University of Groningen

Structure and Dipole Moment of the First Electronically Excited State of Pyridine N-Oxide

Hochstrasser, Robin M.; Wiersma, Douwe A.

Published in:
The Journal of Chemical Physics

DOI:
[10.1063/1.1675676](https://doi.org/10.1063/1.1675676)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1971

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Hochstrasser, R. M., & Wiersma, D. A. (1971). Structure and Dipole Moment of the First Electronically Excited State of Pyridine N-Oxide. *The Journal of Chemical Physics*, 55(11), 5539-5343.
<https://doi.org/10.1063/1.1675676>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

- ¹² H. Bluysen, J. Verhoeven, and A. Dymanus, *Phys. Letters* **25A**, 214 (1967).
¹³ J. Verhoeven, H. Bluysen, and A. Dymanus, *Phys. Letters* **26A**, 424 (1968).
¹⁴ G. Steenbeckeliers and J. Bellet, *Compt. Rend.* **270**, 1039 (1970).
¹⁵ J. Bellet and G. Steenbeckeliers, *Compt. Rend.* **271**, 1208 (1970).
¹⁶ G. Steenbeckeliers (private communication).
¹⁷ D. R. Johnson (private communication). (Data arrived too late to include in analysis.)
¹⁸ E. F. Barker and W. W. Sleator, *J. Chem. Phys.* **3**, 660 (1935).
¹⁹ W. S. Benedict, N. M. Gailar, and E. K. Plyler, *J. Chem. Phys.* **21**, 1302 (1953).
²⁰ W. S. Benedict, N. M. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).
²¹ N. M. Gailar and F. P. Dickey, *J. Mol. Spectry.* **4**, 1 (1960).
²² P. Helminger, R. L. Cook, and F. C. DeLucia, *J. Mol. Spectry.* (to be published).
²³ F. C. DeLucia, P. Helminger, and W. Gordy, *Phys. Rev. A* **3**, 1849 (1971).
²⁴ P. Helminger, F. C. De Lucia, and W. Gordy, *Phys. Rev. Letters* **25**, 1397 (1970).
²⁵ R. Kewley, K. V. L. N. Sastry, M. Winnewisser, and W. Gordy, *J. Chem. Phys.* **39**, 2856 (1963).
²⁶ W. S. Benedict, S. A. Clough, L. Frenkel, and T. E. Sullivan, *J. Chem. Phys.* **53**, 2565 (1970).
²⁷ F. De Lucia, P. Helminger, R. L. Cook, and W. Gordy, Abstract V1, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 14-18 June 1971.
²⁸ E. B. Wilson, Jr., and J. B. Howard, *J. Chem. Phys.* **4**, 260 (1936).
²⁹ D. Kivelson and E. B. Wilson, Jr., *J. Chem. Phys.* **21**, 1229 (1953).
³⁰ J. K. G. Watson, *J. Chem. Phys.* **45**, 1360 (1966).
³¹ J. K. G. Watson, *J. Chem. Phys.* **46**, 1935 (1967).
³² J. K. G. Watson, *J. Chem. Phys.* **48**, 4517 (1968).
³³ W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1970).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 11 1 DECEMBER 1971

Structure and Dipole Moment of the First Electronically Excited State of Pyridine *N*-Oxide*

ROBIN M. HOCHSTRASSER AND DOUWE A. WIERSMA

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 7 July 1971)

A study is presented of the lowest-energy singlet-singlet transition of pyridine *N*-oxide in mixed crystals with *p*-dichlorobenzene at 4.2°K. Polarization and Stark effect measurements on the electronic origin of the transition (at 29 599.6 cm⁻¹) show that the transition is $\pi^* \leftarrow \pi$, ${}^1B_2 \leftarrow {}^1A_1$. The spectrum of *d*₅-pyridine *N*-oxide is blue shifted by 123 cm⁻¹ and its absorption and emission spectra are quite similar to those of *h*₅. The vibrational analysis of the absorption and fluorescence spectrum, and the Franck-Condon patterns, suggest that the equilibrium geometry is little affected by electronic excitation. Stark effect measurements on the electronic origin band yield a value of $\Delta\mu = 0.71 \pm 0.03$ D (assuming $E = 0.60 E_{\text{eff}}$) for the change in dipole moment on electronic excitation; where E and E_{eff} are the applied and effective Stark electric fields corresponding to an external field directed down the *a'* crystallographic axis of the *p*-dichlorobenzene host crystal. This small change is much less than predicted by π -electron theory.

INTRODUCTION

Pyridine *N*-oxide may be regarded as an intramolecular charge-transfer complex of pyridine and an oxygen atom, in which the nitrogen atom is positive with respect to oxygen. The various electronically excited states of pyridine *N*-oxide will be expected to have varying degrees of charge transfer, and it is of interest to learn more about the classification of these states and hence about the structure of this rather unusual prototype molecule.

Three electronic transitions of pyridine *N*-oxide have been discussed previously¹⁻⁴: A weak transition ($f=0.012$) at 3200 Å and two moderately strong transitions at 2800 Å ($f=0.173$) and 2150 Å ($\epsilon_{\text{max}}=18\,000$). There are no definite assignments for any of these states. The 3200-Å transition has been described as an $n \rightarrow \pi^*$ transition⁴ on the basis of solvent shifts, but this characterization was questioned^{5,6} in view of the therefore unusually large f number, and because the

solvent shifts of the 2800-Å transition are apparently similar. The polarization of the fluorescence excitation spectra of other *N*-oxides⁷ gave indications by analogy that the 3200-Å state is most likely not $n\pi^*$.

In a recent theoretical study⁸ the lowest electronic transition is predicted to be $\pi \rightarrow \pi^*$: In addition, the dipole moment is predicted to reverse direction on electronic excitation to this state,^{8,9} changing from the ground-state value of 4.13 D to an excited-state value⁸ of -0.66 D. These contentions are subject to direct experimental test. If the transition is ${}^1B_2 \leftarrow {}^1A_1(\pi^* \leftarrow \pi)$, then it will be polarized in the molecular plane along the short axis. The excited-state dipole moment can be measured using the Stark effect on the individual vibronic transitions.¹⁰ Both of these experiments are conveniently done with mixed crystals, and in this paper the absorption and emission spectra and the Stark effect measurements are presented for pyridine *N*-oxide in a *p*-dichlorobenzene host lattice.

FIG. 1. The *b*- and *c*-polarized absorption spectra of pyridine *N*-oxide (h_5) in *p*-dichlorobenzene at 4.2°K.

TABLE I. Absorption of pyridine *N*-oxide (h_5) in a *p*-dichlorobenzene crystal at 4.2°K. Number in parentheses are for the perdeutero analog.

<i>I</i> ^a	Å	cm ⁻¹ ^b	$\Delta\nu$ (cm ⁻¹)	Interpretation ^c
vs, s	3377.45	29 599.6	0	0-0
vs, b	3374.7	29 624	24	Local lattice mode (<i>llm</i>)
s, b	3372.0	29 647	47	2× <i>llm</i>
m, b	3369.6	29 669	69	3× <i>llm</i>
w, s	3328.1	30 039	439(425)	Fundamental
m, s	3318.3	30 127	527(517)	Fundamental (ν_{8a})
s, s	3315.1	30 156	556(-)	Fundamental
m, b	3312.5	30 180	580	556+ <i>llm</i>
w, b	3310.0	30 203	603	556+2× <i>llm</i>
s, s	3292.3	30 366	766(712)	Fundamental (ν_{12})
m, b	3289.5	30 391	791	766+ <i>llm</i>
w, b	3287.0	30 414	814	766+2× <i>llm</i>
vw, b	3284.1	30 441	841	766+3× <i>llm</i>
w, s	3272.8	30 546	946(809)	Fundamental (ν_{18a} OR ν_{9a})
m, s	3269.4	30 578	978(-)	
s, s	3267.6	30 595	995(847)	Fundamental (ν_{9a} OR ν_{18a})
m, b	3265.1	30 619	1019	995+ <i>llm</i>
w, s	3236.4	30 890	1290	766+527-3
w, s	3233.5	30 917	1317	766+556-5
w, b	3231.2	30 939	1339	1317+ <i>llm</i>
w, s	3228.4	30 966	1366	
m, s	3223.2	31 017	1417(1366)	Fundamental (ν_{19a})
m, b	3220.7	31 040	1440	1417+ <i>llm</i>
m, b	3217.9	31 068	1468	Fund+2× <i>llm</i>
m, s	3215.1	31 094	1494	2×527+439+1
s, s	3213.1	31 113	1513(1485)	Fundamental (ν_{8a})
m, b	3210.6	31 138	1538	1513+ <i>llm</i>
w, b	3207.8	31 165	1565	1513+2 <i>llm</i>

^a In this column the first symbol stands for the intensity: vs, very strong; s, strong; m, medium; and w, weak. The second symbol indicates the line-width: s, sharp and b, broad.

^b Vacuum wavenumbers.

^c The most probable benzene parentage is given for each fundamental.

EXPERIMENTAL PROCEDURES

All materials were purified by zone refining. The pyridine *N*-oxide (h_5) was obtained from Eastman Kodak and the d_5 compound was obtained from Merck, Sharp and Dohme (Canada). The mixed crystals were grown from the melt in Bridgman style, and contained about 0.1% guest. The Stark spectra were photographed on a Jarrell-Ash spectrograph (1.7 Czerny-Turner-Fastie) used in the 17th order with a linear dispersion of 4.3 Å/cm. The remaining spectra were obtained photographically on a Baird Atomic GX-1 Eagle Spectrograph (3 m) with an accuracy of ~2 cm⁻¹. The fluorescence was photographed on 103A-O plates and required about 2-h exposures using two 7-54 (Corning) filters and 30 cm of NiSO₄ (60 g/liter) solution in association with a 1000-W xenon arc for excitation.

THE ABSORPTION SPECTRUM

The *b*- and *c*-polarized absorption spectra of the h_5 compound are shown in Fig. 1. Table I gives the band positions and some possible assignments for the prominent vibronic levels. The vibrational frequencies for the d_5 compound are noted in parenthesis.

The spectrum consists of five prominent groups of bands. Each group consists of both zero-phonon and phonon-assisted transitions that were distinguished from one another by their spectral appearance. For example, the 0, 0 band group shows one very sharp line (≤ 0.6 -cm⁻¹ width) and a number of broader bands (≈ 3 -cm⁻¹ width): The wider lines are assumed to be local lattice excitations, and these same intervals are associated with other vibronic (zero-phonon) transitions. The deuteration shift of the electronic origin is 123 cm⁻¹ ($\bar{\nu}_d - \bar{\nu}_h$).

The fact that the absorption spectrum is considerably stronger for light polarized along *b* than along *c* immediately establishes that the transition is polarized in the molecular plane (see Table II for crystallographic data¹¹) and we conclude that it is a $\pi \rightarrow \pi^*$ type transition. The orientation of the in-plane axes of pyridine *N*-oxide relative to the *p*-dichlorobenzene crystal axes is not known, however our studies of the spectrum in an electric field (see below) have shown conclusively that this transition is polarized perpendicular to the dipolar (twofold) axis, thus providing

TABLE II. Squared direction cosines for the principal axes of the host molecules (*p*-dichlorobenzene) with respect to the host crystallographic axes.

	<i>a'</i>	<i>b</i>	<i>c</i>
<i>L</i>	0.536	0.359	0.106
<i>M</i>	0.462	0.446	0.091
<i>N</i>	0.002	0.194	0.803

a definite assignment of the upper state as 1B_2 . The polarization and the electric field measurements show that pyridine *N*-oxide does not enter into *p*-dichlorobenzene with its principal axes parallel to those of the host molecules. We find $I_b/I_c = 3.3$ and $I_b/I_a \geq 25$, indicating that the short in-plane axis of the guest is almost perpendicular to a' . The host molecules, on the other hand, have their shortest in-plane axis at 47° to a' . Apparently the guest molecules have equilibrated at a position in which the longest in-plane axis is roughly aligned with the a' axis of the crystal: This alignment places the NO axis at about 43° to the C-Cl axis of the host.

THE FLUORESCENCE SPECTRUM

The fluorescence spectrum of pyridine *N*-oxide in *p*-dichlorobenzene is shown in Fig. 2. The $T_1 \leftarrow S_0$ absorption of the host starts at 3585 Å so many host emission lines appear at longer wavelengths. The higher-energy guest emission lines are located above the host singlet-triplet absorption, and the highest-energy guest fluorescence line coincides with the lowest-energy guest absorption line: This establishes our assignment for the electronic origin of the guest transition. Table III lists some of the main fluorescence bands for h_b (and d_b) pyridine *N*-oxide, including the local phonon modes. The agreement between our ground-state frequencies and those obtained by infrared and Raman spectroscopy¹² is not as close as expected indicating that we may have a case where the molecular force field is quite solvent sensitive.

VIBRONIC EFFECTS

The 1B_2 state, under study here, symmetry correlates with the 2600-Å ${}^1B_{2u}$ state of benzene, and if indeed it were just a perturbed version of the benzene state we would expect the benzenelike Herzberg-Teller interactions to show up in the spectrum: The ${}^1B_2 \leftarrow {}^1A_1$ transition has $f \sim 0.012$ whereas the 2600-Å

TABLE III. Emission of pyridine *N*-oxide (h_b) in a *p*-dichlorobenzene crystal at 4.2°K. Numbers in parentheses are for the deuterio analog.^a

<i>I</i>	Å	cm ⁻¹	$\Delta\nu$ (cm ⁻¹)	Interpretation
vs, s	3377.45	29 599.6	0	0-0
vs, b	3381.9	29 561	39	Local lattice mode (llm)
s, b	3386.8	29 518	82	$2 \times llm$
m, b	3391.9	29 474	126	$3 \times llm$
w, s	3429.9	29 147	453 (430)	Fundamental
vw, b	3434.1	29 111	489	$453 + llm$
s, s	3440.5	29 057	543 (528)	Fundamental (ν_{8a})
m, b	3445.2	29 018	582	$543 + llm$
m, s	3448.2	28 992	608 (585)	Fundamental
vw, b	3450.3	28 974	626	$582 + llm$
w, b	3453.8	28 945	655	$+ llm$
w, b	3457.1	28 918	682	$+ llm$
m, s	3473.7	28 780	820 (747)	Fundamental (ν_{12})
w, b	3478.4	28 741	859	$820 + llm$
w, s	3483.6	28 697	903	$2 \times 453 - 3$
vw, s	3495.1	28 603	997	$543 + 453 + 1$
vw, s	3514.4	28 447	1153	$608 + 543 + 2$
w, s	3521.8	28 387	1213 (1218)	$2 \times 608 - 3$ or (ν_{18a} or ν_{9a})
vs, s	3524.1	28 368	1232 (1222)	Fundamental (ν_{9a} or ν_{18a})
s, b	3529.0	28 329	1271	$1232 + llm$
m, b	3530.4	28 317	1283	
m, b	3534.5	28 285	1315	$1232 + 2llm$
s, s	3540.6	28 236	1364	$820 + 543 + 1$
m, b	3545.4	28 197	1403	$1364 + llm$
w, b	3551.6	28 149	1451	$1364 + 2llm$
w, s	3553.1	28 136	1464 (1358)	Fundamental (ν_{19a})
w, s	3562.4	28 063	1537	$2 \times 543 + 453 - 2$
w, s	3563.0	28 058	1542	Fundamental
w, s	3564.4	28 047	1553 (1509)	Fundamental
w, b	3568.8	28 013	1587	$+ llm$
s, s	3579.9	27 926	1674 (1659)	Fundamental (ν_{8a}) or 2×837
w, s	3581.4	27 914	1686	$1232 + 453 + 1$
m, b	3584.7	27 889	1711	$1674 + llm$
w, s	3590.5	27 843	1757	$1213 + 543 + 1$
m, s	3593.1	27 824	1776	$1232 + 543 + 1$

^a See Table I notes for explanation of symbols.

FIG. 2. The emission spectrum of pyridine *N*-oxide (h_b) in *p*-dichlorobenzene at 4.2°K. The line at 3585 Å is the origin of the $T_1 \leftarrow S_0$ absorption spectrum of *p*-dichlorobenzene.

transition of benzene has $f \sim 0.0012$. The benzene e_{2g} mode ν_6' (522 cm⁻¹) will correlate with b_2 - and a_1 -type modes in pyridine *N*-oxide, giving rise to long- and short-axis polarized Herzberg-Teller origins. Actually the whole spectrum is short-axis polarized, including a number of obvious Herzberg-Teller origins. The strongest origins are the 0, 0 band, then the 527- and 556-cm⁻¹ a_1 modes. One or both of these modes probably has significant benzene ν_6' parentage. These two vibronically induced transitions (0+556, and 0+527 cm⁻¹) present what may be a nice example of the Duschinsky effect¹³: The relative intensity of the

FIG. 3. Absorption spectra at high resolution of the origin band of the ${}^1B_2 \leftarrow {}^1A_1$ transition of pyridine *N*-oxide (h_5) in *p*-dichlorobenzene at various electric field strengths. The electric field is directed along the a' axis and the field strength and splittings are as noted on the figure.

two transitions is quite different in the absorption and emission spectrum ($0-608$, $0-543 \text{ cm}^{-1}$). The remainder of the modes appear to be Franck-Condon allowed, although it is easily seen that the absorption and emission spectra are by no means identical in regard to intensity distribution, and the Franck-Condon patterns are not the same for the electronic origin and the false origin spectra. In addition, there are most likely Fermi resonances, such as between $0-1213$ and $0-1232 \text{ cm}^{-1}$: In perdeutero these modes become $0-1218$ and $0-1222 \text{ cm}^{-1}$ and their relative intensities are considerably modified. The spectrum is generally straightforward, and the absence of progressions in any of the modes, the relative strength of the origins compared the remainder of the spectrum, and the occurrence of conventional deuteration shifts for both ground- and excited-state modes leads to the conclusion that the equilibrium geometry (including the N-O bond length) is quite similar for the ground and 1B_2 excited states in the mixed crystal. The absence of b_2 false origins remains puzzling.

Electric Dipole Moment of the Excited State

We have shown previously that a pseudo-Stark splitting of vibronic transitions can be caused by applying an electric field across a molecular crystal (host) while observing, at high resolution, the electronic spectrum of the guest molecules.^{10,14} If the orientation of the guest molecule is known relative to the host

crystal axes, then a single measuring field $\mathbf{E}$ can be found that causes an observable splitting $2\mathbf{E} \cdot \Delta\boldsymbol{\mu}$ of each spectral line: Hence $|\Delta\boldsymbol{\mu}|$ can be measured if the magnitude of $\mathbf{E}$ is known. In the present case the orientation is not known *a priori*, but there are three mutually perpendicular experimental possibilities for $\mathbf{E}$ and these suffice to determine the orientation and magnitude of $\Delta\boldsymbol{\mu}$ in the crystal coordinate system. The most advantageous situation, from the viewpoint of accuracy of determining $|\Delta\boldsymbol{\mu}|$, arises when the three experimental directions form a Cartesian system with $\Delta\boldsymbol{\mu}$ nearly parallel to one of the axes. Such happens to be the case for pyridine *N*-oxide in *p*-dichlorobenzene with the three directions being the a' , b , and c crystallographic axes. It arises that the direction $\Delta\boldsymbol{\mu}$ is very near to a' . With $\mathbf{E}$ parallel to b or c we see only a very slight broadening of the $0, 0$ band of the ${}^1B_2 \leftarrow {}^1A_1$ transition. The absorption line is about 0.6 cm^{-1} wide and the electric field broadening is not more than an additional 10%, for an applied field of 60 kV cm^{-1} along either b or c . For the same field along a' the splitting of the line is about 2 cm^{-1} . Because $\Delta\boldsymbol{\mu}$ is close to a' , there is very little error ($\sim 3\%$) introduced by even a large ($\sim 10^\circ$) uncertainty in the actual angle between a' and $\Delta\boldsymbol{\mu}$.

Figure 3 shows the spectra of the $0, 0$ band for various applied fields, and our experimental data are summarized in Fig. 4. The slope of the line in Fig. 4 is $2.36 \times 10^{-18} \text{ erg esu}^{-1}$. To evaluate $|\Delta\boldsymbol{\mu}|$ we assume $2\Delta\mu = 0.60 \times (\text{slope}) \times 10^{18} \text{ D}$. The factor of 0.60 arises from our assumption¹⁰ that the applied field (along a') is $3(n_a^2 + 2)^{-1}$ times the effective field, where n_a is the refractive index along a' . We hope that it may soon be possible to test this approximation by comparing our results with future results from the Stark effect of pyridine *N*-oxide in the gas phase. From the present study we obtain $|\Delta\boldsymbol{\mu}| = 0.71 \pm 0.03 \text{ D}$ (for $E \equiv 0.60 E_{\text{eff}}$).

The sign of $\Delta\boldsymbol{\mu}$ can be deduced from the spectral shifts between the neat crystal and the nonpolar mixed crystal.¹⁵ Usually a decrease of dipole moment on excitation will result in a shift to higher energy

FIG. 4. Stark splitting vs applied electric field for the origin band of the ${}^1B_2 \leftarrow {}^1A_1$ transition of pyridine *N*-oxide (h_5) in *p*-dichlorobenzene. The electric field is directed along the a' axis of the *p*-dichlorobenzene crystal. For the field directed either along the b or c axes no Stark splitting was observed (see text). The crystal used in this experiment had a thickness of 5 mm.

when the molecule is located in a dipolar lattice. Without knowing the actual crystal structure one cannot be certain of the source of spectral shifts, but since in this case there is a blue shift between *p*-dichlorobenzene and neat crystal (0, 0 at $\sim 30\,300\text{ cm}^{-1}$) this provides a strong indication that the excited-state dipole moment is less than that of the ground state.

Extraneous Influences on Polarity

Our measured dipole-moment change is extremely small compared with that expected on theoretical grounds, and we have therefore tried to eliminate two possible experimental situations that would certainly influence the meaning of our result. One of these situations is that we are observing the spectrum of a weakly polar dimer of pyridine *N*-oxide, and the other is that each pyridine *N*-oxide molecule is associated with one molecule of water in the mixed crystal.

We have eliminated the possibility that our spectra are mainly due to dimers or polymers of pyridine *N*-oxide by studying the spectra of mixtures of perproto and perdeutero in dichlorobenzene. The fact that these spectra show no shifts and no additional prominent lines over those obtained for perproto and perdeutero separately indicates that there is no significant aggregation.

To check the presence of water we deliberately prepared crystals in such a manner that D₂O would replace substantially any H₂O that was incorporated. The resulting spectra were identical with those reported earlier in this paper, and we conclude that our procedures did remove water from pyridine *N*-oxide.

Excited-State Structure

Our observation of a proportionately small change in dipole moment (compared with ground-state moment of 4.13 D) is consistent with conclusions drawn from the vibrational analysis and from the assignment of the state as the analog of the benzene ${}^1B_{2u}$ state. The bonding of O to pyridine appears to be quite similar in the ground and 1B_2 excited states. Our experimental results do not manifest the predictions of molecular-orbital calculations which would indicate significant changes in π -electron polarity following excitation to

this state. Apparently the amount of electron transfer from oxygen in the excited state is smaller than predicted by restricted calculations.¹⁶

These results point once more to the importance of including σ electrons in calculations concerned with charge distributions in polar molecules. Experimental evidence is now available that indicates that π -electron calculations consistently overestimate changes in dipole moment on electronic excitation.¹³ It should be apparent that one cannot usually modify a π -electron charge distribution without thereby seriously influencing the distribution of the other electrons; obviously the tendency is for these other electrons to shift in the opposite direction to the π -electron shift.

* This research was supported in part by the U.S. Army Research Office (Durham) and in part by the Advanced Research Projects Agency.

¹ T. Kubota, J. Chem. Soc. Japan **79**, 930 (1958); **80**, 578 (1959).

² M. Ito and N. Hata, Bull. Chem. Soc. Japan **28**, 260 (1955).

³ T. Kubota, Bull. Chem. Soc. Japan **35**, 946 (1962).

⁴ M. Ito and W. Mizushima, J. Chem. Phys. **24**, 495 (1956).

⁵ J. Sidman, Chem. Rev. **58**, 689 (1958).

⁶ J. N. Murrell, *Theory of Electronic Spectra of Organic Molecules* (Methuen, London, 1963), p. 188.

⁷ B. Ziolkowsky and F. Dörr, Ber. Bunsenges. Physik. Chem. **69**, 448 (1965).

⁸ E. M. Evlieth, Theoret. Chim. Acta **11**, 145 (1968).

⁹ J. Del Bene and H. H. Jaffé, J. Chem. Phys. **49**, 1221 (1968).

¹⁰ R. M. Hochstrasser and L. J. Noe, J. Chem. Phys. **48**, 514 (1968).

¹¹ E. Frasson, C. Garbuguo, and S. Bezzi, Acta Cryst. **12**, 126 (1959).

¹² P. Mirone and B. Fortunato, Atti. Accad. Nazl. Lincei, Rend. Classe Sci. Fis. Mat. Nat. **34**, 168 (1963).

¹³ G. Small, J. Chem. Phys. **54**, 3300 (1971).

¹⁴ R. M. Hochstrasser and L. J. Noe, J. Chem. Phys. **50**, 1684 (1968).

¹⁵ In most crystals of polar molecules the electric fields due to nearby dipoles contribute substantially to the spectral shifts for single molecule excitations. These fields usually introduce an attractive potential energy at a single polar site, such as in a crystal that consists of a card-pack stack of molecules. If the dipole moment of the test molecule is decreased then the attractive potential is decreased. This effect will cause a shift to higher energy, compared with the gas phase, if a transition is accompanied by a decrease in dipole moment.

¹⁶ J. C. D. Brand and K. T. Tang (unpublished results). During the course of preparing this work for publication these authors kindly sent us a preprint of their work on the rotational analysis of a band of pyridine *N*-oxide at 3420 Å. Our work confirms that the upper state symmetry B_2 determined by these authors is the electronic symmetry. They conclude that there is a significant change in NO bond length.