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The Singlet-triplet Absorption Spectra of Heterocyclic Amine *N*-Oxides (I)

Tanekazu KUBOTA, Masumi YAMAKAWA, and Yoshiko MIZUNO
Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka 553

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The singlet-triplet absorption ($T_1 \leftarrow N$) spectra of pyridine *N*-oxide, quinoline *N*-oxide, isoquinoline *N*-oxide, and acridine *N*-oxide have been observed by applying the oxygen-intensification technique. The correlation between the $T_1 \leftarrow N$ absorption bands and the singlet-singlet ($S^* \leftarrow N$) absorption bands of these *N*-oxides has been established and discussed theoretically. The lowest triplet state of the *N*-oxides has been assigned as the π-π^* transition of a ^3L_a (CT) nature. The $T_1 \leftarrow N$ absorption bands obtained show a blue shift in polar solvents. The results have been compared with the case of $S^* \leftarrow N$ transitions and have been reasonably explained by taking into account the contribution from the intramolecular charge transfer.

In the field of the studies of photochemical reactions, heterocyclic amine *N*-oxides constitute one group of substances which are being quite extensively studied at present.[1] Needless to say, the knowledge of excited singlet and triplet states is important for interpreting the mechanism of photochemical reactions. Although the nature of the excited singlet states of heterocyclic amine *N*-oxides has been intensively investigated,[2]

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[1] a) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970). b) C. Kaneko, *Kagaku No Ryoiki, Zokan*, **93**, 235 (1970), (Review in Japanese). c) I. Tanaka and H. Shizuka, *J. Soc. Org. Syn. Chem.*, Tokyo, **26**, 412 (1968), (Review in Japanese). d) C. Kaneko, S. Yamada, I. Yokoe, and T. Kubota, *Tetrahedron Lett.*, **1970**, 2333 (No. 27). e) F. Bellamy, L. G. R. Barragan, and J. Streith, *Chem. Commun.*, **1971**, 456. f) K. Koyano and H, Suzuki, This Bulletin, **43**, 3582 (1970). g) R. Gleiter, D. Schmidt. and J. Streith, *Helv. Chim. Acta*, **54**, 1645 (1971).

[2] a) K. Seibold, G. Wagniere, and H. Labhart, *Helv. Chim, Acta*, **52**, 789 (1969). b) M. Yamakawa, T. Kubota, and H. Akazawa, *Theor. Chim. Acta*, **15**, 244 (1969). c) E. M. Evleth, *ibid.*, **11**, 145 (1968). d) S. Kobinata and S. Nagakura, *ibid.*, **14**, 415 (1969). e) J. D. Bene and H. H. Jaffe, *J. Chem. Phys.*, **49**, 1221 (1968). f) R. M. Hochstrasser and D. A. Wiersma, *ibid.*, **55**, 5339 (1971). g) H. Miyazaki, T. Kubota, and M. Yamakawa, This Bulletin, **45**, 780 (1972). h) J. C. D. Brand and K.-T. Tang, *J. Mol. Spectrosc.*, **39**, 171 (1971).

there have as yet been few studies of their excited triplet states.[3] The main reason for this is some difficulty for measuring the phosphorescence spectra because of their very weak intensity or some instability accompanying a photochemical reaction. In these cases, the observation of the singlet-triplet ($T_1 \leftarrow N$) absorption spectra is very useful in determining the energy level of the lowest triplet state. Several techniques for measuring the $T_1 \leftarrow N$ absorption spectra have already been reported.[4]

In our present case, the technique of high-pressure oxygen perturbation developed by Evans[4a] was the most useful technique for obtaining the $T_1 \leftarrow N$ absorption spectra of the aromatic amine *N*-oxides studied here. In this paper we would like to report on these $T_1 \leftarrow N$ absorption spectra and their interpretations.

Experimental

Absorption Cell. Figure 1 shows the absorption cell employed in this study; it was made of stainless steel and was constructed by referring to the ones used by Evans[4a] and by Robin.[5] A suprasil silica plate 8 mm thick was used as a window. The effective light pass length was ~5.2 cm. This absorption cell was safe for oxygen pressures of ~200 kg/cm². The equilibrium state of the sample solution saturated with compressed oxygen gas was easily obtained by shaking the absorption cell moderately. All the spectral measurements were made at room temperature. The sample concentrations are dependent on the solubility and on the degree of the enhancement of the $T_1 \leftarrow N$ absorption with oxygen. In the case of $CHCl_3$ solution, the most suitable concentrations are 0.93, 0.75, and 0.99 mol/*l* for pyridine *N*-oxide (PNO), quinoline *N*-oxide (QNO), and isoquinoline *N*-oxide (IQNO) respectively. However, a saturated solution was used for acridine *N*-oxide (ANO) because of the low solubility. The instrument used for recording the singlet-triplet absorption spectra was a Beckman DK-2A Far-UV spectrometer.

Solvents and Samples. All the solvents used, except for chloroform, were spectro-grade in purity; they were dried sufficiently with calcium chloride, *etc.*,[6] and then rectified carefully. Spectro-grade chloroform containing about 1% ethanol as a stabilizer was used with no further treatment. As to samples, PNO, QNO, IQNO, and ANO were used in this study. The details of the preparation and the purification of these samples have already been reported.[7] Finally, they were again sublimated or distilled before use. In the case of ANO, an alumina column chromatographic method was also used,[8] the *N*-oxide being eluted first with an ether-pentane mixture and later with ether alone. The pure *N*-oxide has been obtained from the ether fraction.

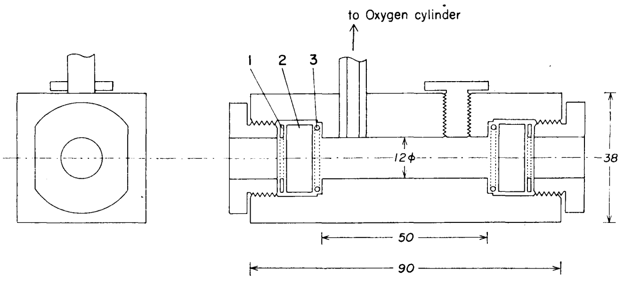

Fig. 1. High pressure cell used for obtaining the singlet-triplet absorption spectra under compressed oxygen perturbation. Dimension is in mm unit. Suprasil silica plate of 8 mm thickness (2) is held between the Teflon O-ring (3) and the Teflon washer (1).

Results and Discussion

$T_1 \leftarrow N$ *Absorption Spectra of PNO, QNO, IQNO, and ANO.* To confirm our experimental technique, we have first examined the $T_1 \leftarrow N$ absorption spectra of naphthalene, *etc.*, under almost the same experimental conditions as those reported by Evans.[4a] The spectra thus obtained reproduced Evans' well. Our experiments can, therefore, be believed to be correct.[9] As a typical example, the oxygen-pressure dependence of the $T_1 \leftarrow N$ absorption spectrum is illustrated in Fig. 2 for a relatively high concentration (~1 mol/*l*) of the PNO chloroform solution. It is now clear that a new absorption band appears in the wavelength region of 370—500 nm and that the intensity of this new band increases in a linear fashion with an increase

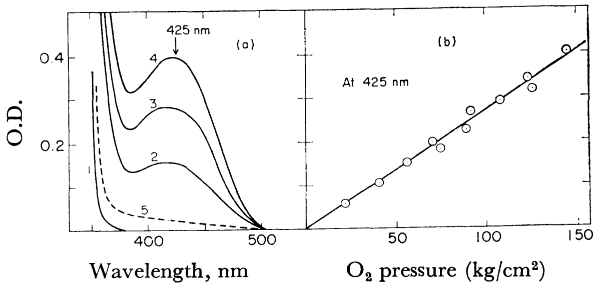

Fig. 2. Oxygen pressure dependence of the $T_1 \leftarrow N$ absorption spectrum of pyridine *N*-oxide in $CHCl_3$ solution (0.93 mol/*l*). (a): The change in the spectrum with no oxygen perturber (curve 1) upon the applied oxygen pressure (kg/cm²) of 57 (curve 2), 108 (3), and 145 (4). The curve 5 is for the spectrum after removal of the oxygen. The intensity of the curve 5 is a little larger than that of the curve 1. The main reasons would be that the removal of oxygen is incomplete, and thus contact charge transfer spectra caused by weak oxygen complex formation may appear as a tail toward a longer wavelength region. (b): The linear relation of the enhanced $T_1 \leftarrow N$ absorption intensity to the applied oxygen pressure.

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3) B. Ziolkowsky and F. Dörr, *Ber. Bunsenges. Phys. Chem.*, **69**, 448 (1965).

4) a) D. F. Evans, *J. Chem. Soc.*, **1957**, 1351, 3885; **1959**, 2753; *Proc. Roy. Soc. Ser A*, **255**, 55 (1960). b) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964). c) E. V. Donckt and C. Vogels, *Spectrochim. Acta*, **27A**, 2157 (1971).

5) M. B. Robin and N. A. Kuebler, *J. Mol. Spectrosc.*, **33**, 274 (1970).

6) J. A. Riddick and W. B. Bunger, "Organic Solvent," (Third Edition) edited by A. Weissberger, Wiley-Interscience, New York (1970).

7) E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Co., Amsterdam (1967), and the other papers cited therein.

8) R. M. Acheson, B. Adcock, G. M. Glover, and L. E. Sutton, *J. Chem. Soc.*, **1960**, 3367.

9) The trial is deemed to have failed in obtaining the $T_1 \leftarrow N$ absorption spectra of the present *N*-oxides in solvents with heavy atoms, such as CH_2Br_2 and CH_2I_2, since the enhancement of the $T_1 \leftarrow N$ absorption intensity in these solvents seems to be small. In addition, there also occurred other kinds of solute-solvent interactions in the case of the present system.

in the oxygen pressure, as may be seen in Fig. 2b. In addition, when the oxygen pressure is reduced to atmospheric pressure, the new absorption band disappears, and the spectrum almost completely returns to that before the introduction of oxygen gas. The reproducibility of this spectral behaviour was quite good. Comparing these expermental results with those found in the literature,[4a,10,11] one can conclude that the above-mentioned new absorption band of PNO is due to the $T_1 \leftarrow N$ transition enhanced by oxygen gas. Quite recently, Bellamy *et al.*[1e] carried out the photochemical sensitization reaction of 2-cyanopyridine *N*-oxide, *etc.*, sensitizers which have triplet energy levels of 74 (Xanthone) and 79 kcal/mol (tetrabuthylammonium phenyltetrazolide) being effective. These results are in accord with our experimental results presented above. Furthermore, the contact charge-transfer (CCT) spectra due to the CCT complex formation of PNO with the oxygen molecule may appear as an end-absorption, overlapped with the spectrum of PNO itself, at the shorter-wavelength region than the $T_1 \leftarrow N$ absorption band, since the existence of this kind of CCT spectrum is well known.[11,12]

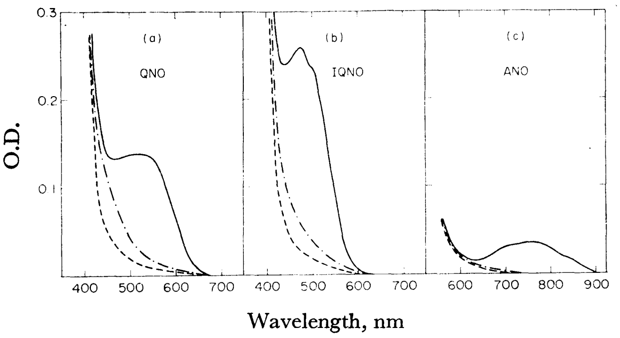

Fig. 3. Singlet-triplet absorption spectra of quinoline *N*-oxide (a), isoquinoline *N*-oxide (b), and acridine *N*-oxide (c) in $CHCl_3$ solution. The concentration (mol/*l*) and the oxygen pressure (kg/cm^2) are in this order: 0.75, 128; 0.99, 100; and the saturated solution, 152; for QNO, IQNO, and ANO, respectively.
----: for initial solution, ——: under high pressure oxygen perturbation, -·-·: after removing the oxygen gas.

A new absorption band brought about by compressed oxygen gas was also clearly found for QNO, IQNO, and ANO. The spectral behaviour for the oxygen-pressure dependence and the reproducibility of the intensified new band were both very similar to those in the case of PNO discussed above. These absorption bands can, therefore, reasonably be assigned to the $T_1 \leftarrow N$ transition, the spectra being shown in Fig. 3. It should be noticed that the accuracy of the $T_1 \leftarrow N$ absorption spectra of ANO seems to be less than that of the other *N*-oxides, because the solubility of ANO in a $CHCl_3$ solvent, *etc.*, is small; thus, the intensity of the $T_1 \leftarrow N$ transition arising from the oxygen perturbation also becomes small. Nevertheless, the wavelength region and the maximum position of the $T_1 \leftarrow N$ absorption of ANO seem correct.[13] The band positions of the obtained $T_1 \leftarrow N$ spectra, the singlet-singlet π-π^* transition energies in intimate correlation with the $T_1 \leftarrow N$ spectra, and the values of the singlet-triplet separation are all shown in Table 1 for the *N*-oxides studied here. Figure 4 depicts a correlation diagram of all the transitions (see Table 1) pertinent to PNO, QNO, and ANO, the correlation curves of the $S^* \leftarrow N$ transitions having previously been reported by us.[14]

Table 1. Transition energies to the T_1, ^1L_b, and ^1L_a (CT) excited states, and the T_1—^1L_a (CT) energy separation (in kK unit)

N-oxide of	$T_1 \leftarrow N$[a]	$^1L_a \leftarrow N$[b]	$^1L_b \leftarrow N$[b]	T_1—^1L_a separation[c]
Pyridine[d]	23.98	35.44	30.7	11.46
Isoquinoline	21.03	32.3	26.5	11.3
Quinoline	18.64	28.6	29.4	10.0
Acridine	13.07	22.1	27.2	9.0

a) Obtained in chloroform.
b) Obtained in *n*-heptane.
c) The $S^* \leftarrow N$ spectra shift considerably to shorter wavelength in $CHCl_3$ (contain ~1% ethanol), in which $T_1 \leftarrow N$ spectra have been recorded, so that the S^*—T_1 separation in $CHCl_3$ should be larger than that listed in this Table.
d) The $T_1 \leftarrow N$ absorption maximum in various solvents is: 23.49 kK (Diethyl oxalate), 23.18 (Benzene), 22.68 (Ether), 23.16 (Ethyl acetate), 23.46 (Dichloromethane), 23.39 (Acetone), 23.87 (Acetonitrile), 24.99 (Ethanol), 25.51 (Methanol), and 25.89 (Water).

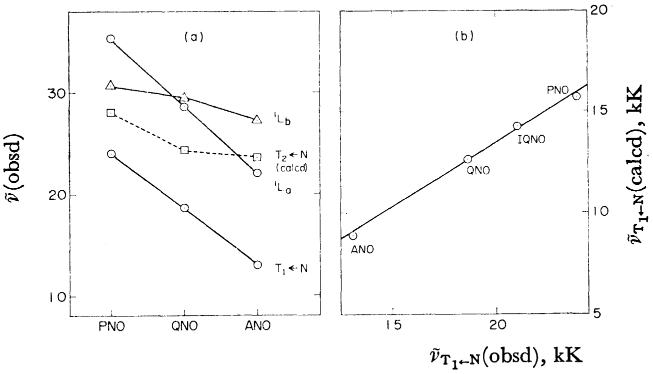

Fig. 4. (a): Correlation curves of the experimentally and the theoretically (only for $T_2 \leftarrow N$ transition) obtained transition energies among the *N*-oxides of pyridine, quinoline, and acridine. (b): Calculated $T_1 \leftarrow N$ transition energies of the *N*-oxides.

Solvent Effect on the $T_1 \leftarrow N$ *Transition of PNO.* It is well known that the singlet-singlet π-π^* bands of aromatic amine *N*-oxides exhibit a dominant blue shift phenomenon in polar solvents, especially in

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[10] R. A. Raubach and A. V. Guzzo, *J. Phys. Chem.*, **75**, 983 (1971).
[11] M. Itoh and R. S. Mulliken, *ibid.*, **73**, 4332 (1969).
[12] H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).
[13] In the present experiment concerning aromatic *N*-oxides, we have found that, roughly, the degree of the $T_1 \leftarrow N$ absorption enhancement with oxygen decreases in the order of PNO, QNO, and ANO, *i.e.*, in the order of increasing molecular size.
[14] M. Yamakawa, T. Kubota, and H. Akazawa, *Theor. Chim. Acta*, **15**, 244 (1969).

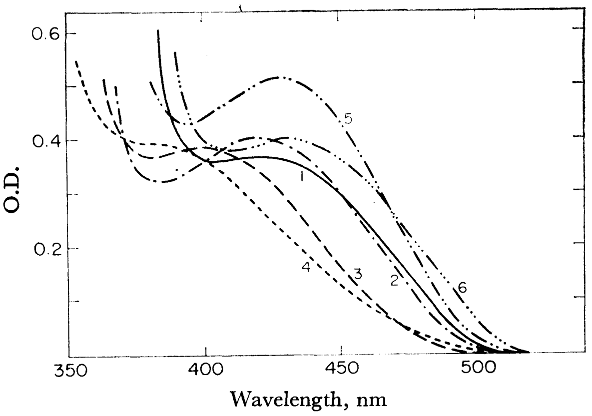

Fig. 5. Enhanced absorption spectra of the $T_1 \leftarrow N$ transition of pyridine *N*-oxide with high pressure oxygen in various solvents.
Solvents; 1: CH_3CN, 2: $CHCl_3$, 3: C_2H_5OH, 4: H_2O, 5: CH_2Cl_2, 6: benzene. All the spectra were drawn so as to give almost the same intensity as that in $CHCl_3$ solution (see Fig. 1) by suitably multiplying the original curves.

protic solvents,[15] where the hydrogen-bonding effect plays an important role.[16] This was attributed to the fact that the solute-solvent interaction, including the hydrogen-bonding effect, is much larger at the ground state than at the π–π^* excited singlet states, because the charge transfer from the oxygen atom of the *N*-oxide group to the ring π electron system is larger at the excited singlet π–π^* states than at the ground state. It is of great interest what kind of solvent shift can be expected for the case of the $T_1 \leftarrow N$ absorption bands. This sort of study was caried out in detail for PNO, the spectra yielded in several solvents being shown in Table 1 and its footnote d), and in Fig. 5. It is clear in Fig. 5 that the $T_1 \leftarrow N$ transition of PNO is quite sensitive to the solvent change and is blue-shifted with an increase in the polarity of the solvents, particularly in protic solvents such as water and ethanol. These are results similar to those observed generally for the singlet π–π^* bands of many *N*-oxides.[15,16] However, note that the degree of the blue shift for the $T_1 \leftarrow N$ transition is smaller than that of the intramolecular CT ($^1A_1$-282 nm) band of PNO. For example, the blue shifts due to the solvent change from CH_3CN (dielectric constant $D=37.5$) to C_2H_5OH (24.55), CH_3OH (32.70), and water (78.38) are 1120, 1360: 1640, 1700: 2020, 3140: (in cm^{-1} units) respectively. Here, in each set the first number should refer to the $T_1 \leftarrow N$ band, and the second, to the above $^1A_1$ CT band. It has been reported that the intramolecular charge transfer from such substituents as OH, and NR_2 to a ring π electron system like benzene and naphthalene is, in general, larger at the singlet excited state than at the lowest triplet state.[17] If the same argument as the above can be applied to the PNO system, since PNO and the phenolate ion are isoelectronic in the π electron system, the aforementioned blue shift of the $T_1 \leftarrow N$ transition, smaller than that of the $^1A_1$ band, seems to be reasonable.[18] Actually, our calculation results obtaind by the PPP method, as well as the CNDO results reported by other authors, all support this kind of consideration, although the difference in CT magnitude between the $^1A_1$ and the $^3A_1$ states of PNO is not very large.[14,19]

Nature of the $T_1 \leftarrow N$ *Transition of PNO, QNO, IQNO, and ANO.* Although it is not easy to discuss the character of the lowest triplet state from the $T_1 \leftarrow N$ transition alone, the nature of the $T_1 \leftarrow N$ absorption spectra will become somewhat clear if we check the singlet-triplet splitting values (see Table 1) and the correlation diagram shown in Fig. 4a, where the energies of the $T_1 \leftarrow N$ and $S^* \leftarrow N$ transitions are plotted in order to make the comparison clear. We can see there that the T_1 energy level is smoothly red-shifted according to the increase in the ring number. This tendency is very similar to that of the ^1L_a (CT) correlation curve among PNO, QNO, and ANO. In addition, the ^1L_a–T_1 energy separation turns out to become smaller with the increase in the ring size, but just the reverse order holds for the energy separation between the ^1L_b and the $T_1 \leftarrow N$ bands. These results are the same as those of the experiments and the theoretical S^*-T_1 energy separations of cata-condensed aromatic hydrocarbon;[20] they lead to the conclusion that the T_1 states of these *N*-oxides correspond to ^3L_a (π-π^*): $^3A_1$ for PNO and ANO, and to $^3A'$ for QNO. The conclusion is also supported by the quite large values of singlet-triplet energy separation listed in Table 1.

In the case of IQNO, systematic discussions based on the correlation diagram can not be applied. Nevertheless, it may be said that the T_1 state has the character of the π-π^* transition because of the fact that there is a good correlation between the observed T_1 energy levels and the calculated values (*vide infra*) for the PNO, QNO, IQNO, and ANO compounds, as may be seen in Fig. 4b.

In order to examine the above-mentioned character of the T_1 states theoretically, we undertook molecular orbital calculations. The calculations were made by the PPP-type SCF–MO–CI method.[14] Special attention was paid to the two-electron repulsion integral, $\gamma_{\mu\nu}$. We used the form given by Beveridge and

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[15] a) T. Kubota and H. Miyazaki, *Chem. Pharm. Bull.* (Tokyo), **9**, 948 (1961). b) See Chapter 4 of Ref. 7.

[16] T. Kubota and M. Yamakawa, This Bulletin, **35**, 555 (1962), and the other papers cited therein.

[17] a) K. Kimura and H. Tsubomura, *Mol. Phys.*, **11**, 349 (1966). b) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York (1970), p.364.

[18] Here, the following discussion seems appropriate. In the lowest equilibrium triplet state, the electron distribution and the molecular geometry can be expected to be different from those in the singlet excited state. Thus, the solute-solvent interaction potential curve in the triplet state may differ from that in the ground state or in the singlet excited state. Light absorption occurs, according to the Frank-Condon principle, from the ground state. In the present case, therefore, these circumstances would bring about a more exaggerated blue shift than the energy difference of the solute-solvent interaction in the equilibrium state between the lowest triplet and the ground states.

[19] C. Leibovici and J. Streith, *Tetrahedron Lett.*, **1971**, 387 (No. 5).

[20] S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet States," Prentice-Hall, New Jersey (1969).

Hinze:[21] $\gamma_{\mu\nu}=e^2/[a_{\mu\nu}\cdot\exp(-r_{\mu\nu}^2/2a_{\mu\nu}^2)+r_{\mu\nu}]$; here $a_{\mu\nu}=2e^2/[\gamma_{\mu\mu}+\gamma_{\nu\nu}]$.[22] The calculated results are given in Fig. 4, along with the observed ones. We found that the calculated lowest triplet energy level, T_1, lies quite apart from the other calculated triplet levels T_2, T_3, *etc.* For example, the T_2–T_1 and T_3–T_2 separations (in cm^{-1} unit) are 12296, 1988; 11610, 3408; and 14734, 1045 for PNO, QNO, and ANO respectively. In other words, the change in the character of the T_1 states, which become the ^3L_a species from a consideration of the molecular symmetry, may not occur even if more rigorous calculations are performed.[22] The calculated T_1 state also shifts smoothly to a longer wavelength in the order of PNO, QNO, and ANO, just the observed T_1 states do. Therefore, these calculated results support the previous discussion of the character of T_1 states, although the calculated values themselves are unsatisfactory compared with the observed values because the parametrization seems to be insufficient for a better description of the triplet energy levels of the *N*-oxides. Quite recently, Leibovici and Streith[19] calculated the triplet energy levels of pyridine *N*-oxide using the CNDO–CI method as modified by Bene and Jaffé.[23] They concluded that (i) the lowest triplet state, T_1, is of a π-π^* nature, with its polarization along the molecular axis, and (ii) the charge transfer from the *N*-oxide-group oxygen atom to the pyridine ring π system occurs, to thus reducing the dipole moment at the T_1 state, but the degree is smaller than for the $^1A_1$ CT band. Therefore, the blue shift of the T_1 band can be expected in polar solvents. These theoretical predictions are in accord with our experimental and calculated results discussed hitherto.

Here it should be noticed that, in general, the character of the T_1 state can also be obtained from a study of the phosphorescence spectra if the substances in question phosphoresce. In the case of some heterocyclic amine *N*-oxides, the phosphorescence spectra and their characteristics have been examined by means of the *photographic method.*[3] We repeated these measurements carefully using a Hitachi fluorescence-phosphorescence spectrophotometer, Model MPF-2A, using a red-sensitive photomultiplier for recording the spectra appearing in the longer-wavelength region. However, our experiment on the rigid glass solution at the temperature of liquid nitrogen indicated that, in the present case, the phosphorescence spectra obtained consist of those of heterocyclic amine *N*-oxide and its photochemical reaction product, and that the ratio of these two components is dependent on the solvents and samples. For example, the phosphorescence spectrum of QNO in alcohol reported by Dörr *et al.*[3] may be identified as that of 2-quinolone produced by a photochemical reaction.[24] The true phosphorescence spectra of the *N*-oxides can, then, be estimated by extrapolating the somewhat time-dependent spectra to time zero. Because of these circumstances, the experimental data of the $T_1 \leftarrow N$ absorption spectra are very important.

Next, let us pay attention to the intensity of the enhanced $T_1 \leftarrow N$ absorption bands. Recent theoretical studies have indicated that the enhancement of $T_1 \leftarrow N$ absorption is mainly brought about by the electron-exchange interaction[25] and by the contact charge-transfer interaction[12,26] occurring in the contact-weak complex formed from an electron donor (organic molecules) and an acceptor (a perturber like oxygen). Here, note that these quantum mechanical interactions may lead to the $T_1 \leftarrow N$ absorption stealing a part of the strong intensity of the singlet-singlet transitions. The degree of the intensity borrowing is, however, dependent on the molecular orbitals and on the energies of the electron donor and the acceptor. In our experimental results reported here, the $T_1 \leftarrow N$ absorption of PNO is most strongly enhanced by the oxygen perturber. However, the oxygen perturbation effect is in the order: PNO>QNO>ANO. This means that the above-mentioned quantum mechanical interactions may decrease with an increase in the π-conjugate system in the present *N*-oxides. The quantitative theoretical treatment of these experimental results is thus quite interesting; it is now proceeding in our laboratory.

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21) D. L. Beveridge and J. Hinze, *J. Amer. Chem. Soc.*, **93**, 3107 (1971). See also P. Knowlton and W. R. Carper, *Mol. Phys.*, **11**, 213 (1966); A. Matsuyama and H. Baba, This Bulletin, **44**, 1162 (1971).

22) From the viewpoint of correlation energy, the importance of the parametrization and the approximation was recently discussed for the case of the PPP-type calculation of triplet and singlet transition energies.[21] In the present case, however, the adoption of the Nishimoto-Mataga approximation[14] for $\gamma_{\mu\nu}$, and the calculation according to Zahradnik *et al.* (who suggested simple modifications of the parametrization to fit the experimental triplet energy levels to the calculated ones) both gave the same results for the state symmetry and for the relative correlation among the energy levels, as is stated in the text (see Fig. 4), although the absolute values themselves are different, especially for the NM approximation. R. Zahradnik, I. Tesarova, and J. Pancir, *Collect. Czech. Chem. Commun.*, **36**, 2867 (1971).

23) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

24) T. Yamamuro, I. Tanaka, and N. Hata, This Bulletin, **44**. 667 (1971).

25) a) G. J. Hoytink, *Accounts Chem. Res.*, **2**, 114 (1969). b) G. J. Hoijtink, *Mol. Phys.*, **3**, 67 (1960). c) C. Dijkgraaf and G. J. Hoijtink, *Tetrahedron*, **19**, Suppl. 2, 179 (1963).

26) J. N. Murrell, *Mol. Phys.*, **3**, 319 (1960).