# Structural Effects on Photophysical Processes in Saturated Amines. II[1]

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**Abstract:** The photophysical properties of the diamine *N,N'*-dimethylpiperazine (NNDMP) are compared with those of certain monoamines. Whereas the uv absorption and photoelectron spectral data for NNDMP are consistent with (ground state) NNDMP's being a noninteracting bonded dimer of trimethylamine, fluorescence spectral and decay properties suggest that structural reorganization occurs in the excited state producing a species having a markedly different radiative rate constant compared with monoamines. The low pressure extrapolated lifetimes of trimethylamine and NNDMP are 45 and 770 nsec, respectively. The respective quantum yields of these amines (in the vapor phase) are 0.97 and 0.23. On the basis of certain spectral and temporal characteristics of NNDMP, it is proposed that emission occurs both from the initially formed and structurally relaxed states, and that these two states can undergo interconversion. Two possible geometries for the relaxed excited state are suggested. The values of the amine self-quenching constants are discussed.

The ground-state interaction between the nonbonding orbitals of the diamine 1,4-diazabicyclo[2.2.2]octane, DABCO, is a well-documented phenom-
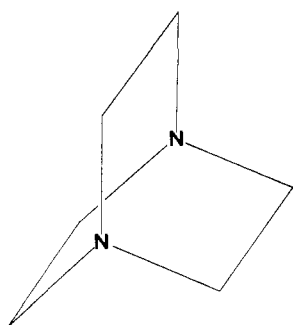


DABCO

enon.[2,3] This coupling, which is facilitated by the favorable (and relatively rigid) orientation of the three intervening ethylene bridges, is made manifest by the splitting of the nonbonding orbitals $(n_\pm)$ as determined from the photoelectron spectrum.[3]

This paper reports the results of a photophysical investigation of a related diamine which has a lower degree of constraint than DABCO, namely, *N,N'*-dimethylpiperazine (NNDMP). In this study, the photophysical properties of this amine are compared with those of several monoamines, such as *N*-methylpiperidine (NMP), 4,*N*-dimethylpiperidine (4NDMP), trimethylamine (TMA), triethylamine (TEA), and *N*-methylmorpholine (NMM). The latter compound possesses an oxygen heteroatom in the 4 position.

This study was undertaken in order to determine the importance of structural rigidity on the degree of lone pair interaction in a system such as DABCO. It has already been observed that apparently slight cage (and



NMP   NNDMP   NMM

symmetry) distortions in DABCO (*e.g.*, in 2-methyl-1,4-diazabicyclo[2.2.2]octane) dramatically affect both the radiative and nonradiative transition probabilities pertaining to the lowest excited singlet state.[4] On the other hand, it was shown that the nature and degree of the nonbonding orbital coupling in 2-methyl-1,4-diazobicyclo[2.2.2]octane was nearly identical with that in DABCO.

## Experimental Section

**Materials.** All amines with the exception of 4NDMP were procured from Aldrich Chemical Co. 4NDMP was provided by Mr. H. Friedman. The amines were distilled over BaO under an atmosphere of dry nitrogen, and were stored *in vacuo*. Toluene was obtained from Mallinckrodt Chemical Co. and was distilled prior to use.

**Pressure Measurements.** An MKS Baratron Type 77 Electronic Pressure Meter (MKS Instruments) was used to determine pressures up to *ca.* 10 Torr, and a Wallace and Tiernan Absolute Pressure Gauge was employed for higher pressures (up to 50 Torr).

**Spectral Measurements.** Absorption spectra used in conjunction with quantum yield determinations were obtained with a Beckman DK-2 recording spectrophotometer which was capable of producing spectral data at wavelengths down to *ca.* 185 nm. Other spectra were obtained with a Cary Model 15 spectrophotometer. Fluorescence spectra were obtained using a conventional dc fluorimeter described elsewhere.[4a]

**Fluorescence Decay Curves.** Time-dependent fluorescence was measured using the time-correlated single-photon technique. Data from the multichannel analyzer were either fed directly or *via* paper tape to a Univac 1108 computer. A TSP-212 X-Y plotter (Time Share Peripherals Corp.), which was interfaced with the computer, was used to obtain decay curves. Convolution calculations and scattered light corrections were performed *via* an interactive program.[5]

**Quantum Yield Measurements.** Toluene vapor was chosen as the absolute standard because fluorescence quantum yield data are available for this compound over a range of specified conditions such as excitation wavelength, band pass, and pressure.[6] Further-

(1) Part I: A. M. Halpern and R. M. Danziger, *Chem. Phys. Lett.*, **16**, 72 (1972). The research was carried out in Nichols Laboratory, Department of Chemistry, New York University, University Heights (RIP).

(2) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

(3) (a) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, **46**, 4025 (1969). (b) E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3818 (1970).

(4) (a) See reference in ref 1; (b) A. M. Halpern, *Chem. Phys. Lett.*, **6**, 296 (1970).

(5) B. Blumberg, private communication.

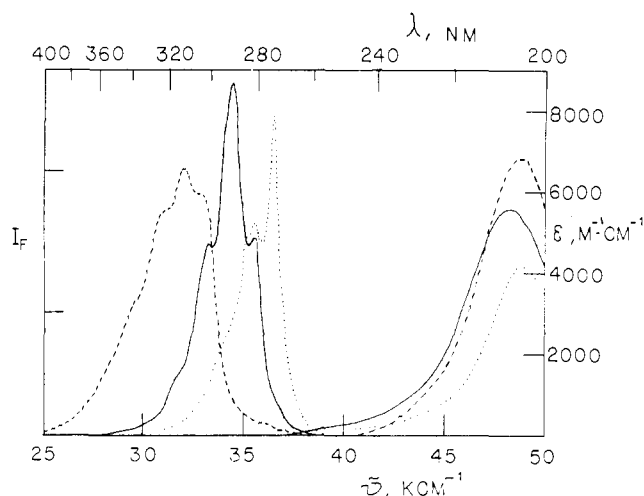(6) C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49**, 1705 (1968).

**Figure 1.** Corrected emission spectra (left-hand side) and absorption spectra (right-hand side) of NMP (——); NMM (·······); and NNDMP (-------) vapors at 23°.

more, since the fluorescence spectra of toluene and triethylamine lie in the same region, problems introduced by spectral correction are minimized. Thus, toluene at pressures between 12 and 18 Torr excited at 248 nm with a band pass of 2 nm and at room temperature was taken to have a fluorescence quantum yield of 0.092. The absence of any quenching impurities in the toluene was confirmed by lifetime measurements. The value obtained (56 nsec) is in excellent agreement with that reported by Breuer and Lee.[7] Toluene and TEA were directly compared and then TEA was subsequently used as the standard for quantum yield measurements of other amines. The toluene and TEA spectra were corrected according to standard techniques. This correction was not employed for the other amine measurements (except for NNDMP) because respective spectral overlap was satisfactory. The optical densities of the samples were always less than 0.1 at the exciting wavelength (248 nm) and were accurately measured by first independently determining the extinction coefficients both at 248 and 210 nm where the samples absorbed more strongly. Then the measured optical density at 210 nm was converted to the respective value at 248 nm by using the ratio of the previously determined extinction coefficients at 210 and 248 nm. Quantum yield values for the amines were corrected for whatever self-quenching occurred at the pressures used. For TEA, seven independent measurements were performed; for the other amines, at least three measurements were carried out.

## Results and Discussion

NNDMP can be viewed as a flexible form of DABCO, with one of the 2–3 carbon–carbon bonds having been severed. On a time-averaged basis, the interaction between the nonbonding orbitals (which could be affected *via* the two intervening ethylene bridges) would be expected to be very small as a result of rapid ring and nitrogen atom inversions. Some photoelectron spectral data support this expectation, since, in piperazine, the splitting of the nonbonding orbitals is "about zero."[3a] Furthermore, evidence of splitting is also apparently absent from the photoelectron spectrum of NNDMP itself.[8] Interestingly, the value of the lowest IP for NNDMP was found to be 8.41 eV (vertical). This presumably corresponds to the energy of the (unsplit) nonbonding orbitals and can be compared with the first vertical IP of 8.5 eV[9] for trimethylamine.

(7) G. M. Breuer and E. K. C. Lee, *Chem. Phys. Lett.*, **14**, 404 (1972).

(8) We are indebted to Drs. M. B. Robin and G. N. Taylor for their cooperation in obtaining the photoelectron spectra of NMM and NNDMP.

(9) A. B. Cornfield, D. C. Frost, F. G. Herring, and C. A. McDowell, *Can. J. Chem.*, **45**, 1135 (1971); K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957).

Thus, it seems that it is the number of carbon atoms in the alkyl groups per nitrogen atom which is important in determining the IP in the absence of N–N coupling. It is reasonable, therefore, to consider NNDMP in the ground state as a noninteracting bonded dimer of trimethylamine.

The absorption strength of NNDMP (as indicated by the $\epsilon_{max}$ value) seems to confirm this conclusion because its value (6800 $M^{-1}$ sec$^{-1}$) is about twice that of trimethylamine's (3270 $M^{-1}$ sec$^{-1}$). The absorption spectra of NNDMP, NMP, and NMM are depicted in Figure 1. It is immediately apparent that there is no obvious low-lying transition present in these compounds. The NNDMP spectrum provides no evidence for any other transition below 45,000 cm$^{-1}$ and, in fact, resembles that of a monoamine, having $\lambda_{max}$ at 205 nm. Furthermore, examination of the NNDMP spectrum under higher sensitivity (10 Torr, 10-cm path length) does not reveal any distinct transition (or inflexion point) at longer wavelengths.

The fluorescence spectra of these amines, on the other hand, are distinctly different. Whereas the emission spectrum of NMP lies in the same region as a monoamine with a similar degree of alkylation (*e.g.*, trimethylamine or triethylamine),[10] the fluorescence spectrum of NNDMP is considerably red-shifted with $\lambda_{max}$ at 313 nm. Moreover, the emission spectra of NNDMP and triethylamine are very different, both in appearance and in position. This spectral difference may be a consequence of excited-state interaction between the nitrogen centers in NNDMP. Absorption and emission spectral data for several amines are listed in Table I.

**Table I.** Absorption and Fluorescence Spectral Characteristics of Several Vapor Phase Amines at 300°K

| Amine | $\lambda_{max}$ (abs), nm | $\epsilon_{max}$, $M^{-1}$ sec$^{-1}$ | $\lambda_{max}$ (fluor), nm | IP (vert), eV |
|-------|------|------|------|------|
| TMA | 198 | 3720 | 287[a] | 8.5[b] |
| TEA | 211 | 6020 | 279 | 8.06[c] |
| NMP | 207 | 5500 | 290 | |
| NMM | 204 | 4150 | 274 | 8.62[d] |
| NNDMP | 205 | 6800 | 313 | 8.41[d] |

[a] Emission spectrum is structured. [b] Reference 9. [c] Reference 11. [d] Reference 8.

For NMM, a considerably blue-shifted emission spectrum is observed. In this case, there is a rather sharp maximum (resembling a 0–0 band) at 274 nm. It is possible that the higher electronegativity of the oxygen atom results in a reduction of electron density at the nitrogen center, stabilizing the nonbonding orbital (centered on nitrogen) and thereby increasing the transition energies in NMM. The value of the vertical ionization potential of NMM (8.62 eV)[8] is somewhat higher than those of triethylamine (8.06)[11] or trimethylamine (8.5 eV).[9] In this case, one would expect that the $S_n \leftarrow S_0$ transition energies of NMM would be larger relative to the other amines.[12]

(10) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **8**, 77 (1971); A. M. Halpern and T. Gartman, unpublished data.

(11) S. F. Nelson, private communication.

(12) This follows from the assumption that, in the amines, the excited state are Rydberg in nature; see ref 13 and 14.

The results of fluorescent lifetime and quantum yield measurements of these amines imply that there is a distinct difference in the relaxed lowest electronically excited state of NNDMP relative to NMP and other monoamines. The fluorescence lifetimes and quantum yields for the amines studied are contained in Table II.

**Table II.** Self-Quenching Constants, Lifetimes, Quantum Yields, and Radiative Rate Constants for the Amines Studied

| Amine | $k_q$, $M^{-1}$ sec$^{-1}$ [a] | $\tau_{p \to 0}$, nsec[b] | $\varphi_f$[c] | $k_R$, sec$^{-1}$ [d] |
|-------|-----------------|-----------------|---------------|-----------------|
| TMA | $3.2 \times 10^{10}$ | $45 \pm 1$ | $0.97 \pm 0.06$ | $2.1 \times 10^7$ |
| TEA | $6.5 \times 10^9$ | $61 \pm 1$ | $0.98 \pm 0.05$ | $1.6 \times 10^7$ |
| NMP | $5.5 \times 10^{10}$ | $60 \pm 1$ | $0.95 \pm 0.05$ | $1.6 \times 10^7$ |
| 4NDMP | $3.3 \times 10^{10}$ | $50 \pm 1$ | $1.0 \pm 0.1$ | $1.5 \times 10^7$ |
| NMM | $1.5 \times 10^{10}$ | $66 \pm 1$ | $0.78 \pm 0.06$ | $1.2 \times 10^7$ |
| NNDMP[e] | $1.3 \times 10^9$ | $770 \pm 3$ | $0.23 \pm 0.05$ | $3.2 \times 10^5$ |
| DABCO[f] | | 1040 | 0.9 | $8.6 \times 10^5$ |

[a] Obtained from the slope of a $1/\tau$ vs. pressure plot; $\lambda_{exc}$ is 240 nm. [b] Obtained from the intercept of a $1/\tau$ vs. pressure plot; $\lambda_{exc}$ is 240 nm. [c] Contains a correction for any self-quenching at the pressure at which $\varphi_f$ was measured. [d] $k_R = \varphi_f/\tau_{p \to 0} \times 10^9$. [e] NNDMP data pertain to the long-lived component. [f] Data from ref 4b; notation (b) does not apply.

The lifetime values listed in Table II are obtained from extrapolations of $1/\tau$ vs. pressure plots to zero pressure. The slopes of these plots, which are linear over the pressure range studied (0.5–20 Torr), provided values of the amine self-quenching constants which are also listed in Table I. These data will be discussed below.

Although the absorption spectral characteristics for NNDMP and several monoamines appear to be rather similar (vide supra), the radiative rate constants for fluorescence ($k_R$) for these amines are quite different. For example, $k_R$ for NNDMP is a factor of 50 smaller than $k_R$ for NMP and triethylamine, and about 65 times smaller than $k_R$ for TMA.

This rather large difference in $k_R$ values implies that, in NNDMP, there is some degree of interaction between the nitrogen atoms. This coupling can be thought of as arising at the orbital level (i.e., via ground-state coupling between the two n-type orbitals), or at the state level (e.g., excitation dipole–dipole interaction). The apparent absence of splitting in the highest filled MO (as determined from the photoelectron spectrum vide supra), seems to rule out the former possibility. It appears more likely that, in NNDMP, there is a low-lying excited state, which is fluorescent, and which is apparently not directly populated via a radiative transition from the ground state.

Thus, we interpret this $k_R$ difference in terms of a structural and electronic reorganization which characterizes the lowest excited state of NNDMP. The electronic coupling in the excited state of NNDMP can possibly arise via a through-bond or through-space type of mechanism wherein the molecular configuration is adjusted in order to accommodate this interaction. Several (relaxed) excited-state geometries can be proposed, e.g., structures I and II.

In structure I, stabilization would be affected by the electronic coupling which can be thought of as arising



I        II
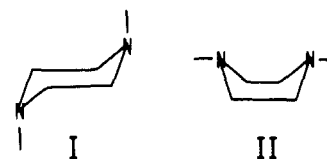
via a "through bond" mechanism, while in structure II, a "through space" type of coupling would apply.[2,15] Another possible form is II, in which the two methyl groups point in the same direction (i.e., up). This structure, while resembling DABCO, would be unfavorable due to strong steric interactions between the methyl groups. A similar type of structure has been proposed by Nelson and Hintz in explaining the relative stabilities of certain hydrazine radical cations, as determined from polarographic half-wave potentials.[16] Both structures I and II represent conformational changes which would occur subsequent to optical excitation, because in the ground state (and therefore the Franck–Condon excited states(s)), the predominant form of NNDMP is the conformation with both methyl groups in the equitorial positions.[17] Thus, direct transitions to either of these electronically relaxed states from the ground state would be unfavorable because of the small Franck–Condon factors.

Fluorescence decay measurements provide additional insight into the proposed excited state electronic reorganization in NNDMP. The fluorescence decay curve of NNDMP vapor (1.0 Torr), excited at 240 nm, and at 23°, is nonexponential and can be represented by

$$I_f(t) = 0.47 \exp(-t/134) + 0.53 \exp(-t/743)$$

where $t$ is in nsec. In this experiment, a Corning glass 9-54 filter is placed between the sample and the photomultiplier tube. This filter eliminates approximately 9% of the emission spectrum (from the high-energy end). If a small overpressure of thoroughly degassed n-hexane (5–10 Torr) is added (to ensure vibrational relaxation), the nonexponentiality of the decay curve remains. With the addition of 4 Torr of n-hexane, for example, the decay curve changes so that the amplitudes and time constants are: 0.46 and 0.54; and 54 and 610 nsec. With 10 Torr of n-hexane added, the NNDMP decay curve is invariant with excitation wavelength between ca. 240 and 210 nm, but is still nonexponential. These two decay curves are illustrated in Figures 2 and 3, respectively.

As the 9-54 filter is replaced by filters which remove increasingly larger amounts of the high-energy end of the emission spectrum, the amount of the short component observed in the NNDMP decay curve monotonically decreases. Thus, there is a sharp reduction in the amplitude of the fast component as the spectral cutoff point begins to move to longer wavelengths, and this effect then tapers off. With an 0-52 filter, which removes about 89% of the fluorescence spectrum, the fast component, while considerably reduced, is still observed.

These results, which are contained in Table III, are interpreted in terms of two emitting states which have different radiative rate constants. The fast component

(13) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, p 151 et seq.
(14) A. M. Halpern, J. L. Roebber, and K. Weiss, J. Chem. Phys., 49, 1348 (1967).
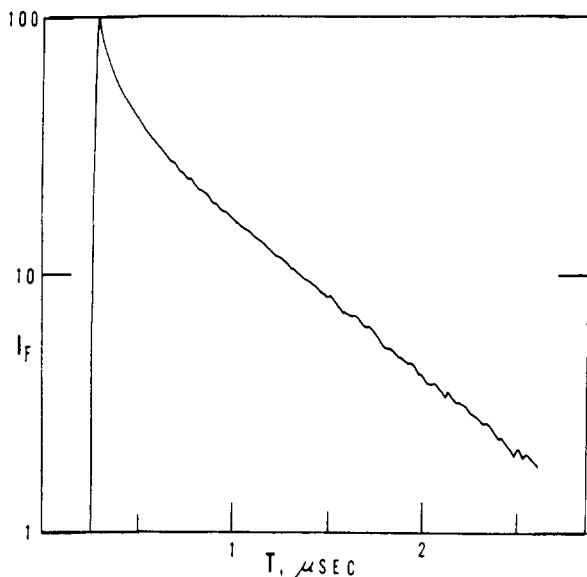(15) R. Hoffman, Accounts Chem. Res., 4, 1 (1971).
(16) S. F. Nelson and P. J. Hintz, J. Amer. Chem. Soc., 94, 7108 (1972).
(17) N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, J. Amer. Chem. Soc., 87, 1232 (1965).

**Figure 2.** Fluorescence decay curve for NNDMP vapor excited at 240 nm. Pressure is 1.0 Torr. The decay equation is given in the text.
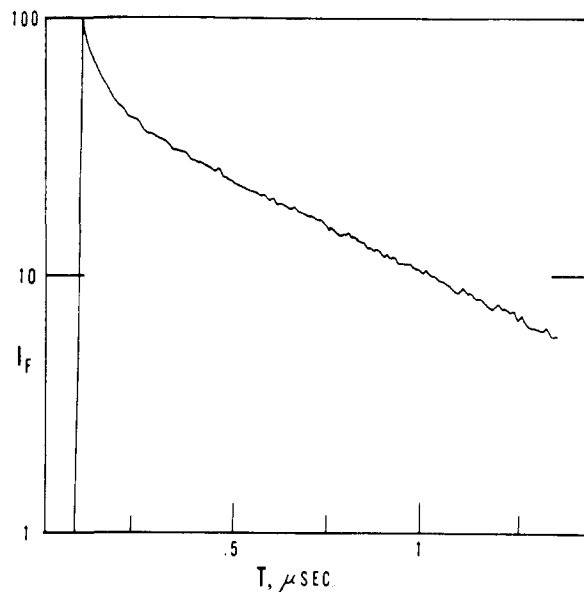


**Figure 3.** Fluorescence decay curve for NNDMP vapor excited at 240 nm. Partial NNDMP pressure is 1.0 Torr and partial *n*-hexane pressure is 4.0 Torr. Decay parameters are given in the text.

**Table III.** Relationship between the Amplitude of the Fast Component of NNDMP Vapor (1 Torr) Fluorescence Decay and the Amount of the Emission Spectrum Removed by Various Filter Combinations

| Filter combination[a] | % removed[b] | Rel amplitude of the fast component |
|---|---|---|
| 9-54 + 9-54 | 9 | 57 |
| 9-54 + 0-53 | 27 | 46 |
| 9-54 + 0-54 | 45 | 32 |
| 0-54 + 0-54 | 54 | 29 |
| 0-54 + 0-52 | 89 | 23 |

[a] Corning glass filters. [b] Measured relative to having no filters present.

is ascribed to the "prompt" emission, *i.e.*, fluorescence from the Franck–Condon (initially formed) state, and the long component is assigned to emission from the conformationally (and electronically) relaxed state.

The cutoff filter data imply that the short-lived emission component has most of its intensity at the high-energy end of the spectrum, and then tails off toward longer wavelengths. One would expect that the emission from the unrelaxed state would lie at higher energies relative to the fluorescence from the reorganized state. Time-resolved fluorescence spectra of NNDMP should reveal two distinct spectra: the unrelaxed one at short times, and the relaxed emission at longer times subsequent to excitation.

The effects of added *n*-hexane vapor were examined continuously between 0 and 30 Torr, with an NNDMP partial pressure constant at 1 Torr. As the *n*-hexane pressure increased, both the long and short components of the NNDMP decay curve decreased, and a $1/\tau$ *vs.* pressure plot for each at the components was linear. For the long component, however, $1/\tau$ reached a plateau at *ca.* 15–20 Torr of *n*-hexane. The *n*-hexane quenching constants obtained from the slopes of the linear portions of these plots are $5.0 \times 10^{10}$ $M^{-1}$ sec$^{-1}$ and $1.3 \times 10^{9}$ $M^{-1}$ sec$^{-1}$ for the short and long components, respectively.

It is premature to speculate in detail about the mechanism of the *n*-hexane quenching of the NNDMP lowest excited (long lived) state, but it is noteworthy that the quenching constant for DABCO fluorescence by *n*-hexane vapor was reported to be also about $10^{9}$ $M^{-1}$ sec$^{-1}$.[1] It is possible that in the DABCO and NNDMP lowest excited states, collisions between these amines and inert bodies (such as *n*-hexane) are effective in lowering the formal (chromophore) symmetry and/or perturbing the molecular configuration sufficiently so that certain selection rules are relaxed and transition probabilities are enhanced.

The quenching constant obtained for the fast component of the NNDMP fluorescence decay seems somewhat smaller than that for an efficient vibrational relaxation process. It is possible to interpret the reduction of the short component lifetime by proposing that *n*-hexane vapor is required for complete vibrational relaxation of the structurally (and electronically) *reorganized* form of the NNDMP excited state. This reorganization is a unimolecular process in which a vibrationally excited species is formed. If NNDMP in this conformation (*e.g.*, I or II, *vide supra*) is unable to dissipate the released electronic energy *via* internal degrees of freedom, then the vibrationally excited species could revert back to its initial configuration (at low total pressures), presuming that the barrier to interconversion is not too high. Thus, it is suggested that at low total pressures, the reorganization which appears to take place subsequent to optical excitation is a reversible one, each state being fluorescent. This is summarized in the schematic NNDMP state diagram in Figure 4.

$S_1$** and $S_1$* may correspond to different electronic states, or alternatively, the Franck–Condon and relaxed vibronic states, respectively, of the lowest excited state. Higher lying electronic states are not indicated. $S\dagger$ represents NNDMP in the ground state but possessing the same configuration as the relaxed excited state, and may actually be a metastable species if the barrier to conversion to $S_0$ is high enough (*vide infra*).

$k_1$ and $k_2$ are the unimolecular rate constants which pertain to the excited-state reorganization. This would be expected to be an activated process, in analogy with both the boat–chair and diequatorial–diaxial interconversions in ground-state NNDMP. For example, the free energy of activation for the conversion of the diequatorial to the diaxial conformer in NNDMP (methanol solution) is 12–14 kcal/mol.[18]

The persistence of nonexponentiality in the fluorescence decay of NNDMP even after sufficient $n$-hexane is added to ensure vibrational relaxation in both the $S_1^{**}$ and $S_1^*$ manifolds lends additional support to the reversibility of the proposed configuration change (vide supra). The reversibility of the two proposed states, $S_1^{**}$ and $S_1^*$, does not imply that the states are in equilibrium (on a time scale of hundreds of nanoseconds subsequent to pulsed excitation). The continued observation of the fast decay component when $n$-hexane is added implies that the "reversible" rate constant, $k_2$ (see Figure 4), is relatively small as compared with relaxation within the $S_1^*$ manifold.

It is difficult to estimate values of $k_1$ and $k_2$ because for this system, i.e., two coupled emitting states, the observed decay parameters are functions of specific rate constants such as $k_1$ and $k_2$. The decay laws which apply to this case are analogous to those which pertain to excimers and exciplexes,[19] except that this is an unimolecular system and the usual concentration-dependent terms would be absent (except for self-quenching).

It is also consistent with the suggested reversibility of the excited state configurations that the decay curve of NNDMP vapor at pressures as low as 0.1 Torr are nonexponential. At a pressure of ca. 0.1 Torr, NNDMP is under nearly collision-free conditions, assuming an effective collision frequency of $2 \times 10^{11}$ $M^{-1}$ sec$^{-1}$. At these low pressures, the degree of nonexponentiality is observed to be a function of excitation wavelength; at shorter excitation wavelengths, the nonexponentiality increases. These observations imply that (1) an initially formed species in the $S_1^*$ manifold is unable to undergo intramolecular vibrational relaxation during a time comparable with the $S_1^{*,v}$ lifetime, and (2) as the excitation energy is increased, some nonradiative process(es) is (are) increased more rapidly within the $S_1^*$ manifold relative to the $S_1^{**}$ manifold. For a given excitation energy, there is a smaller amount of vibrational energy produced in $S_1^{**}$ than in an isoenergetic state $S_1^{*,v}$ and electronic relaxation processes will reflect this difference (in the absence of vibrational relaxation). Therefore presuming that the $k_{NR}$'s are a stronger function of energy than $k_R$'s for both $S_1^{**}$ and $S_1^*$ states, then the quantum yield for emission of $S_1^{**}$ relative to $S_1^*$ should increase as the excitation wavelength decreases.

To test this hypothesis, the emission spectrum of NNDMP was examined at lower pressures. In order to obtain satisfactory signal-to-noise ratios, a pressure of 0.5 Torr was chosen. These results are shown in Figure 5 in which each spectrum is maximum normalized. It is obvious that as the excitation wavelength decreases from 244 to 210 nm, the total emission spectrum shows a considerable relative intensification
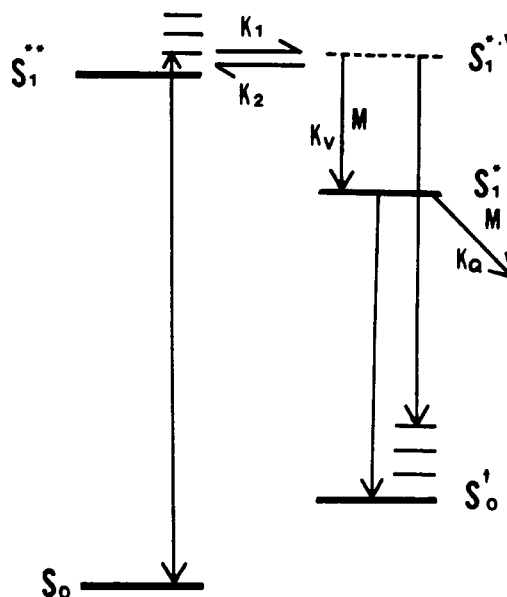


Figure 4. Schematic state diagram for NNDMP.

at shorter wavelengths. At wavelengths between 244 and 210 nm (237 and 220 nm), spectra are observed which are intermediate in appearance between those depicted in Figure 5. The completely relaxed spectrum is produced with the addition of $n$-hexane (in this case 50 Torr). Presumably, even with the added $n$-hexane, the total spectrum represents both emission systems, as deduced from the fluorescence decay nonexponentiality discussed above.

If under appropriate conditions it is possible to obtain "pure" $S_1^{**}$ and $S_1^*$ emission spectra, e.g., from time-resolved studies or from very low pressure emission spectra, one might proceed to examine quantitatively the nature of the suggested conformational relaxation in the excited state of NNDMP. Then the $S_0 \leftarrow S_1^{**}$ and $S_0 \leftarrow S_1^*$ transition energies could be assigned (see schematic state diagram), and after estimating the difference in ground-state energies for the initially formed and relaxed configurations (i.e., $\Delta E$ for $S_0$ and $S_0\dagger$), the electronic reorganization energy for the excited state (i.e., $\Delta E$ for $S_1^{**}$ and $S_1^*$) can be obtained. With this information, the type of excited-state conformational stabilization might be inferred.

Finally, it may be noteworthy to point out some differences in the self-quenching constants for the amines listed in Table II. It is not surprising that $k_q$ for TEA is about five times smaller than $k_q$ for TMA. This may be a consequence of the greater steric shielding of the nitrogen atom in TEA.[20,21] It is unexpected that $k_q$ for NNDMP is about 40 times smaller than $k_q$ for NMP and 4NDMP. The lower reactivity of electronically excited NNDMP toward self-quenching indicates possibly that one of the consequences of the structural reorganization is a diminution of the spacial extent of the (relaxed) excited-state orbital. It is tempting to speculate, on the basis of this observation, that to some degree, the excited-state MO encompasses a portion of the $\sigma$-bonded framework of NNDMP. This type of conjecture leads one to think in terms of structure I as

(18) R. G. Lett, L. Petrakis, A. F. Ellis, and R. K. Jensen, J. Phys. Chem., 74, 2816 (1970), and references cited therein.
(19) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970, Chapter 7.

(20) H. C. Brown and S. Sujushi, J. Amer. Chem. Soc., 70, 2878 (1948).
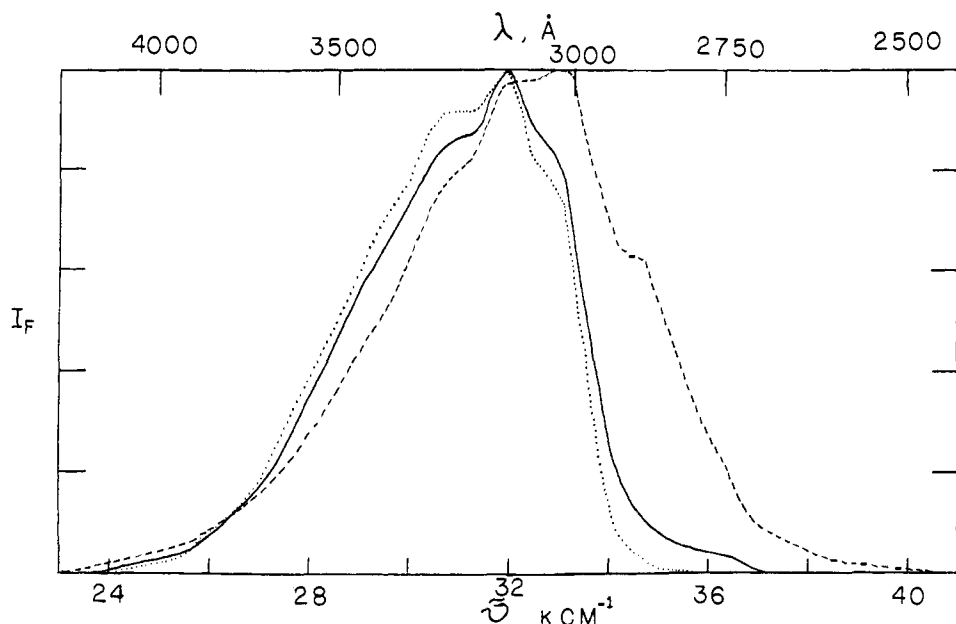(21) H. C. Brown and N. R. Eldred, J. Amer. Chem. Soc., 71, 445 (1949).

**Figure 5.** Fluorescence spectrum of NNDMP vapor (0.5 Torr) excited at: 210 nm (------); 244 nm (———); and 244 nm plus 50 Torr of *n*-hexane (· · · · · ·). Each spectrum is maximum normalized.

a possible model for the relaxed excited state of NNDMP.

# Radicals and Scavengers. III. The Cage Effect in the Decomposition of *tert*-Butyl Diphenylperacetate

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**Abstract:** The title perester, I, on thermal decomposition in cumene at 60°, affords $CO_2$ quantitatively when allowance is made for the presence of the impurities benzophenone and *tert*-butyl benzhydryl ether (II). The cage effect resulting in the formation of II is found by both scavenger and product isolation methods to be 16.5 ± 2%, not 35% as implied by previously reported yields of II from I now known to have been impure. Decomposition of I in 88% mineral oil–12% chlorobenzene gives a much reduced yield of *tert*-butyl alcohol and an increase in the yield of II, further supporting the postulated cage effect. In addition, a "phantom" *ca.* 10% cage effect, probably involving p coupling of *tert*-butoxy and benzhydryl radicals, is postulated to explain the deficient material balance.

S tudies of *tert*-butyl perester decomposition in these laboratories[2] have progressed from kinetics to cage effects,[3] as the possibility of obtaining information

about radical combination has become evident. A few such studies,[3,4] as well as of cage effects in photolytic perester decompositions,[5] have now been reported. Our own studies faltered for a considerable time on *tert*-butyl diphenylperacetate, I,[6] which alone among reac-

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