of the electronic spectra of aromatic nitrile *N*-oxides were done by the following procedures. First, simple molecular orbitals (SMO) of benzonitrile and phenylacetylene were calculated using some parameters determined by the use of the overlap integrals and valence state ionization potentials. Then, by comparing the eigenvalues of the SMO thus obtained with the observed spectra the spectroscopic exchange integrals have been obtained for $^1A_1$ and $^1B_1$ bands, where interactions between two configurations were taken into consideration for the $^1B_1$ bands. The SMO of benzonitrile *N*-oxide was next calculated on reference to the physicochemical nature of aromatic nitrile *N*-oxides studied before. The parameters were chosen so as to fit with the observed values of dipole moments of benzonitrile *N*-oxide and its some methyl derivatives. Electronic spectra of the nitrile *N*-oxides were then analyzed using the above SMO's and spectroscopic exchange integrals. The substituent effect on the electronic spectrum of benzonitrile *N*-oxide was also discussed by the similar treatment. Characteristic strong band appearing in the near UV region was assigned to the $^1A_1$ band having a change transfer (CT) nature, where the CT from the oxygen atom to the residual conjugated system makes a larger contribution than that of the reverse direction. In addition, the physicochemical nature and reactivity of nitrile *N*-oxides were discussed on the basis of their molecular diagrams, which were obtained from the SMO's mentioned above.

In the previous papers,[1,2] the electronic spectra of substituted benzonitrile *N*-oxides and 9-anthronitrile *N*-oxide were recorded in various solvents and compared with those of the corresponding nitriles. In addition, molecular complexes of aromatic nitrile *N*-oxides with iodine, β-naphthol and phenol were studied quantitatively by electronic and infrared (IR) spectroscopic methods.[1-3] Discussions were made from the viewpoints of solvent and substituent effects on the above electronic spectra and of charge-transfer (CT) type complexing ability. It was concluded that the π-conjugated systems of benzonitrile *N*-oxide (BNO) are well illustrated as I,



(I)

where the CNO group has a character of a partial triple bond consisting of π and $\overline{\pi}$ system (see I) This conclusion was led from the experimental evidences that (i) CT type complexing ability of aromatic nitrile *N*-oxides is very weak, (ii) the N–O stretching vibration, $\tilde{\nu}_{NO}$, appears at higher frequency than that of pyridine *N*-oxide, and (iii) substituted benzonitrile *N*-oxides exhibit an absorption band with high intensity ($\varepsilon > 10000$) in a near ultraviolet (UV) region where the corresponding nitriles do not show such a high intensity band. The absorption band pertinent to the nitrile *N*-oxides was found to undergo a blue shift with an increasing polarity of solvents, although the shift is small compared with some other kinds of tertiary amine *N*-oxides. It seems to be now interesting to examine the stated experimental results from theoretical points of view. The present paper describes the molecular orbital (MO) treatment of BNO and its derivatives to discuss the UV spectra and other physicochemical natures. The results will be compared with those of nitrones reported previously,[4,5] because benzylidene methylamine *N*-oxide (BMANO)[6] and BNO are isoelectronic on the π-electron system except for the presence of $\overline{\pi}$-system in BNO (see I).

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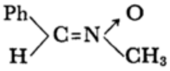
[1] M. Yamakawa, T. Kubota and H. Akazawa, This Bulletin, **40**, 1600 (1967).

[2] T. Kubota, M. Yamakawa, M. Takasuka, K. Iwatani, H. Akazawa and I. Tanaka, *J. Phys. Chem.*, **71**, 3597 (1967).

[3] T. Kubota, K. Ezumi, M. Yamakawa and Y. Matsui, *J. Mol. Spectroscopy*, **24**, 378 (1967).

[4] T. Kubota and M. Yamakawa, This Bulletin, **36**, 1564 (1963).

[5] T. Kubota, M. Yamakawa and Y. Mori, *ibid.*, **36**, 1552 (1963).

[6] The structure is  $\mathrm{Ph(H)C{=}N(\to O)CH_3}$ a typical nitrone.

Experimental

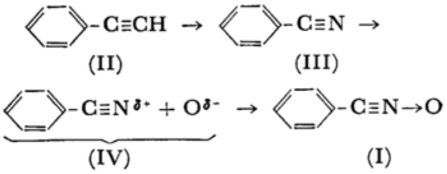
Measurement of electronic and IR spectra and the purification of solvents employed were the same as were described in the foregoing papers.[1,2]

Materials. In addition to the aromatic nitrile *N*-oxides reported already,[1] 4-dimethylamino-2,6-dimethylbenzonitrile *N*-oxide (DMABNO) was newly synthesized to get the spectra. DMABNO (new compound) was obtained by the reaction of the corresponding oxime with NaOBr according to Grundmann's method,[7] and was recrystallized several times with methanol: mp 134.0—136°C; IR, $\tilde{\nu}_{NO}=1341$ cm^{-1} and $\tilde{\nu}_{C\equiv N}=2287$ cm^{-1} in CCl_4. The above oxime, 4-dimethylamino-2,6-dimethylbenzaldoxime (new compound, mp 135.0—137.5°C, a mixture of syn and anti forms) was prepared by the reaction of hydroxylamine with the corresponding aldehyde (mp 82.5—83.5°C) which was obtained by Vilsmeyer-Haackschen's method[8] from *N,N*-dimethyl-3,5-dimethylaniline (125°C/37 mmHg) prepared by dimethylation of 3,5-dimethylaniline with trimethylphosphate ($(CH_3O)_3PO$).[9]

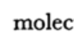
The nitrile, DMABN, corresponding to DMABNO was synthesized by the dehydration of 4-dimethylamino-2,6-dimethylbenzaldoxime mentioned above with acetic anhydride.[10,11] The pure material of DMABN, mp 89°C, was obtained by chromatograph passing through the alumina and by recrystalliation from petroleum ether; $\tilde{\nu}_{C\equiv N}=2213$ cm^{-1} (CCl_4). The main absorption maxima (mμ) and intensities (ε_{max}), latter being shown in parentheses, of DMABNO and DMABN in *n*-heptane are: 292.7 (22900), 229.0 (11500), and 206.8 (23000) for DMABNO and 282.3 (27600), 233.7 (14100), 227.2 (14700), 206.2 (19300), and 188.0 (17800) for DMABN. The purity of the samples was carefully checked on by elementary analyses and UV, IR, and NMR spectroscopic measurements. Commercial phenylacetylene (GR grade of Kanto Chemical Co.) and benzonitrile (special grade of Wako Chemical Co.) were first purified by repeated distillations. Then these were subjected to rectifying distillation through a good efficient column to collect the middle portions; bp 142.4°C and 46.0—46.5°C/5 mmHg for phenylacetylene (PA) and benzonitrile (BN), respectively.

Calculation and Experimental Results

As was mentioned in the introductory section of this paper the π-electronic structures of aromatic nitrile oxides and nitrones seem to bear some resemblance to each other. Therefore, the calculations of MO and transition energies were carried out with the similar treatment to that adopted to interpret the electronic spectra and electronic structures of BMANO.[4),*1] Namely, based on simple MO (SMO) calculation, and taking account of configuration interaction (CI) partly, the character of electronic spectra of BNO and its derivatives has been analyzed using the spectroscopic exchange integrals, β_s's, for the series of the following compounds,[14] in which the spectra of II[15] and III[16-18] were already analyzed by several authors.



Hypothetical molecule, IV, is obtained by dividing I into the composite systems consisting of the oxygen atom, $O^{\delta-}$, and its residual part, IV. It seems to be valuable to compare the π energy level of the $O^{\delta-}$ with the levels of IV.

SMO Calculation of I—IV. First we evaluated the parameters for SMO calculations of II, III and IV. The parameters pertaining to an atom, X, and a bond, X=Y, are, respectively, expressed by k_X in the Coulomb integral $\alpha_X=\alpha+k_X\cdot\beta$, and by ρ_{XY} in the resonance integral $\beta_{XY}=\rho_{XY}\cdot\beta$. The valence state ionization potential (IP) due to a π electron of carbon and nitrogen atoms is insensitive for the change of σ-core hybridization from sp^2 to sp type[19,20] whether or not these atoms are neutral or cation.[19,20] Thus it may be allowed to assume that the k_X values for the atoms appearing in $-C\equiv N$ and $-C\equiv N^{\delta+}$ (IV) bonds are the same as those reported previously for pyridine[21] and benzylidene methylamine[4] and its hypothetical molecule[4] $-C=N^{\delta+}$. That is, the values are as follows: $k_C=0$ and $k_N=0.5$ for C≡N bond, and in the case of IV $k_{N^{\delta+}}=1.6$ and

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[7] a) C. Grundmann and J. M. Dean, *Angew. Chem. Intern. Ed.*, **3**, 585 (1964); b) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

[8] C. Grundmann and J. M. Dean, *Angew. Chem.*, **77**, 966 (1965).

[9] D. G. Thomas, J. H. Billman and C. E. Davis, *J. Am. Chem. Soc.*, **68**, 895 (1946).

[10] L. F. Fieser and J. L. Hartwell, *ibid.*, **60**, 2555 (1938).

[11] C. Grundmann and H. D. Frommeld, *J. Org. Chem.*, **30**, 2077 (1965).

[*1] This type of theoretical treatment was originally applied by Baba and Suzuki,[12] and Goodman and Shull[13] to the analyses of the electronic spectra of substituted aromatic hydrocarbons.

[12] H. Baba, This Bulletin, **34**, 76 (1961); H. Baba and S. Suzuki, *ibid.*, **34**, 82 (1961); *J. Chem. Phys.*, **32**, 1706 (1960).

[13] L. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957).

[14] The comparison of the spectra of $Ph-C\equiv N^+-H$ with those of BNO *etc.* seems to be interesting. However, our trial under various conditions to get the accurate spectra was not successful.

[15] a) E. M. Layton, Jr., *J. Mol. Spectroscopy*, **5**, 181 (1960); b) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951); c) J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256, 5260 (1950); d) A. K. Chandra, *ibid.*, **83**, 4177 (1961).

[16] T. E. Peacock and P. T. Wilkinson, *Proc. Phys. Soc.*, **79**, 105 (1962).

[17] H. E. Popkie and J. B. Moffat, *Can. J. Chem.*, **43**, 624 (1965).

[18] K. Kimura and S. Nagakura, *Theort. Chim. Acta*, **3**, 164 (1965).

[19] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[20] J. Hinze and H. H. Jaffé, *J. Phys. Chem.*, **67**, 1501 (1963).

inductive effect $=(1/3)^n \times k_N^{\delta+}$ for carbon atoms. Adopting the Mulliken approximation,[22] $\rho_{C\equiv N}$ was estimated using Eq. (1), where $\beta_{C=N}$ is for pyridine type C=N bond. Here the relation $\beta_{C=N} \approx \beta_{C=C} \equiv \beta$ was assumed, this assumption being commonly employed in our previous calculations of nitrone,[4] pyridine *N*-oxide and their related compounds[21b,c] and also in usual SMO calculation of *N*-heterocyclic compounds.[21a,23]

$$\rho_{C\equiv N} \approx \frac{\beta_{C\equiv N}}{\beta_{C=N}} \approx$$

$$\frac{(1/2)\cdot K\cdot S_{C\equiv N}(IP_C{}^{sp}+IP_N{}^{sp})}{(1/2)\cdot K\cdot S_{C=N}(IP_C{}^{sp_2}+IP_N{}^{sp_2})} \propto \frac{S_{C\equiv N}}{S_{C=N}} \qquad (1)$$

It would be understood that Eq. (1) is satisfied, since $IP_{C\text{ or }N}{}^{sp} \approx IP_{C\text{ or }N}{}^{sp_2}$ is closely held for a π electron as was discussed before. The Mulliken Table[24] for overlap integrals, *S*'s, gave the values: $S_{C\equiv N}{}^{\pi}=0.302$ at 1.15 Å (triple covalent bond length) and $S_{C=N}{}^{\pi}=0.199$ at 1.37 Å, so that we got $\rho_{C\equiv N}=1.52$. As a reference, this value should be referred to 1.50[16] and 1.35[17] for $\rho_{C\equiv N}$ estimated from the data in literatures.[16,17,25] We have now used the $\rho_{C\equiv N}=1.50$ for C≡N and C≡C bonds in I, II, III, and IV for the sake of simplicity.[26]

Next our attention was paid to the parameters of ρ_{NO} and k_O in I. Keeping in mind the conclusion of previous studies[1,2] that the net electronic charge on the oxygen atom in nitrile oxides would be decreased because of a partial triple bond nature of an N→O bond in C≡N→O group, the following boundary conditions are expected. Namely, both the k_O and ρ_{NO} in the present case is larger than those of BMANO[4] and pyridine *N*-oxide,[21b,c] *etc.* The values of $k_O=1.2$ for BMANO, $k_O=0.8$ for pyridine *N*-oxide, and $\rho_{NO}=1$ for both the compounds were already derived. Many calculations were carried out so as to fit with the observed dipole moments of BNO and 2,4,6-trimethylbenzonitrile *N*-oxide (TMBNO), *etc.* by using the various sets of k_O and ρ_{NO} under the above boundary conditions.[27] The best values were determined as $k_O=1.55$ and $\rho_{NO}=1.2$. The energy levels of MO's were thus calculated for I, II, III, and IV using the above mentioned parameters, and the results were drawn in Fig. 1 with the symmetry and numbering of each orbital.

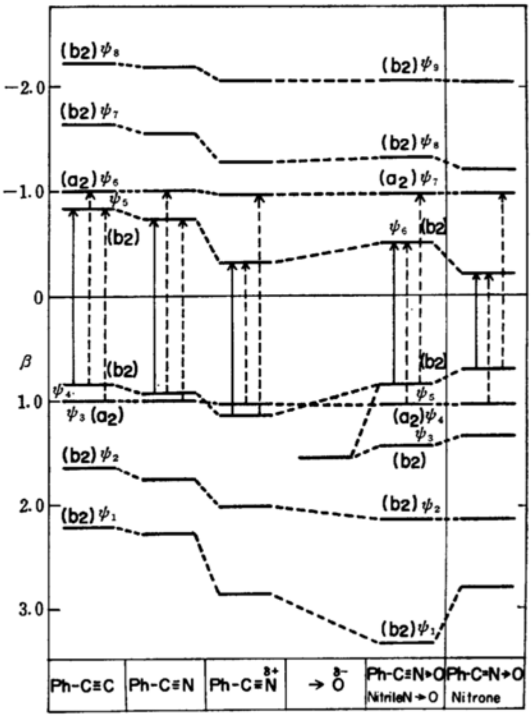

Fig. 1. The orbital energies and their numberings of phenyl acetylene, benzonitrile, and benzonitrile *N*-oxide and its composite ststems. The values of nitrone are cited from a previous paper[4] for comparison. Solid and broken vertical lines represent, respectively, $^1A_1$ and $^1B_1$ transitions responsible for near UV spectra. See "Appendix" for calculating conditions.

The present calculation of dipole moment has been based on the summation of σ and π moments. The values used for the former were cited from our previous paper[21c] and the latter values were taken from the present MO calculations. The molecular dimension of BNO was determined from molecular diagrams by employing the same treatment as in the previous work.[4] However, in the present molecule there are two π conjugated systems (π and $\overline{\pi}$) which are orthogonal to each other, and therefore MO calculation results for these two systems were taken into consideration to obtain the bond order and charge density. Although the bond length of the N→O bond (R_{NO}) is unknown, it was estimated as about 1.25 Å by the aid of N→O stretching frequency ($\tilde{\nu}_{NO}=\sim 1350\ \mathrm{cm}^{-1}$) and $\tilde{\nu}_{NO}$-bond length relationship.[28] In the present study we used the

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[21] a) N. Mataga and K. Nishimoto, *Z. Physik. Chem. N. F.*, **13**, 140 (1957); b) T. Kubota, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **80**, 578 (1959); This Bulletin, **35**, 946 (1962); c) T. Kubota and H. Watanabe, *ibid.*, **36**, 1093 (1963).

[22] R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949); M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.*, **20**, 837 (1952).

[23] R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry Methods and Application," Interscience Publishers, Inc., New York, N. Y. (1959), pp. 77, 211.

[24] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[25] In these papers[16,17] Pariser-Parr-Pople calculations of benzonitrile *etc.* were carried out. Using the data given therein, $\rho_{C\equiv N}$'s have been obtained from the ratio: $\beta_{C\equiv N}{}^{core}/\beta_{C=N}{}^{core}$.

[26] When we calculate the $\rho_{C\equiv C}$ for a –C≡CH bond using the equation, $\rho_{C\equiv C}=[S_{C\equiv C}/S_{C=C}]$, the value of $\rho_{C\equiv C}=1.38$ is led. A Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, London (1961), p. 105.

[27] Here was included the inductive effect, $(1/3)^n \cdot k_N{}^{\delta+}=(1/3)^n \times 1.6$, in the calculations.

[28] W. Lüttke, *Z. Elektrochem.*, **61**, 976 (1957).

value ranging from 1.21 to 1.30 Å tentatively, but uncertainty of the R_{NO} in this range resulted in only small differences in the calculated dipole moments. The lone pair moment ($\overrightarrow{\mu_{1\cdot\mathrm{sp}^2}}$) of N atom in sp² hybridization was previously assessed 1.0 D.U.[21c] The N atom of C≡N group is, however, in sp hybridization, so that its lone pair moment ($\overrightarrow{\mu_{1\cdot\mathrm{sp}}}$) was estimated to be 1.06 D.U. from the equation, $\overrightarrow{\mu_{1\cdot\mathrm{sp}}} = [\overrightarrow{\mu^{\mathrm{cal.}}_{1\cdot\mathrm{sp}}}/\overrightarrow{\mu^{\mathrm{cal.}}_{1\cdot\mathrm{sp}^2}}] \times \overrightarrow{\mu_{1\cdot\mathrm{sp}^2}}$. Here $\overrightarrow{\mu^{\mathrm{cal.}}_{1\cdot\mathrm{sp}}}$ and $\overrightarrow{\mu^{\mathrm{cal.}}_{1\cdot\mathrm{sp}^2}}$ are, respectively, the calculated lone pair moments for sp and sp² hybridized orbitals by the aid of the Slater orbital. Since both atoms of C≡N bond is in the sp type, the σ moment for the C≡N bond was here put as 0.00 D.U. because of the same reason as that for the C=N bond mentioned in the previous work.[21c] The σ-moment of the N→O dative bond assumed to be the same (4.55 D, see Ref. 21c) among three kinds of the bonds; aliphatic type $\rightarrow$N→O, pyridine *N*-oxide type ⪢N→O, and nitrile *N*-oxide type ≡N→O; although some difference in the N-atom σ-donor orbital (that is, sp³, sp², and sp orbitals in the above given order) would cause somewhat the variation of σ-electron distribution in the N→O σ bond itself as was discussed in Ref. 2. On the other hand, the non-bonding electrons at the oxygen atom in the N→O bond would be in almost no-hybridization[29] just like the oxygen atom in free carbonyl group,[30] so that no lone pair moment was supposed for the oxygen atom. Now, dipole moments of BNO, benzonitrile, and acetonitrile were calculated and compared with those observed.[31]

Evaluation of Spectroscopic Exchange Integrals, β_s's. In Fig. 2 are depicted the absorption spectra of PA, BN and 2,6-dimethylbenzonitrile *N*-oxide (DMBNO) in *n*-heptane. The band position of a quite strong band ($^1A_1$ under C_{2v}) appearing in 210—250 mμ region is considerably different to each other between PA and BN, but that the ^1L_b band ($^1B_1{}^-$ under C_{2v}) occurs in almost the same wavelength region for both compounds. As will be mentioned later it would be allowed that the β_s value ($\beta_s(^1A_1)$) for the former band ($^1A_1$) is evaluated on the basis of a single electronic configuration. However, this resulted in two relatively different $\beta_s(^1A_1)$ values for PA and BN, mainly because of different band ($^1A_1$) positions. Some difference in intramolecular interaction ability of –C≡CH and –C≡N groups with phenyl residue might be the principal origin for observed difference in the band ($^1A_1$) position, because the $^1A_1$ band in question is closely associated with the above mentioned intramolecular interaction. Hence, the $\beta_s(^1A_1)$ value was estimated from the observed band position of BN. This $^1A_1$ band will be mainly attributed to a one electron transition from ψ_4 to ψ_5, $^1\chi_{4\to5}$. Assuming the calculated energy difference ($^1\chi_{4\to5} = 1.653\,\beta$) to be equal to the observed value (5.510 eV) of BN, we get $\beta_s(^1A_1) = 3.33$ eV. This value will be used to discuss the $^1A_1$ bands in the UV spectra of BNO. It is worthwhile to point out that the other transitions having the symmetry $^1A_1$ seem to occur at much shorter wavelength than in $^1\chi_{4\to5}$, as is seen in Fig. 3, in which the calculated energy levels of excited states are shown. Therefore, the interaction of $^1\chi_{4\to5}$ transition with the other $^1A_1$ configurations would be small. The assumption to derive the above $\beta_s(^1A_1) = 3.33$ eV may be qualitatively allowed.

Next the evaluation of β_s for $^1B_1$ bands was carried out. The mutual interaction between two one-electron transitions, $^1\chi_{4\to6}$ and $^1\chi_{3\to5}$, may be the main origin for the $^1B_1$ bands appearing in near UV region. Assuming that the contribution to the $^1B_1$ bands from the other configurations might be neglected, two $^1B_1$ states, $^1B_1{}^-$ and $^1B_1{}^+$, of PA and BN are respectively written as Eqs. (2) and (3).

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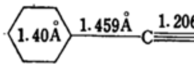
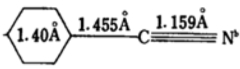
[29] T. Kubota, M. Yamakawa and I. Tanaka, *J. Mol. Spectroscopy*, **20**, 226 (1966).

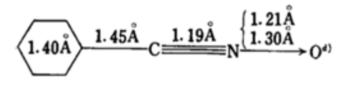
[30] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen & Co., Ltd., London (1963), p. 159.

[31] Adopted molecular dimensions and experimental and calculated dipole moments are shown below.

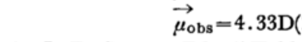




$\overrightarrow{\mu_{\mathrm{calc}}} = 4.11$D
$\overrightarrow{\mu_{\mathrm{obs}}} = 4.13$D(25°C in Benzene),[c]
4.14D(Microwave)[b]



$\overrightarrow{\mu_{\mathrm{calc}}} = 4.36$D($R_{NO} = 1.21$ Å),
4.18D($R_{NO} = 1.30$ Å)
$\overrightarrow{\mu_{\mathrm{obs}}} = 4.00$D(15°C in Benzene)[e]



$$\mathrm{H_3C}\overset{1.458\,\text{Å}}{\text{———}}\mathrm{C}\overset{1.157\,\text{Å}}{\equiv}\mathrm{N}^{\mathrm{b)}}$$

$\overrightarrow{\mu_{\mathrm{calc}}} = 3.28$D
$\overrightarrow{\mu_{\mathrm{obs}}} = 3.92$D(Microwave),[b]
3.47D(25°C in Benzene)[f]

2,4,6-Trimethylbenzonitrile *N*-oxide

$\overrightarrow{\mu_{\mathrm{obs}}} = 4.38$D(25°C in Benzene),[c]
4.39D(25°C in Dioxane)[e]

2,3,5,6-Tetramethylbenzonitrile *N*-oxide

$\overrightarrow{\mu_{\mathrm{obs}}} = 4.33$D(25°C in Benzene)[e]

a) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London (1958).

b) B. Bak, D. Christensen, W. B. Dixon, L. H. Nygaard and J. R. Andersen, *J. Chem. Phys.*, **37**, 2027 (1962).

c) Dipole moments for these compounds were measured by Dr. H. Watanabe and Miss N. Mōri, thanks of authors being due to them.

d) These values were estimated by using the order-length relation, *etc.* (see text).

e) G. Speroni, *Ricerca sci*, **27**, 1199 (1957).

f) J. W. Smith and L. B. Witten, *Trans. Faraday Soc.*, **47**, 1304 (1951).

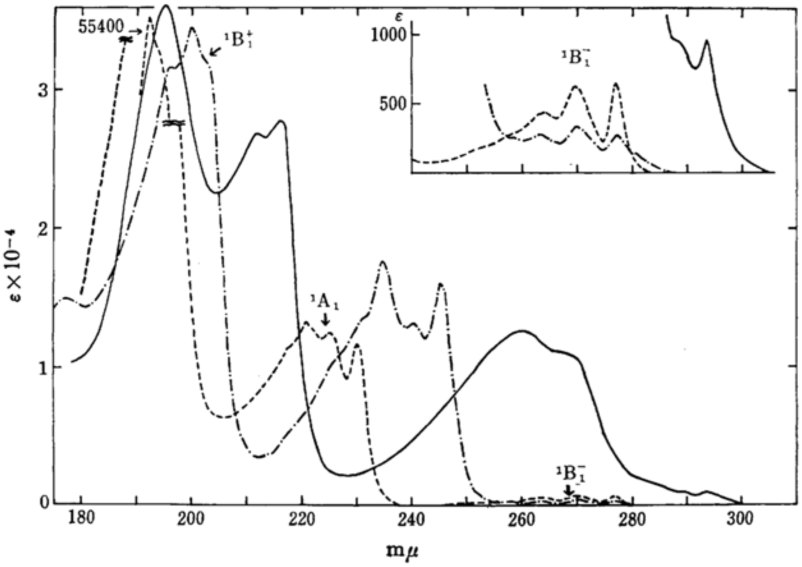


Fig. 2. Absorption spectra of phenylacetylene (—·—·), benzonitrile (------), and 2,6-dimethylbenzonitrile *N*-oxide (———) in *n*-heptane.

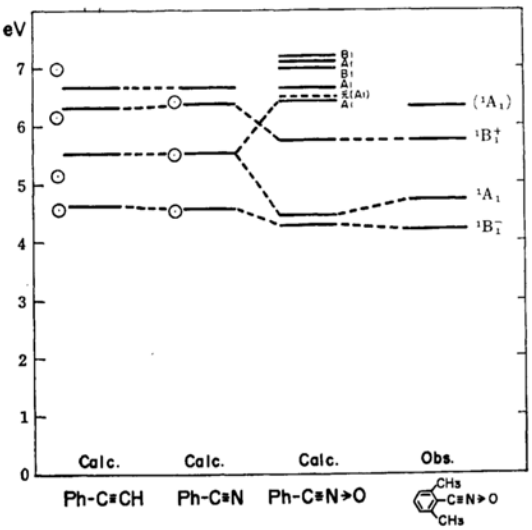


Fig. 3. The calculated and observed transition energies of the compounds indicated in this figure. Observed values for phenyl acetylene and benzonitrile are shown by circles.

$$({}^1B_1{}^- \text{ or } {}^1B_1{}^+) = \frac{1}{\sqrt{2}}({}^1\chi_{3\to5} \mp {}^1\chi_{4\to6}) \tag{2}$$

$$({}^1B_1{}^- \text{ or } {}^1B_1{}^+) = a{}^1\chi_{3\to5} \mp b{}^1\chi_{4\to6} \tag{3}$$

Here, minus and plus signs on the right hand side of the equations stand for the $^1B_1{}^-$ and $^1B_1{}^+$, respectively. The interaction energy is given by $\mathscr{H}^{3\to5}_{4\to6} = \langle {}^1\chi_{4\to6}|\mathscr{H}|{}^1\chi_{3\to5}\rangle = 2\langle 36|G|54\rangle^{MO} - \langle 36|G|45\rangle^{MO}$. Using the one-center and two-center π-Coulomb repulsion integrals, which were already given by Eq. (5) in Ref. 4, $\mathscr{H}^{3\to5}_{4\to6}$ is calculated to be 0.8653 eV for PA and 0.8583 eV for BN. In the case of PA the $\mathscr{H}^{3\to5}_{4\to6}$ will be also given experimentally by the half of energy difference between the two absorption bands of 4.59 eV and 6.20 eV (see Fig. 4) under the above assumption to derive Eqs. (2) and (3). The value of 0.804 eV thus derived is a value consistent with the theoretical ones stated above.

Figure 4 shows the relation of the transition energy obtained by SMO calculation to the observed $^1B_1{}^-$ and $^1B_1{}^+$ bands. The spectroscopic exchange integral, $\beta_s({}^1B_1)$, for $^1B_1$ state was evaluated to satisfy the observed values using the theoretical $\mathscr{H}^{3\to5}_{4\to6}$ values mentioned above and the SMO transition energies shown in Fig. 4. For the case of PA we obtained the $\beta_s({}^1B_1) = 2.978$ eV and 2.911 eV for $^1B_1{}^-$ and $^1B_1{}^+$ excited states, respectively. The mean values is 2.945 eV. However, the spectrum of BN gave $\beta_s({}^1B_1) = 2.983$ eV and 3.029 eV for $^1B_1{}^-$ and $^1B_1{}^+$ bands, respectively. The mean value results in 3.006 eV, and in this case the values of a and b for $^1B_1{}^-$ state in Eq. 3 were found to be 0.8142 and 0.5806, respectively. We would now understand that PA and BN give almost the same value of $\beta_s({}^1B_1)$ as far as the $^1B_1{}^\mp$ bands are concerned. The value of $\beta_s({}^1B_1) = 3.006$ eV was then used to discuss the spectra of BNO and its related compounds in relation to the choice for the $\beta_s({}^1A_1)$ value mentioned before.

Calculation of Transition Energies and Oscillator Strength. Combination of the SMO calculation results and the values of $\beta_s({}^1A_1)$ and $\beta_s({}^1B_1)$ make it possible to calculate the transition energies and their oscillator strengths, f_{calc}, the latter being carried out by the standard method.[29,32] The re-

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[32] R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

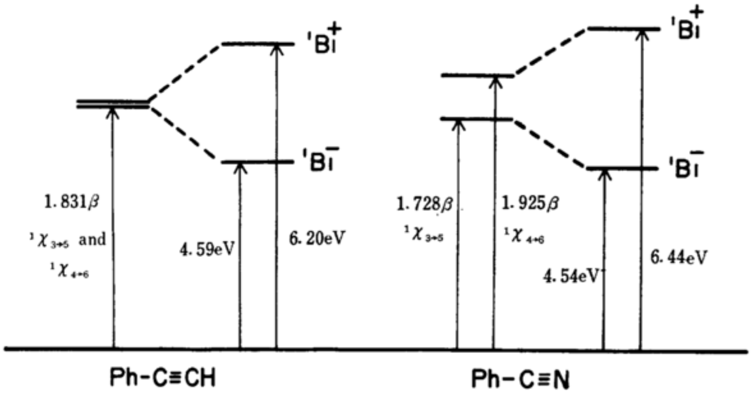

Fig. 4. The state energy splitting owing to the configuration interactions between two ${}^1B_1$ states yielded by SMO calculation, and the correlation, and the correlation with observed ${}^1B_1$ bands.

TABLE 1. THE CALCULATED AND OBSERVED VALUES OF TRANSITION ENERGIES, ΔE (IN eV), AND OSCILLATOR STRENGTHS, f, IN THE ${}^1A_1$ AND ${}^1B_1\pm$ STATES

		$\Delta E({}^1B_1{}^-)$ eV	$f({}^1B_1{}^-)$	$\Delta E({}^1A_1)$ eV	$f({}^1A_1)$	$\Delta E({}^1B_1{}^+)$ eV	$f({}^1B_1{}^+)$	The wave function of ${}^1B_1{}^-$ state
Ph-C≡C	Calcd.	4.609	0	5.540	1.058	6.340	0.862	$1/\sqrt{2}({}^1\chi_{4\to6}-{}^1\chi_{3\to5})$
	Obs.	4.592	0.002—0.003	5.166	0.314	6.196	0.778[a]	
Ph-C≡N	Calcd.	4.583	0.0113	5.510	1.079	6.399	0.872	$0.5806{}^1\chi_{4\to6}-0.8142{}^1\chi_{3\to5}$
	Obs.	4.541	0.007	5.510	0.240	6.441	0.914[a,b]	
Ph-C≡N→O	Calcd.	4.311	0.0306	4.486	1.490	5.749	0.512	$0.8869{}^1\chi_{4\to6}-0.4619{}^1\chi_{5\to7}$
	Obs.[c]	4.224	0.009	4.775	0.258	5.766	0.308[a]	

a) The f value estimated experimentally is not very accurate, because the absorption bands corresponding to ${}^1B_1{}^+$ state overlapped quite strongly with the other absorption bands of higher transition energies.

b) See footnote 18. The value of $f_{obs}=1.6$ was reported[18] for the case where the integration was carried out over the three far UV bands in vapor phase; 6.61, (6.88), and 7.44 eV.

c) In addition to the absorption bands listed in this row another band with a high intensity was observed at 6.352 eV ($f_{obs}=0.768$, $\varepsilon=36100$).

sults for compounds I, II, and III are listed in Table 1 with the state functions obtained and with the observed transition energies. The transition moment, $\vec{Q}$, is given by

$$\vec{Q} = \langle \Psi_g({}^1\Gamma) | \Sigma \vec{r} | \Psi_{exc}({}^1\Gamma) \rangle,$$

where $\Psi_g({}^1\Gamma)$ and $\Psi_{exc}({}^1\Gamma)$ are singlet state wave functions in the ground and excited states, respectively (see Table 1). In Table 1 are included the oscillator strengths, f_{obs}, obtained experimentally from the recorded spectra by the aid of the equation: $f_{obs}=4.32\times10^{-9}\int\varepsilon(\tilde{\nu})d\tilde{\nu}$. The integrated intensity $\int\varepsilon(\tilde{\nu})d\tilde{\nu}$, was obtained using a planimeter from an enlarged absorption curve which was divided into each electronic transition component by the usual method.[29]

The Effect of Electron Donating Substituents on the Electronic Spectrum of 2,6-Dimethylbenzonitrile *N*-Oxide (DMBNO). It is of interest to elucidate theoretically the substituent effect on the UV spectrum of DMBNO. Some experimental results obtained here and reported in the foregoing paper[1] are shown in Table 2. The substituent effect was now introduced in the SMO calculation by such a way that k_X of Coulomb integral (α_X) for a substituent is varied in the range of 0.5—3.5, while ρ_{C-X} for the resonance integral (β_{C-X}) between a substituent and a benzene ring carbon atom to which the substituent is attached is assumed to be unity. Then many MO calculations were carried out using different values of the parameters. The calculation of transition energy is based on the same treatment as that in the preceding chapters except that $\beta_s({}^1A_1)=3.55$ eV, which reproduces completely the 259.7 mμ band of DMBNO, is employed in stead of $\beta_s({}^1A_1)=3.33$ eV mentioned before. Calculations were made using the above two $\beta_s({}^1A_1)$ values, but the two ${}^1A_1$ curves calculated were nearly parallel to each other. That is, the two $\beta_s({}^1A_1)$ values give almost the same results, as far as

TABLE. 2. OBSERVED TRANSITION ENERGIES (ΔE) AND ε_{max}'S IN n-HEPTANE, CALCULATED TRANSITION ENERGIES, AND THE COULOMB PARAMETERS, k_X, OF SUBSTITUENTS FOR MO CALCULATIONS OF 4-SUBSTITUTED-2,6-DIMETHYLBENZONITRILE N-OXIDES

X	k_X	$^1B_1{}^-$			$^1A_1$			$^1B_1{}^+$			($^1A_1$)	
		ΔE (calc) eV	ΔE (obs)	ε_{max}	ΔE (calc) eV	ΔE (obs)	ε_{max}	ΔE (calc) eV	ΔE (obs)	ε_{max}	ΔE (obs)	ε_{max}
H	∞	4.31	4.224	968	4.775	4.775	12700	5.75	5.766	28000	6.352	36100
CH_3-	3.5	4.31	4.214	667	4.66	4.720	15000	5.64	5.687	27000	6.249	37300
Br-	2.5	4.32	4.229	1350	4.56	4.626	19000	5.56	5.732	25700	6.069	31000
CH_3O-	2.0	4.29	(4.188)$^{a)}$	(1300)$^{a)}$	4.46	4.628	17900	5.50	5.801	24700	6.122	34400
$(CH_3)_2N$-	1.2	4.16	—	—	4.06	4.235	22900	5.29	5.414	11500	5.996	23000

a) Since this band occurs as shoulder, the band position and intensity is not so accurate.

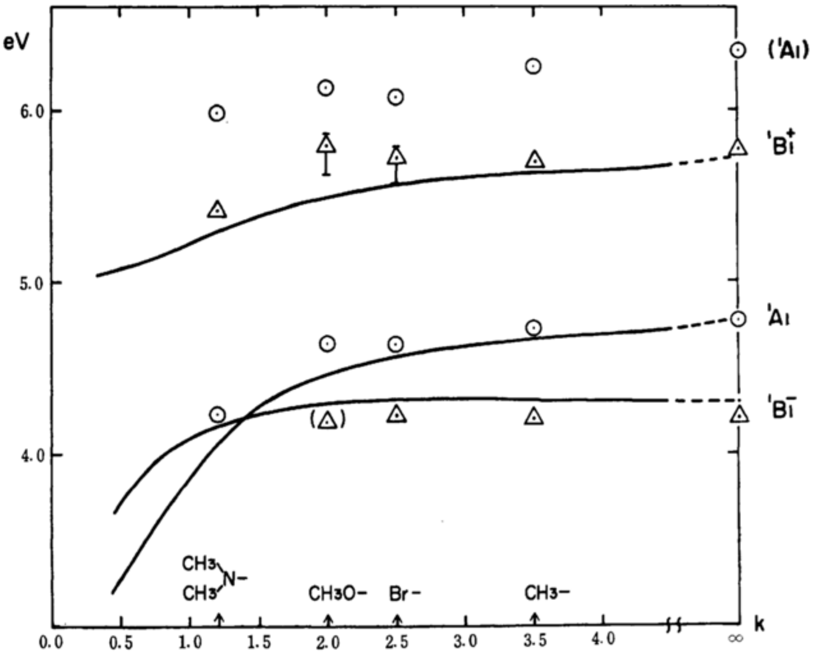

Fig. 5. The effect of substituents on the transition energies of 2,6-dimethylbenzonitrile N-oxide. Calculated and observed values are, respectively, shown by solid lines and by circles and triangles.

the comparison of magnitude of substituent effect is concerned. Altnough the present choice of the $\beta_s(^1A_1)=3.55$ eV is somewhat arbitrary, we deem that it would lead to more satisfactory results in the investigation of the substituent effect and in the deviation of the calculated $^1A_1$ state energies from the observed ones when the 259.7 mμ band of DMBNO is taken as a standard. The results are shown in Table 2 and drawn in Fig. 5, in which the observed values are plotted at the following parameter positions:

$$k_{N(CH_3)_2}=1.2,\ k_{OCH_3}=2.0,\ k_{Br}=2.5 \text{ and } k_{CH_3}=3.5.$$

These are determined by referring the values recommended by Baba,[12] and by Goodman and Shull.[13]

Discussion

Electronic Spectra of Benzonitrile *N*-Oxide and Its Related Compounds. As Table 1 shows, the comparison of the calculated and the observed results on the absorption spectrum of DMBNO indicates clearly that the 259.7 mμ band with high intensity should be assigned to $^1A_1$ band having the transition moment along the long axis of DMBNO (C_2 asis under C_{2v}). Now we may say that the $^1A_1$ band occurs in quite longer wavelength than in $^1A_1(^1L_a)$ band of benzonitrile, and thus would be thought to be a characteristic band for benzonitrile N-oxides. This is due to the fact that the 2pπ

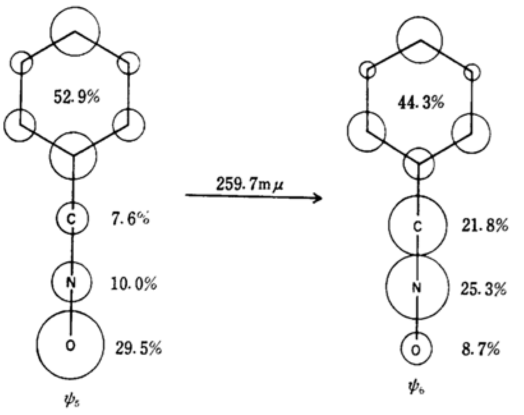

Fig. 6. The electron distribution in the highest occupied (ψ_5) and the lowest vacant (ψ_6) orbitals of benzonitrile *N*-oxide.

electrons of the oxygen atom coordinated to benzonitrile group can newly enter into π-conjugation, so that the charge transfer of $2p\pi$ electrons on the oxygen atom to the residual electron system, as well as the charge transfer of the reverse direction to the above, is brought about. In Fig. 6 we showed the change of orbital charge distribution caused by the $^1A_1$ (259.7 mμ) transition of DMBNO, which mainly consists of the $^1\chi_{5\to6}$ configuration. It is seen that the charge density on the oxygen atom decreases at the $^1\chi_{5\to6}$ excited state because of the charge transfer from the oxygen atom to the residual π-electronic system. However, calculations showed that the above charge transfer at the $^1A_1$ state is weaker than in the cases of BMANO[4,33] and pyridine *N*-oxide,[33] indicating that the solvent effect on the absorption band of nitrile *N*-oxides is less than that found in the case of nitrones and heterocyclic *N*-oxides, with which the considerable effect was observed.[1] The other two bands of DMBNO which appeared at 293.5 mμ and 215 mμ were assigned to $^1B_1^-$ (^1L_b, weak intensity) and $^1B_1^+$ (^1B_b, strong intensity) bands, respectively. The assignment was made by comparing the experimental results with the calculated ones as shown in Fig. 3. The band assignment made hitherto was consistent with that derived experimentally from the substituent- and solvent-effects and from the intensity consideration.[34] Tentative assignment of absorption bands appearing in far UV region are also given in Fig. 3. The assignment, however, would not be certain from the present study, because configuration interaction seems to play an important role for interpreting the electronic spectra in the above region. We suppose that the above band assignment, except for the one in far UV region, is also supported from the comparison of the calculated and experimental results concerning the substituent effect on the spectra of DMBNO, as is seen in Fig. 5. It is found there that the results of the calculation are parallel to the experimental ones at least semiquantitatively.

As was mentioned in the introduction of the present paper, nitrone and nitrile *N*-oxide have the π-electronic system similar to each other. The main difference in their UV spectra is the position of longer wavelength $^1A_1$ band. The band for nitrone occurs at longer wavelength than that of the corresponding nitrile *N*-oxide. For example, the $^1A_1$ band (259.7 mμ) of DMBNO in *n*-heptane appears at shorter wavelength than that (298.3 mμ)[5] of BMANO, a typical nitrone. It has been already known that the longer wavelength $^1A_1$ band is sensitive to substituents and shows an apparent red shift when electron donating power of substituents becomes stronger, as was reported for the system of mono-substituted benzenes.[12,13] The above difference in the $^1A_1$ band position between nitrone and nitrile *N*-oxide would be explained by the larger values of parameters k_O and ρ_{CN} for C≡N→O group, which make the separation of the lowest vacant and the highest occupied orbitals larger (see also Fig. 1).[35]

Molecular Diagrams and Physicochemical Natures of Nitrile *N*-Oxides. In connection with the analyses of the UV spectra discussed above it seems to be also valuable to make the discussion on the correlation between the molecular diagram and some physicochemical natures of nitrile *N*-oxides in the ground state. The molecular diagrams calculated for BN and BNO are designated in Fig. 7. Since these compounds have the two resonance systems, π and $\bar{\pi}$, their bond orders and charge densities are relatively different from those of benzylidenemethylamine and BMANO except for benzene part, where the above differences are not very large. Let us now consider the nature of –C≡N→O group. The π-bond order (0.779) of ≡N→O bond in BNO is much larger than that (0.406) of BMANO,[4] although partial bond order for π and $\bar{\pi}$ systems is less than the above 0.406. At the same time the C≡N bond order is also large (1.704), indicating that the bond exhibits a triple bond nature. These values should now be compared with those given by Wagner[36] who calculated the molecular diagram of fulminic acid, H–C≡N→O, by the method

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[33] T. Kubota and M. Yamakawa, This Bulletin, **35**, 555 (1962).

[34] It is noted that the oscillator strengths calculated for $^1A_1$ band appearing in near UV region of PA, BN, and BNO are high from the quantitative viewpoint. The same tendency was also found for the calculated results of *p*-substituted DMBNO. Although MO calculation gives usually oscillator strength larger than that obtained experimentally, the above discrepancy would be ascirbed to the model of calculation which is not rigorous for the present case.

[35] The spectral change similar to the above is naturally found between BN (225 mμ) and benzylidenemethylamine[5] (244.0 mμ), and between PA (240 mμ) and styrene (247.5 mμ).[4]

[36] E. L. Wagner, *J. Chem. Phys.*, **43**, 2728 (1965).

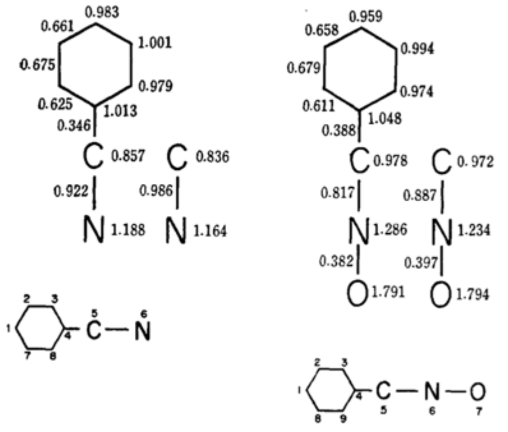

Fig. 7. Molecular diagrams of benzonitrile and its *N*-oxide.

of linear combination of group orbitals, and obtained the values: 0.939 and 1.729 for the π-bond order of N→O and C≡N bonds, respectively. Both his and our results seem to reflect the character of C≡N→O bond well. Therefore we may say that the stretching vibration of N→O bond, $\tilde{\nu}_{NO}$, of BNO occurs in higher frequency than in pyridine *N*-oxide, *etc.* Actually this prediction was verified experimentally as we discussed in the foregoing paper.[1]

It is known that $\tilde{\nu}_{NO}$ has the close correlation with N–O bond distance, R_{NO}. Using Lüttke's correlation curve[28] and also applying the Kharitonov's equation[37] which connects $\tilde{\nu}_{NO}$ and R_{NO}, the N–O bond distance was estimated to be 1.25 and 1.22 Å, respectively. On the other hand, the examination of the relation between $\tilde{\nu}_{NO}$ and R_{NO} reported for many aromatic and aliphatic amineoxides, oximes, nitroso compounds, *etc.*[1,4,5,38] led to R_{NO}=1.28—1.23 Å. Anyway it appears likely that R_{NO} of nitrile *N*-oxides in free state becomes relatively short.

Finally attention is directed to the π-electron density of BNO, *etc.* Comparing the molecular diagrams of BNO (see Fig. 7) and BMANO,[4] we can find that the charge distributions in the benzene ring are not very different between those of BNO and BMANO, but large change occurs in the part of C≡N→O group. Total π-electron net charges on the oxygen- and C_5 carbon-atoms (see Fig. 7) are +0.415 and +0.050 for BNO, but were +0.283 and +0.017 for the corresponding values of BMANO.[4] The increment of the positive net charge on the oxygen atom of BNO is responsible for weak complexing ability of aromatic nitrile *N*-oxides. Although the π net charge on the oxygen atom of C≡N→O group is positive, as has been discussed above, it is sure that the total charge on the oxygen atom is negative. This is because the N→O σ dative bond (σ moment, $\vec{\mu}_{NO}=4.55$ D.U.)[21c] shows a large shift of charge in the σ system. If we define $q_O=q_O^{\sigma}+q_O^{\pi}=(\vec{\mu}_{NO}/R_{NO})+q_O^{\pi}$, the value of $q_O\approx-0.368$ is derived. In addition to that, the net charge on the carbon atom of C≡N→O group (see Fig. 7) is positive and its value is considerably larger than that for C=N→O in BMANO, whereas the π net charge on nitrogen atom of C≡N→O is negative. These results may suggest that nitrile *N*-oxide group can also be expressed as a resonance formula, $-C^{\delta+}=\ddot{N}-O^{\delta-}$. This fact seems to be the reason why nitrile *N*-oxides are rich in reactivity[39] and bring about easily the reaction of 1.3 dipole addition[39] unless bulky substituents prevent the reagent from coming closely enough to nitrile *N*-oxide groups.[7]

The authors wish to express their thanks to Professor Saburo Nagakura of the Institute for Solid State Physics, the University of Tokyo and to Professor Noboru Mataga of Osaka University for discussions.

Note Added in Proof: After the manuscript of this paper had been sent to the Chemical Society, we learned of two papers in which the N→O bond length (R_{NO}) of nitrile *N*-oxide group was reported. One is a paper by M. Winnewisser and H. K. Bodensch, *Z. Naturforsch.*, **A22**, 1724 (1967), in which they reported R_{NO} of H–C≡N→O molecule to be 1.207 Å based on the analyses of the microwave spectrum. Another paper by M. Shiro *et al.* in our laboratory showed R_{NO} of 4-methoxy-2,6-dimethylbenzonitrile *N*-oxide to be 1.249 Å by the method of X-ray analyses at about −140°C; the paper presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April 1968. The above R_{NO} values pertinent to nitrile *N*-oxide group are short and almost agree with theoretically predicted values reported in this paper.

Appendix

The MO's obtained here for BNO and its related compounds are listed below for the sake of comparison with those of BMANO and its related compounds.

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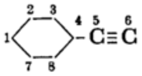
37) Y. Y. Kharitonov, *Izvest. Akad. Nauk. S.S.S.R.*, **No. 11**, 1953 (1962).

38) a) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London (1958), p. M112, and b) its supplement (1965), pp. M24S, M25S, M119S, M126S, M127S, M137S, M138S and M155S; c) A. Caron, G. J. Palenik, E. Goldish and J. Donohue, *Acta Cryst.*, **17**, 102 (1964); d) K. Folting, W. N. Lipscomb and B. Jerslev, *ibid.*, **17**, 1263 (1964); e) N. B. H. Jonathan, *J. Mol. Spectroscopy*, **4**, 75 (1960); f) E. Ochiai and H. Mitarashi, *Ann. Rept. ITSUU Lab.*, **No. 13**, 19 (1963); g) W. Lüttke, *Z. Elektrochem.*, **61**, 302 (1957); h) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958); i) Y. Matsui, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **83**, 990 (1962); i) H. Shindo, *Chem. Pharm. Bull.*, **6**, 117 (1958).

39) R. Huisgen, *Angew. Chem. Intern. Ed.*, **2**, 565 (1963); R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960).

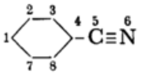
Simple molecular orbitals of phenyl acetylene, benzonitrile, and benzonitrile *N*-oxide. Ψ and $\bar{\varepsilon}$ stand for the wave function and eigenvalue for $\bar{\pi}$ conjugated system (see Fig. 1 in text), respectively. Eigenvalue stands for the δ in the equation; $E=\alpha+\delta\cdot\beta$, and the calculating conditions are included in each table.



($\beta_{56}=1.5\,\beta$, $\beta_{45}=\beta$)

	Eigen-value	Symmetry	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i5}	C_{i6}
ϕ_1	2.21380	b_2	+0.24551	+0.27176	+0.35610	+0.51658	+0.43140	+0.29230
ϕ_2	1.63042	b_2	−0.45136	−0.36795	−0.14856	+0.12574	+0.50213	+0.46196
ϕ_3	1.00000	a_2	0	−0.5	−0.5	0	0	0
ϕ_4	0.83116	b_2	+0.48580	+0.20189	−0.31800	−0.46619	+0.24851	+0.44850
ϕ_5	−0.83116	b_2	+0.48580	−0.20189	−0.31800	+0.46619	+0.24851	−0.44850
ϕ_6	−1.00000	a_2	0	−0.5	+0.5	0	0	0
ϕ_7	−1.63042	b_2	−0.45136	+0.36795	−0.14856	−0.12574	+0.50213	−0.46196
ϕ_8	−2.21380	b_2	−0.24551	+0.27176	−0.35610	+0.51658	−0.43140	+0.29230

$C_{i2}=\pm C_{i7}$; $C_{i3}=\pm C_{i8}$ (+ and − represent b_2 and a_2 orbitals respectively.)



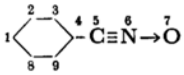
($\alpha_6=\alpha+0.5\,\beta$, $\beta_{56}=1.5\,\beta$, $\beta_{45}=\beta$)

	Eigen-value	Symmetry	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i5}	C_{i6}
ϕ_1	2.27521	b_2	+0.19955	+0.22701	+0.31695	+0.49411	+0.49031	+0.41430
ϕ_2	1.74886	b_2	−0.43090	−0.37679	−0.22805	−0.02204	+0.41756	+0.50153
ϕ_3	1.00000	a_2	0	−0.5	−0.5	0	0	0
ϕ_4	0.92500	b_2	−0.51574	−0.23853	+0.29510	+0.51149	−0.11707	−0.41319
ϕ_5	−0.72824	b_2	−0.45606	+0.16606	+0.33513	−0.41012	−0.37160	+0.45382
ϕ_6	−1.00000	a_2	0	+0.5	−0.5	0	0	0
ϕ_7	−1.53893	b_2	−0.47625	+0.36646	−0.08770	−0.23149	+0.53165	−0.39113
ϕ_8	−2.18189	b_2	−0.27150	+0.29619	−0.37476	+0.52150	−0.38833	+0.21719

$C_{i2}=\pm C_{i7}$; $C_{i3}=\pm C_{i8}$ (+ and − represent b_2 and a_2 orbitals, respectively.)

$\bar{\varepsilon}_1=1.77069$ $\bar{\phi}_1=0.64637\varphi_C+0.76302\varphi_N$

$\bar{\varepsilon}_2=-1.27069$ $\bar{\phi}_2=0.76302\varphi_C-0.64637\varphi_N$



($\alpha_6=\alpha+1.6\beta$, $\alpha_7=\alpha+1.55\beta$, $\beta_{56}=1.5\beta$, $\beta_{67}=1.2\beta$, Ind.$=((1/3)^n\times1.6)$

	Eigen-value	Symmetry	C_{i1}	C_{i2}	C_{i3}	C_{i4}	C_{i5}	C_{i6}	C_{i7}
ϕ_1	3.34037	b_2	+0.01373	+0.02293	+0.06240	+0.18184	+0.45043	+0.72179	+0.48378
ϕ_2	2.14272	b_2	−0.31002	−0.33214	−0.39512	−0.49119	−0.17528	+0.13935	+0.28213
ϕ_3	1.44351	b_2	+0.46001	+0.33201	+0.01272	−0.31441	−0.42363	−0.04754	+0.53574
ϕ_4	1.03954	a_2	0	−0.49506	−0.50489	0	0	0	0
ϕ_5	0.84945	b_2	−0.41450	−0.17605	+0.26842	+0.38822	−0.27578	−0.31700	+0.54300
ϕ_6	−0.49650	b_2	−0.37320	+0.09265	+0.32537	−0.27339	−0.46662	+0.50252	−0.29466
ϕ_7	−0.96084	a_2	0	+0.50489	−0.49506	0	0	0	0
ϕ_8	−1.29626	b_2	+0.50412	−0.32674	−0.07415	+0.42722	−0.48112	+0.30192	−0.12729
ϕ_9	−2.04459	b_2	+0.35619	−0.36413	+0.39548	−0.46780	+0.24830	−0.11481	+0.03833

$C_{i2}=\pm C_{i8}$; $C_{i3}=C_{i9}$ (+ and − represent b_2 and a_2 orbitals respectively.)

$\bar{\varepsilon}_1=3.26401$ b_1 $\bar{\phi}_1=0.41032\varphi_C+0.74705\varphi_N+0.52302\varphi_O$

$\bar{\varepsilon}_2=1.18034$ b_1 $\bar{\phi}_2=0.56354\varphi_C+0.24320\varphi_N-0.78948\varphi_O$

$\bar{\varepsilon}_3=-0.76135$ b_1 $\bar{\phi}_3=0.71698\varphi_C-0.61868\varphi_N+0.32121\varphi_O$