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Intramolecular Fluorescence Quenching Effect by *p*-Nitrophenyl and *p*-Nitrophenoxy Groups

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The intramolecular fluorescence quenching efficiency of *p*-nitrophenyl and *p*-nitrophenoxy groups in homologous series of *p*-$O_2NC_6H_4(CH_2)_n$NH-1-Naphthyl (I, $n=1$—7) and *p*-$O_2NC_6H_4O(CH_2)_n$NH-1-Naphthyl (II, $n=2$—6), respectively, has been determined. The quenching effect is observed even in the highest homologs of both series. From the fact that the fluorescence intensity of $n=2$ homolog of I is higher than that of $n=1$, together with spectroscopic data it is concluded that the higher intensity of $n=2$ than $n=1$ of the across-space intramolecular charge-transfer band is due to the larger absorbance per interacting molecule of n=2, the origin of which might be attributed to the different interacting conformations of these homologs. The effect of the number of methylene groups (n) on the fluorescence spectral shape has also been found.

Although *intermolecular* charge-transfer (CT) interaction has been studied extensively, it is only recently that across-space *intramolecular* CT interaction has begun to draw the attention of chemists.[1] One of the characteristics of the latter type interaction is that the interaction under more or less restricted conditions can be observed, and accompanying CT spectral features may provide valuable data for a further understanding of the CT phenomenon. In this paper some conformational effects on the CT spectrum are shown by the aid of fluorescence spectroscopy.

The *p*-nitrophenyl, *p*-$O_2NC_6H_4$–, group can play the role of electron-acceptor in the across-space intramolecular CT interaction in a series of *p*-$O_2NC_6H_4$-$(CH_2)_n$-NHAr.[2] It has been found that the intensity of the CT band of $n=2$ homolog is higher than that of $n=1$ homolog regardless of the Ar group. For instance, the ratios of the apparent absorption coefficients, $\varepsilon(n=2)/\varepsilon(n=1)$, observed in carbon tetrachloride solution for the derivatives of Ar=phenyl, =*p*-methoxyphenyl, and =1-naphthyl are 3.0, 1.7, and 1.4, respectively. A similar phenomenon has been reported in other homologous series of compounds.[1a,1f] On the other hand, the position of the CT band of the $n=1$ homolog is a little longer in wavelength, that is, the transition energy is smaller in this homolog. These spectral characteristics could be attributed to the presence of intramolecular N—H$\cdots\pi$ interaction, but the same order of intensities observed in the *N*-alkylated derivatives of I[3] suggests that this explanation is incorrect. In connection with the CT interacting state there are

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[1] a) W. N. White, *J. Amer. Chem. Soc.*, **81**, 2912 (1959); b) S. Shifrin, *Biochem. Biophys. Acta*, **96**, 173 (1966); c) J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *Tetrahedron Lett.*, **1966**, 4399; d) A. J. de Gee, J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *Tetrahedron*, **25**, 3407 (1969); e) J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *ibid.*, **25**, 4037 (1969); f) H. A. H. Craenen, J. W. Verhoeven, and Th. J. de Boer, *Tetrahedron Lett.*, **1970**, 1167; g) R. Carruthers, F. M. Dean, L. E. Houghton, and A. Ledwith, *Chem. Commun.*, **1967**, 1206; h) M. Ōki and K. Mutai, *Tetrahedron Lett.*, **1968**, 2019; i) M. Itoh and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 1843 (1968); j) J. P. Carrión, D. A. Deranleau, B. Donzel, K. Esko, P. Moser, and R. Schwyzer, *Helv. Chim. Acta*, **51**, 459 (1968); k) P. Moser, *ibid.*, **51**, 1831 (1968).

[2] M. Ōki and K. Mutai, *Tetrahedron*, **26**, 1181 (1970).

[3] K. Mutai, to be published.

two possibilities for the interpretation of the spectral features. (1) The CT interaction is favorable in $n=1$ as is noted in the transition energy, and the number of interacting molecules per mole is larger than that in $n=2$. This situation is probable from the viewpoint of entropy for the two interacting groups to meet, but the interacting conformation subject to the restrictions caused by the shorter methylene chain diminishes the CT intensity per interacting molecule. (2) The interaction in the higher homolog ($n=2$) is favored with regard to the interacting energy, since a scale model indicates that the π-electron clouds of the two group can overlap more sufficiently in this homolog, and its higher intensity reflects larger population of the interacting molecule than in $n=1$.

It would be easy to find a correct explanation if the absorption intensities per interacting molecule or the ratios of the interacting to non-interacting molecule for both homologs could be determined. Unfortunately, only a part of the molecules interact and there is no reliable way to determine their values. However, for the present purpose, it is not necessary to know the precise values. It is adequate only to determine in which of the two homologs the population is larger or, in other words, the interacting groups have a greater chance of access to each other.

The approach employed in the present study is fluorescence quenching effect,[4] since the phenomenon is known to be greatly dependent on the distance between a fluorescer and a quencher by whichever mechanism it takes place.[5,6] This characteristic is convenient for comparing the degree of proximity of the two groups in a homologous series of compounds, if one group is fluorescer and the other can quench it. In the present case the 1-naphthyl group is introduced to the amino nitrogen, thus producing a 1-naphthylamino group known as a strong fluorescent moiety. This group, of course, can work as an electron-donor in across-space intramolecular CT interaction with the p-nitrophenyl group.

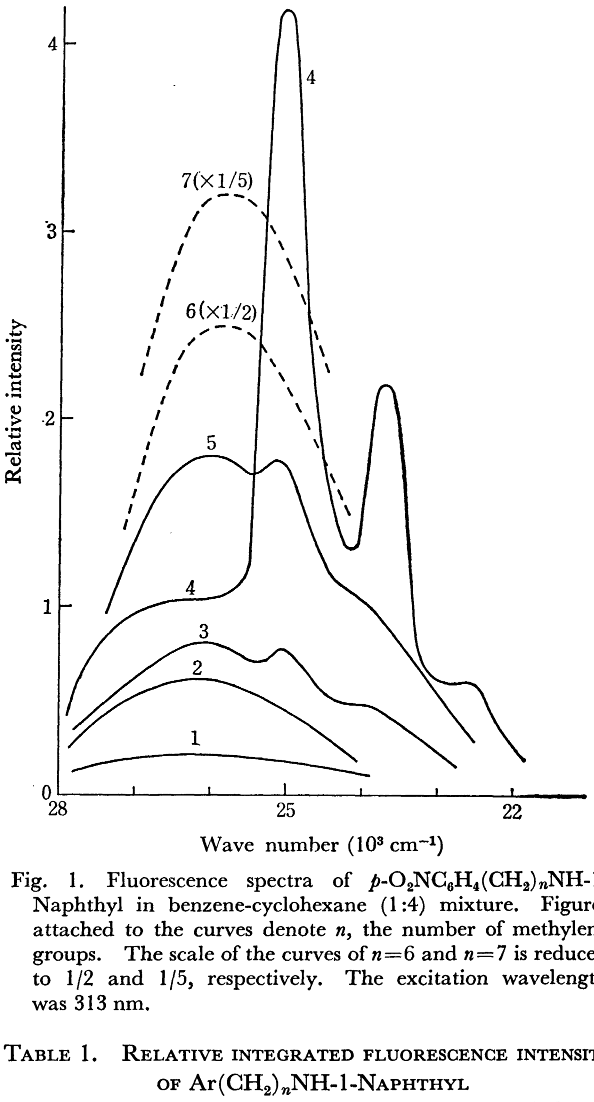

Fig. 1. Fluorescence spectra of p-$O_2NC_6H_4(CH_2)_nNH$-1-Naphthyl in benzene-cyclohexane (1:4) mixture. Figures attached to the curves denote n, the number of methylene groups. The scale of the curves of $n=6$ and $n=7$ is reduced to 1/2 and 1/5, respectively. The excitation wavelength was 313 nm.

Table 1. Relative integrated fluorescence intensity of $Ar(CH_2)_nNH$-1-Naphthyl

Ar=p-$O_2NC_6H_4$ (I)		Ar=p-$O_2NC_6H_4O$ (II)	
n	Rel. intensity[a]	n	Rel. intensity[a]
1	1.0		
2	2.8		
3	3.9	2	1.7
4	10	3	1.6
5	8.6	4	12
6	23	5	12
7	73	6	17

Compounds	Rel. intensity[a]
EtNH-1-Naphthyl	4.4×10^3
$PhCH_2NH$-1-Naphthyl	5.7×10^3
p-$ClC_6H_4CH_2NH$-1-Naphthyl	5.1×10^3

a) The integrated region is from 21×10^3—28×10^3 cm^{-1}, and the values in the Table are relative to that of p-$O_2NC_6H_4CH_2NH$-1-Naphthyl.

Results

Fluorescence spectra due to the 1-naphthylamino moiety in p-$O_2NC_6H_4(CH_2)_nNH$-1-Naphthyl (I) are reproduced in Fig. 1 and data given in Table 1. Benzene-cyclohexane mixture (1:4) was used as a solvent because benzene increases the dissolving power of the solvent. A slight decrease in the fluorescence intensity was observed in this solvent as compared with cyclohexane which is a typical inert solvent with poor dissolving power, but no appreciable change in spectral shape was found. The order of fluorescence intensity is $n=1<2<3<5<4<6<7$. Obviously the quenching effect increases as n or chain length decreases with the exception of $n=4$. Even in the highest homolog studied ($n=7$) in which neither the CT interaction nor N–H$\cdots\pi$ interaction, hence no intramolecular force advantageous for the two groups to be close together, has been detected, the quenching effect by p-nitrophenyl group

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[4] The author wishes to thank Dr. Jun-ichi Aihara, University of Hokkaido, for his suggestion of this effect.

[5] T. Förster, *Discuss. Faraday Soc.*, **27**, 1 (1959).

[6] For recent reviews, see a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y. (1965), p. 97; b) A. A. Lamola, "Technique of Organic Chemistry," Vol. XIV, ed. by P. A. Leermakers and A.Weissberger, Interescience Publishers, New York, N. Y. (1969), p. 17.

is obvious in comparison with *N*-ethyl-, *N*-benzyl-, or *N*-(*p*-chlorobenzyl)-1-naphthylamine (Table 1). The latter compounds can be regarded as model ones which exhibit fluorescence free of any quenching effect. For this purpose, the latter two which are solid at room temperature have an advantage with respect to easy handling and stability over liquid *N*-ethyl derivative which becomes wine-red on standing overnight in the dark after distillation.

In the spectra of $n=3$, 4, and 5, vibrational progressions were observed, especially well-developed in that of $n=4$. The separation between the peaks is approximately 1330—1350 cm^{-1}.

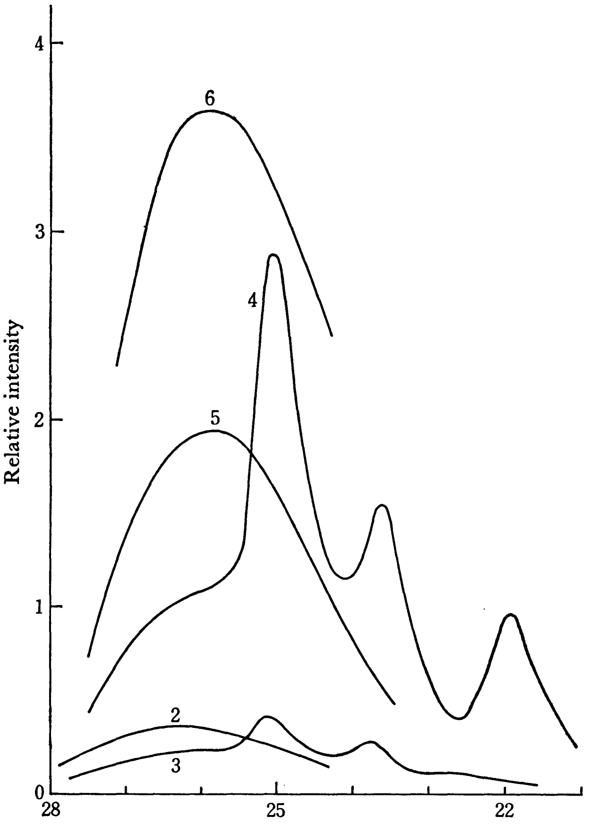

Fig. 2. Fluorescence spectra of p-$O_2NC_6H_4O(CH_2)_nNH$-1-Naphthyl in benzene-cyclohexane (1:4) mixture. The figures attached to the curves denote *n*. The excitation wavelength was 313 nm.

The *p*-Nitrophenoxy group in a homologous series of p-$O_2NC_6H_4O(CH_2)_nNH$-1-Naphthyl (II) also showed fluorescence quenching effect, the fluorescence spectra of which are reproduced in Fig. 2. The lowest homolog of this series used in the present study is $n=2$, since the $n=1$ homolog is too unstable. In this series the chain length (the number of atoms combining two groups) with *n* methylenes corresponds to that with $n+1$ methylenes in I, since an ether oxygen is inserted between p-$O_2NC_6H_4$- and CH_2 groups in II. Probably the different bond distance of C–O and C–C makes no significant effect on quenching efficiency. Thus it is noteworthy that vibrational structure also appeared in II only when $n=3$ and 4.

The relative intensities of I and II measured in a common medium are summarized in Table 1. Since the fluorescent moiety is common to both series, the values could be a measure of efficiency of the quenchers.

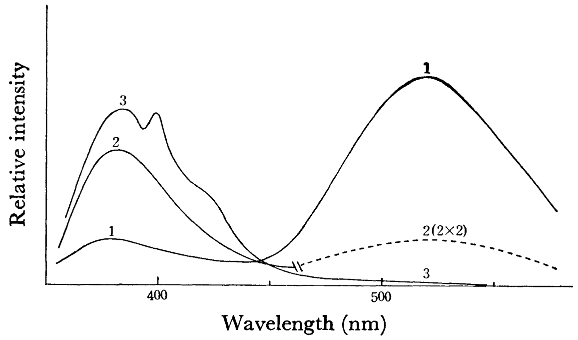

Fig. 3. Fluorescence spectra of p-$O_2NC_6H_4(CH_2)_nNH$-1-Naphthyl in benzene-cyclohexane (1:4) mixture. The scale of the curve of $n=2$ in longer wavelength region is doubled The excitation wavelength was 313 nm.

In the longer wavelength region than that of the fluorescence due to 1-naphthylamine moiety, a broad peak appears in the lower homologs of I (Fig. 3) and II. The origin of this peak has been assigned to the excited CT state on the basis of its intramolecular characteristics and excitation spectrum.[7,8]

Discussion

From the fluorescence intensities of I, we might conclude that naphthylamino and *p*-nitrophenyl groups have a greater chance of access in $n=1$ homolog than in $n=2$. However, the conclusion should be scrutinized from the viewpoint of quenching or energy transfer mechanism.

In the higher homologs ($n \geqq 4$) in which the CT interaction of N–H$\cdots\pi$ interaction is scarcely observed, the quenching effect takes place undoubtedly beyond collisional diameters of the two aromatic groups. This long-range effect suggests that a resonance-energy transfer mechanism is predominating.

In the lower ones, exchange transfer mechanism as well as resonance mechanism is possible as suggested by the occurrence of the intramoledular CT interaction, because both exchange mechanism and the CT interaction require the overlap of the π-electron clouds of the aromatic rings. Examination of a scale molel shows that only partial overlap of the electron clouds is allowed for $n=1$ owing to the limitation of bond angles but sufficient overlap is possible for $n \geqq 2$ in which two aromatic rings can assume a parallel face-to-face arrangement. In the study of the excimer, this latter conformation is regarded as an important, if not essential, condition for excimer formation on theoretical[9] and experimental[10] grounds. As an example, in a series of diphenyl end-substituted alkanes $Ph(CH_2)_nPh$, only

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[7] K. Mutai, *Chem. Commun*, **1970**, 1209.

[8] K. Mutai, *Tetrahedron Lett.*, **1971**, in press.

[9] a) G. J. Hoijtink, *Z. Elektrochem.*, **64**, 156 (1960); b) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1963—1964); c) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3131 (1964); d) T. Azumi, A. T. Armstrong, and S. P. McGlynn, *ibid.*, **41**, 3839 (1964); e) T. Azumi and S. P. McGlynn, *ibid.*, **42**, 1675 (1965).

$n=3$ shows excimer emission[10a] which is not observed in $n=2$. Therefore, as far as exchange mechanism is concerned, the greater quenching efficiency and lower fluorescence intensity are expected for $n=2$ if the population of the CT interacting molecule is the same as or greater than $n=1$.

As for resonance mechanism, which does not require the overlap of the electron clouds, and is largely dependent on the distance between two groups, the intensity of $n=2$ should be lower if the population of $n=2$ is the same as or greater than $n=1$, since the flexibility of the longer chain of $n=2$ permits closer approach of the aromatic rings with each other. The above supposition may be cited as an evidence that in a series of alkanes substituted by 1-naphthyl on one end, $Ar(CH_2)_n$-1-Naphthyl, the intramolecular energy transfer efficiency is nearly the same in $n=2$ and $n=3$ when Ar is 9-anthryl (energy acceptor),[11] and $n=2<n=3$ when Ar is 4-benzoylphenyl[12] (here, $n=2$ and $n=3$ correspond to $n=1$ and $n=2$ homologs of I, respectively, in the number of chain atoms). The same order of interaction effects has also been reported in a series of 9,9′-polymethylene-bisadenines from a study of their hypochromism of absorption spectra and emission spectra.[13] This suggests that in I higher fluoroescence intensity or lower quenching effect should be observed in $n=1$.

In order to explain the results the presence of the intramolecular CT interaction should be taken into account. The overlap of the π-electron clouds is insufficient in $n=1$, but if the population of the CT, interacting molecule of $n=1$ exceeds that of $n=2$, then more quenching effect on lower fluorescence intensity is expected for $n=1$. As is seen in Fig. 3, the transition from the excited intramolecular CT state to the ground state in another radioactive process. In this sence, as far as the fluorescence of the amine moiety is concerned, the CT interaction is a quenching process, since the interacting molecules absorb a part of incident light to decrease the apparent quantum yield of the fluorescence process of the amine moiety. The order of intensities of the CT fluorescence bands ($n=1>n=2$) may be an evidence of the difference of population of the CT interacting molecules. Another evidence has been obtained from the infrared study of I. It has been shown that in the lower homologs there exists intramolecular N-H$\cdots\pi$ interaction which fixes molecular conformation to prohibit the overlap of the π-electron clouds of the aromatic rings, and the population of the free molecule from this interaction is abnormally large in $n=1$.[14] It has also been established that this "free" state is competitive with or more stable than the N-H$\cdots\pi$ interacting state,[15] indicating that the "free" state contains another interacting state, *viz.*, the CT interaction. This shows the population of the CT interacting molecule is larger in $n=1$ than in $n=2$. This conclusion, in turn, suggests the larger intensity of the CT absorption for an interacting molecule of $n=2$. The difference is probably due to the different interacting conformations of the compounds in which more sufficient orbital overlap is possible for $n=2$, resulting in larger value of the transition moment of the CT absorption of $n=2$.[16,17] If the explanation is correct, this may be an example of the conformational effects on the spectral features of the CT interaction.

The quenching effect of both *p*-nitrophenyl and *p*-nitrophenoxy groups is due to the overlap of their absorption spectra with the fluorescence spectrum of the naphthylamine moiety. The region of the overlap is larger in *p*-nitrophenoxy group. This is probably the reason why larger quenching efficiency is observed in II when the fluorescence intensities of the homologs of I and II with the same number of chain atoms are compared. Lack of the quenching effect in benzyl and *p*-chlorobenzyl groups can be attributed to the small overlap of their absorption spectra with the fluorescence.

It is interesting that the appearance of vibrational structure depends strongly on the number of methylene groups. The peak separation suggests its relation with C–N stretching vibtation. Perhaps certain numbers of methylenes make a contribution through a certain type of their vibrational mode to allow the transition to the upper vibrational levels of the ground state.[18] The structure is most remarkable in $n=4$ of I and II in which the fluorescence intensities are more than those expected from the values of their next lower and higher homologs. This suggests that the originally radiationless or forbidden transition becomes radiative due to the same cause as the appearance of the structure.

Experimental

Materials. The compounds used were purified through the known methods.

N-[ω-(*p*-Nitrophenyl)alkyl]-1-naphthylamines (I, $n=4$, 5, and 6). Syntheses of this series of compounds were performed as described previously.[2,14]

N-[ω-(*p*-Nitrophenoxy)alkyl]-1-naphthylamines (II, $n=2$—6). These compounds were prepared by the same procedure as has been reported.[20]

The mp's and results of elemental analyses of the products are given in Table 2.

Spectral Measurement. Fluorescence spectra were recorded on an Aminco-Bowman spectrophotofluorometer. In every series of measurements, the CT fluorescence band was used as a reference of intensity in order to determine a factor for adjusting photomultiplier sensitivity and fluctuation of the intensity of incident light. A Hanovia xenon mercury

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[10] a) F. Hirayama, *ibid.*, **42**, 3163 (1965); b) M. T. Vala, Jr., J. Haebig, and S. A. Rice, *ibid.*, **43**, 886 (1965); c) J. W. Longworth and F. A. Bovey, *Biopolymers*, **4**, 1115 (1966); d) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967).

[11] O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, **84**, 172 (1962).

[12] A. A. Lamola, P. A. Leermakers, B. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965).

[13] D. T. Browne, J. Eisinger, and N. J. Leonard, *ibid.*, **90**, 7302 (1968).

[14] M. Ōki and K. Mutai, This Bulletin, **38**, 393 (1965).

[15] M. Ōki and K. Mutai, *ibid.*, **39**, 809 (1966).

[16] R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y. (1969), p. 23.

[17] J. N. Murrell, *J. Amer. Chem. Soc.*, **81**, 5037 (1959).

[18] The overtones of the accordion like vibration of polymethylene chains may be responsible for this phenomenon.[19]

[19] R. F. Schaufele and T. Shimanouchi, *J. Chem. Phys.*, **47**, 3605 (1967).

[20] M. Ōki and K. Mutai, *Spectrochim. Acta*, **25A**, 1941 (1969).

TABLE 2. ELEMENTAL ANALYSES AND YIELDS OF NEW COMPOUNDS

n	Yield %	mp, °C	Molecular formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd	Found	Calcd	Found	Calcd	Found
			p-$O_2NC_6H_4(CH_2)_nNH$-1-$C_{10}H_7$						
4	47	94—95	$C_{20}H_{20}N_2O_2$	74.97	74.80	6.29	6.21	8.74	8.93
5	38	109—110	$C_{21}H_{22}N_2O_2$	75.42	75.29	6.63	6.59	8.38	8.46
6	8	88—89	$C_{22}H_{24}N_2O_2$	75.83	75.99	6.94	6.76	8.04	7.94
			p-$O_2NC_6H_4O(CH_2)_nNH$-1-$C_{10}H_7$						
2	39	143—144	$C_{18}H_{16}N_2O_3$	70.11	70.28	5.23	5.09	9.09	9.17
3	28	110—111	$C_{19}H_{18}N_2O_3$	70.79	70.50	5.63	5.62	8.69	8.50
4	18	117—118	$C_{20}H_{20}N_2O_3$	71.41	71.54	5.99	6.08	8.33	8.14
5	35	93—94	$C_{21}H_{22}N_2O_3$	71.98	72.28	6.33	6.19	8.00	7.73
6	36	93—94	$C_{22}H_{24}N_2O_3$	72.50	72.67	6.64	6.60	7.69	7.50

lamp of 150 W was used as a light source. The photomultiplier used is 1P28. The emission curves shown in Figs. 1—3 were not corrected for the wavelength dependence of the sensitivity of the spectrometer and photomultiplier.

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