The Singlet-Triplet Absorption Spectra of Heterocyclic Amine *N*-Oxides. II. Pyridine *N*-Oxide Derivatives

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(Received July 4, 1974)

The singlet-triplet absorption spectra of various pyridine *N*-oxide derivatives with an electron-donating substituent have been observed by applying the oxygen-intensification technique. The nature of the lowest triplet (T_1) states of these *N*-oxides and the substituent effect on the T_1 state of pyridine *N*-oxide have been discussed experimentally and theoretically. The T_1 states of the above substituted pyridine *N*-oxides were assigned to a π-π^* transition of a ^3L_a (CT) nature; $^3A_1$ for the *p*-substituted pyridine *N*-oxides. All the singlet-triplet absorption bands as well as the singlet π-π^* bands recorded here show a blue shift in polar solvents; this phenomenon is also discussed. Last, the mutual relation between the contact charge-transfer bands and the singlet-triplet absorption bands, both enhanced by compressed oxygen, has been discussed, since, for pyridine *N*-oxides with *p*-$N(CH_3)_2$, *p*-OCH_3, and *m*-NH_2, we could not record the singlet-triplet absorption band clearly.

In our foregoing papers[1,2] we discussed the characteristics of the lowest triplet state (T_1) of such basic heterocyclic amine *N*-oxides as pyridine *N*-oxide and quinoline *N*-oxide, and of nitro-substituted pyridine and quinoline *N*-oxides. The former was obtained by measuring the singlet-triplet ($T_1 \leftarrow S$) absorption spectra using the technique of high-pressure oxygen perturbation, and the latter, by recording the phosphorescence spectra as well as the $T_1 \leftarrow S$ absorption spectra. As one of the most remarkable conclusions obtained from those studies, the T_1 state of pyridine *N*-oxide (PNO) and 4-nitropyridine *N*-oxide (4NPO) was identified as $^3A_1$ (π-π^*), which corresponds to the $^1A_1$ strong absorption band appearing in a longer-wavelength region;[1,2] this information is valuable for interpreting the primary process of the photochemical reaction of these compounds.[3] As an extension of these investigations, we would like to report, in this paper, on the $T_1 \leftarrow S$ absorption spectra and the contact charge-transfer (CCT) spectra of PNO derivatives with an electron-donating substituent, these spectra being obtained under compressed-oxygen perturbation. The substituent effect on the $T_1 \leftarrow S$ band of PNO as well as the solvent effect on it has also been discussed on the basis of the experimental results and also by applying the PPP SCF-MO-CI calculation.

Experimental

The high-pressure absorption cell employed for recording the $T_1 \leftarrow S$ absorption spectrum under compressed-oxygen perturbation is the same as was described in our previous paper.[1]

The samples used in this paper are listed in Table 1. These, except for 3-aminopyridine *N*-oxide (3APNO), were synthesized and carefully purified by methods previously reported.[4] The 3APNO free base has been obtained by neutralizing its HCl salt with Na_2CO_3 in CH_3OH, and purified by repeated sublimations:[5] mp 124.5—125.0 °C. The above 3APNO HCl salt was crystallized from a reflux solution of a 3M HCl aqueous solution of 3-acethylaminopyridine *N*-oxide, which had been synthesized by the oxidation of the corresponding pyridine base with *m*-chloroperbenzoic acid.[5,6] The solvent used were CH_2Cl_2, CH_3CN, and CH_3OH, all of which were spectrograde in purity; they were dried sufficiently with a Mg ribbon (for CH_3OH alone) or $CaCl_2$, and then rectified carefully.

Results and Discussion

$T_1 \leftarrow S$ Absorption Spectra of PNO Derivatives. The effects of the compressed-oxygen perturbation on the electronic spectra of PNO derivatives with an electron-donating substituent may be experimentally classified

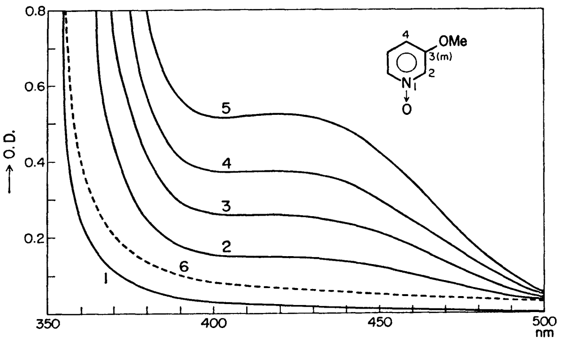

Fig. 1. Singlet-triplet absorption spectra of *m*-methoxy pyridine *N*-oxide (0.925 mol/l in CH_3CN) caused by applied oxygen pressure. The oxygen pressure is 0, 30, 60, 92, and 140 kg/cm² for curves 1, 2, 3, 4, and 5, respectively. Curve 6 is for the spectrum after removal of the oxygen.

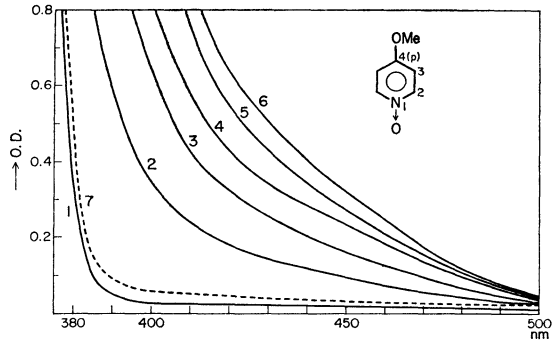

Fig. 2. The spectral change of *p*-methoxy pyridine *N*-oxide (0.290 mol/l in CH_3CN) in visible region with the applied oxygen pressure, which is 0, 37, 65, 93, 120, and 140 kg/cm² for the curves 1, 2, 3, 4, 5, and 6, respectively. Curve 7 is for the spectrum after removal of the oxygen.

TABLE 1. OBSERVED AND CALCULATED TRANSITION ENERGIES TO THE LOWEST TRIPLET STATE (T_1), OBSERVED ^1L_a ENERGY, AND OBSERVED ^1L_a–T_1 ENERGY SEPARATION (in kK unit) FOR SUBSTITUTED PYRIDINE *N*-OXIDES

Substituent	$T_1 \leftarrow S$ band			^1L_a band	^1L_a–T_1	T_1 (calcd)	ΔT_1[b]	T_1^*[c]	T_1^{**}[d]
	CH_2Cl_2	CH_3CN	CH_3OH	CH_2Cl_2	Separation[a]				
H	23.46	23.87	25.51	36.18	12.72	15.63	7.83	23.55	23.28
p-CH_3	23.55	22.8	24.9	35.86	12.04	16.04	7.51	23.23	23.69
p-Cl	22.46	22.75	24.36	35.15	12.69	15.71	6.75	22.52	23.36
p-CH_3O	CCT	CCT	CCT	35.46	—	14.51	—	22.83	22.16
p-$(CH_3)_2N$	CCT	CCT	CCT	32.87	—	11.99	—	20.24	19.64
m-CH_3	23.61	23.87	25.71	36.06	12.45	15.68	7.93	23.43	23.33
m-Cl	22.68	22.76	24.58	35.80	13.12	15.66	7.02	23.17	23.31
m-CH_3O	23.80	23.95	25.64	36.28	12.48	14.97	8.83	23.65	22.62
m-NH_2	—[e]	CCT	CCT	36.06	—	15.04	—	23.41	22.69

a) The values in CH_2Cl_2. b) Differences between the observed and the calculated T_1 energies. c) The estimated T_1 energies using the equation 1 in Text. d) The estimated T_1 energies using the equation 2 in Text. e) The $T_1 \leftarrow S$ spectrum could not be recorded in CH_2Cl_2 because of its low solubility.

into two groups. In the first group, the $T_1 \leftarrow S$ absorption band appears clearly in a visible region. The substituents belonging to this group are *m*- and *p*-CH_3, *m*- and *p*-Cl, and *m*-OCH_3; all are in a relatively weak interaction between the substituent and the N→O group. A typical example is given in Fig. 1 for *m*-methoxy-PNO. The substituents belonging to the other group are *p*-$N(CH_3)_2$, *m*-NH_2, and *p*-OCH_3; in this group, the $T_1 \leftarrow S$ absorption band is not clearly observed, as Fig. 2 shows for the case of *p*-methoxy-PNO. In this case, however, the oxygen-sensitive end absorption appears in a visible region with quite a strong intensity; the nature of this band will be discussed below. The observed values of the $T_1 \leftarrow S$ absorption spectra are listed in Table 1, along with the other relevant spectroscopic and theoretical data.

The characteristics of the ^1L_a band given in Table 1 have already been discussed in detail;[7] it has the nature of an intramolecular CT band from the *N*-oxide-group oxygen atom to the conjugated residue. In the first paper[1] in this series, we also identified the lowest triplet state (T_1) of PNO as ^3L_a (*i.e.*, $^3A_1$) on the basis of a detailed discussion of the T_1 state of basic heterocyclic amine *N*-oxides. Thus, only the substituent effect on the T_1 state of PNO will be discussed here. Checking the data in Table 1, we can see that the $T_1 \leftarrow S$ band and the ^1L_a band both shift parallel with the electron-donating substituent introduced into PNO. A *p*-substituent with a strong electron-donating ability may be especially effective for the red shift of the $T_1 \leftarrow S$ band, as may be inferred from the values of T_1^*, T_1^{**}, and the ^1L_a band listed in Table 1. In Fig. 3 the above relation is illustrated using the observed values, where a linear relation holds qualitatively between the ^1L_a and the $T_1 \leftarrow S$ bands. Conversely, this experimental fact seems to support the idea that the T_1 state of these compounds is of a ^3L_a π-π^* nature.[1,8] Next, let us examine the value of the singlet-triplet separation—in the present case, the ^1L_a—T_1 separation. This value is larger than 12000 cm^{-1} throughout all the compounds, as Table 1 shows. This also supports the idea that the T_1 state is of a π-π^* nature.[9] Moreover, the above ^1L_a—T_1 separation value is in the 12.5—13 kK (1 kK = 1000 cm^{-1}) range and is almost constant—*i.e.*, 12.63 kK on the average. The T_1-state energy of the compounds used here may then be calculated from Equation 1:

$$T_1^* = {}^1L_a\,(\text{obsd}) - 12.63 \qquad (1)$$

The values thus obtained are indicated by T_1^* and are included in Table 1, in which the T_1^* values for the PNO derivatives with *p*-OCH_3, *p*-$N(CH_3)_2$, and *m*-NH_2 substituents are also shown, although attempts to measure these were unsuccessful. The agreement between T_1 (obsd) and T_1^* is quite good.

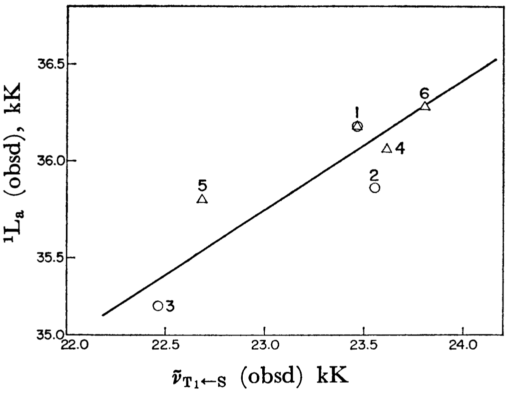

Fig. 3. Mutual correlation between the observed $T_1 \leftarrow S$ absorption band and the observed ^1L_a band for substituted pyridine *N*-oxides. The substituent is *p*-CH_3, *p*-Cl, *m*-CH_3, *m*-Cl, and *m*-OCH_3 for the number 2 to 6, respectively. The number 1 is for pyridine *N*-oxide itself.

The characters of the T_1 states experimentally discussed hitherto were also supported by the PPP-type SCF-MO-CI calculation, the method of which was the same as was employed for the singlet- and triplet-energy calculation of PNO, *etc.*;[1] *i.e.*, the two-electron repulsion integral, $\gamma_{\mu\nu}$, is estimated by means of the Beveridge and Hinze equation.[10] The parameterization for the atoms pertinent to the pyridine *N*-oxide part is the same as that given in a previous paper.[1] For substituents, the valence-state ionization potential (I_p) and the electron affinity (E_A) were determined by referring to the papers by Zahradnik *et al.*[11] The values of β_{XY}^{core} pertaining to the substituents were also estimated according to Zahradnik *et al.*[11] The values (eV) of I_p and E_A for the substituents are in this order: 25.07 and 13.80 for Cl; 32.90 and 10.00 for $-\ddot{O}-$; 27.30 and 9.30 for $-\ddot{N}H_2$; and 25.46 and 8.11 for $-\ddot{N}(CH_3)_2$. For the CH_3 group of the type, $\rangle$-CH_3, the inductive model was adopted; *i.e.*, the I_p of the carbon atom bonded to the CH_3 group is reduced by 1 eV.[12] The $-\beta_{XY}^{core}$ (eV)[13] and the bond-length (Å) values pertaining to the substituents are in this order: 0.948 and 1.730 for $\rangle$C–Cl; 1.000 and 1.356 for $\rangle C-\ddot{O}-$ and 1.896 and 1.431 for $\rangle C-\ddot{N}-$. The calculation showed that the nature of the lowest T_1 state is always ^3L_a; $^3A_1$ for *p*-substituted PNO derivatives and that the T_1 energy level is quite a bit lower (12—8 kK for *p*-substituents and 13—5 kK for *m*-substituents) than that of the T_2-energy level. These facts support the discussions about the assignment of the T_1 state on the basis of the experimental results presented above. The calculated T_1 energies are listed in Table 1. The fact that the calculated values are always lower than the observed values is a well-known general tendency in the PPP semi-empirical calculation of T_1-state energy unless a special refinement is used in the estimation of the electron-repulsion terms.[14] However, note that the difference, ΔT_1, between the observed and the calculated T_1 energies is in the range of 7—8 kK, except for the *m*-OCH_3 derivative, and almost constant; average $\Delta T_1 = 7.65$ kK. Thus, the observed T_1 energies can also be expressed by Equation 2, the values of T_1^{**} being listed in Table 1:

$$T_1^{**} = T_1(\text{calcd}) + 7.65 \qquad (2)$$

It is noticeable that the T_1^{**} values are quite close to the T_1^{*} values obtained from Equation 1. This may also support the assignment of the present T_1 states. The T_1 energy of the compounds with *p*-OCH_3, *p*-$N(CH_3)_2$, and *m*-NH_2 substituents, whose triplet energies were not obtained here experimentally (*vide infra*), seems to be between T_1^{*} and T_1^{**} values in magnitude (see Table 1).

Solvent effect on the $T_1 \leftarrow S$ Absorption Spectra of PNO Derivatives. It was reported in the foregoing papers[1,2] that the blue-shift phenomenon on the $T_1 \leftarrow S$ absorption band of PNO, *etc.* is observed in polar solvents, especially in protic solvents such as alcohols; this is just like the π-π^* singlet bands of those *N*-oxides behave in solvents.[7] The mechanism was then discussed in detail. We have now examined whether or not this kind of solvent effect is also observed in the $T_1 \leftarrow S$ band of PNO derivatives. As a result, it can safely be said that all of the $T_1 \leftarrow S$ bands recorded on PNO derivatives (see Table 1) show a blue shift due to the solvent change from CH_2Cl_2 to CH_3CN and CH_3OH; methanol particularly brings about a larger blue shift than acetonitrile. Of course, this is attributable to the hydrogen-bonding interaction of methanol with *N*-oxides, as has well been verified.[15,16] These phenomena indicate a smaller solute-solvent interaction at the T_1 excited state than in the ground state;[1] this can reasonably be explained by taking into account the intramolecular charge transfer from the oxygen atom of the *N*-oxide group, or from the substituent, to the conjugated ring residue. In turn, by comparing the magnitude of the above blue-shift ability between the $T_1 \leftarrow S$ and $^1L_a \leftarrow S$ (a strong singlet band appearing in the near-ultraviolet region) absorption bands, we have found that the former band shows almost the same magnitude as, or is a little smaller than, that of the latter.[17] However, taking account of the difference in the solute-solvent interaction potential curves among the ground, T_1, and ^1L_a states,[18] and also referring to the light-absorption mechanism according to the Franck-Condon principle,[18] the above fact may suggest that the ability of solute-solvent interaction, especially of hydrogen-bonding interaction, may be larger at the T_1 state than at the ^1L_a state, since the above-mentioned intramolecular charge-transfer effect would be smaller in the T_1 state than in the ^1L_a state.

Contact Charge-transfer Spectra with Oxygen. As has been described above, the compounds with the substituents of *p*-$N(CH_3)_2$, *p*-OCH_3, and *m*-NH_2, where quite a strong resonance of the substituent with the PNO ring is to be expected, do not exhibit a well-defined $T_1 \leftarrow S$ absorption band, but the oxygen-sensitive end absorption appears in the visible region with quite a strong intensity. Keeping these facts in mind, it should also be remembered that many organic compounds bring about contact charge-transfer spectra in the visible-to-near-ultraviolet region by means of interaction with oxygen,[19] and that the smaller the ionization potential of the compounds is, the larger is the red shift of the contact charge-transfer spectra.[20] Our molecular orbital calculation described above led us to the conclusion that the highest MO energies of *p*-N-

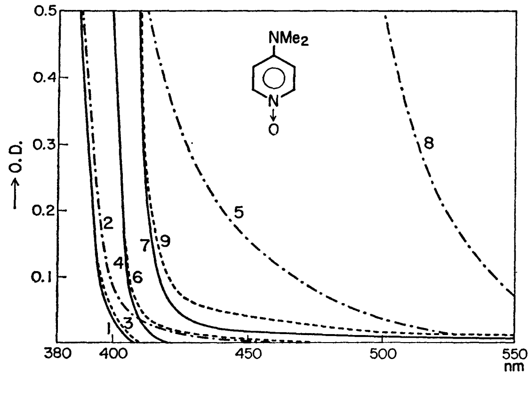

Fig. 4. The effect of oxygen pressure on the absorption spectra in a visible region of *p*-dimethylaminopyridine *N*-oxide at several concentrations in CH_3CN. The sample concentrations for curves 1, 2, and 3 are 6.61×10^{-4} mol/l; for 4, 5, and 6 7.81×10^{-3} mol/l; and for 7, 8, and 9 saturated solution. The oxygen pressure is zero for curves 1, 4, and 7; 130 kg/cm² for 2, 5, and 8. Curves 3, 6, and 9 are for the spectra after removal of the oxygen.

$(CH_3)_2$, *p*-OCH_3, and *m*-NH_2 substituted PNO's are considerably higher, particularly for the *p*-$N(CH_3)_2$ substituent, than those of the others, so that there is a possibility that the CCT spectra of these compounds occur in quite a longer-wavelength region. In addition, this possibility may be much greater in our case, since those experiments have been done under a high oxygen pressure. For these reasons, the end absorption in the visible region of the CCT spectra observed for the above three substances may cover the $T_1 \leftarrow S$ absorption band enhanced by compressed-oxygen perturbation, so we could not record the $T_1 \leftarrow S$ absorption band clearly in these cases. To check the effect of the oxygen pressure on the visible-end absorption of *p*-dimethylamino-PNO, a typical example, dissolved (in several concentrations) in CH_3CN, the experiments illustrated in Fig. 4 were carried out. The change in the spectra upon introducing compressed oxygen gas or on removing it is reversible. However, a careful check of many experiments of this kind indicates that, although the end absorption is intensified strongly and monotonously with an increase in the oxygen pressure, no absorption maximum appears there (see Fig. 4). One may, then, conjecture that the band maxima of the CCT spectra may exist in a much shorter wavelength region than that shown in Fig. 4.

References and Notes

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3) a) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970); b) I. Ono and N. Hata, This Bulletin, **46**, 3658 (1973); c) N. Hata, I. Ono, and K. Osaka, *ibid.*, **46**, 3363 (1973); d) C. Kaneko, Chemistry Review (in Japanese), No. 1, 131 (1973), The University of Tokyo Press.

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8) If the T_1 state is of triplet n-π^* nature, the substituent such as *p*-$N(CH_3)_2$, *p*-OCH_3, *etc.* would bring about the blue shift of the $T_1 \leftarrow S$ band.

9) Detailed discussions on this point were given in the references 1 and 2.

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11) R. Zahradnik, I. Tesařova, and J. Panciř, *Collet. Czech. Chem. Commun.*, **36**, 2867 (1971); J. Pancir̆ and R. Zahradnik, *Theor. Chim. Acta*, **14**, 426 (1969); See also K. Nishimoto, *ibid.*, **7**, 207 (1967), the treatment of this reference being applied for determining the I_P and E_A of $\ddot{N}(CH_3)_2$ by connecting with those of $\ddot{N}H_2$ given in Zahradnik *et al.* (*vide supra*).

12) P. Lazzeretti and F. Taddei, *Mol. Phys.*, **22**, 941 (1971).

13) These values were obtained by multiplying the ratio of (β_{cx}/β_{cc}) given by Zahradnik *et al.*[11] to the present β_{cc}^{core} value (−2.370 eV). For $\beta_{C-O:}^{core}$, however, we estimated it so as to reproduce the UV spectrum of azoxyanisole. Detail was presented at the Symposium of Structure Chemistry and the Electronic State of Molecules (Sendai, October 1972, Abstract p. 65) by Ezumi *et al.*

14) K. Nishimoto, *Theor. Chim. Acta*, **5**, 74 (1966); *ibid.*, **7**, 207 (1967).

15) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Chapters 6 and 7, Dekker, New York (1970).

16) Here note that the dielectric constant, which plays an important role for the solvent shift due to long range electrostatic terms, of acetonitrile and methanol is 37.5 and 32.63, respectively, and almost the same in magnitude.

17) See also reference 1.

18) For detailed description on these points, see footnote 18 in our previous paper.[1] This is attributed to the problem of Franck-Condon stabilization energy.[15]

19) H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960); H. Ishida, H. Takahashi, H. Sato, and H. Tsubomura, *ibid.*, **92**, 275 (1970); This Bulletin, **43**, 3130 (1970).

20) This kind of CCT spectra may be thought to take place by the charge transfer from the highest occupied molecular orbital of electron donors to thee lectron accepting orbitals (degenerated π and $\bar{\pi}$ orbitals) of oxygen (electron acceptor), and to borrow the intensity from strong π-π^* transition of the donor in CCT complexes.[19] In several amines *etc.* the CCT full spectra with maxima were observed by oxygen perturbation.[19]