

Photorearrangement mechanism of 1-nitro-naphthaldehyde and application to three-dimensional optical storage devices

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Received 12 May 1997; received in revised form 28 July 1997; accepted 5 August 1997

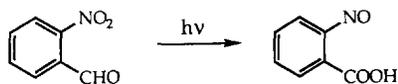
Abstract

The photorearrangement of 1-nitro-2-naphthaldehyde to the nitroso acid has been studied by means of time-resolved picosecond and nanosecond spectroscopy. Based on the experimental data we propose that the photoreaction proceeds via both the $^1n\pi^*$ excited singlet state and the low lying $^3\pi\pi^*$ triplet state. 1-Nitro-2-naphthaldehyde is the critical component used to generate a new memory material, which has been successfully utilized by us in two-photon three-dimensional optical storage devices. © 1998 Elsevier Science S.A.

Keywords: Photochromism; Kinetics; Picosecond spectroscopy; Electronic materials

1. Introduction

The photoisomerization of aromatic nitro compounds to nitroso compounds was reported initially by Ciamician and Silber [1], who observed that *o*-nitrobenzaldehyde was converted to *o*-nitrosobenzoic acid when exposed to sunlight. This process was found to take place both in solution and in the crystalline state.



Since that time a number of other ortho-substituted nitro-aromatic compounds, which undergo similar photorearrangement, have been studied [2]. In addition the *o*-nitrobenzaldehyde photoreaction has been used as an actinometer to measure solar UV radiation [3].

Because of its importance as a model for photorearrangement and its possible application to optical devices, the mechanism of *o*-nitrobenzaldehyde phototransformation has been studied by several investigators in detail [4–9]. It was shown that the photorearrangement of *o*-nitrobenzaldehyde proceeds via formation of a ketene intermediate [4,7–9] whose decay into nitroso acid is accelerated by the presence of water. The ketene intermediate generated by UV excitation of matrix-isolated *o*-nitrobenzaldehyde was stabilized at low temperature (10 K) and characterized by means of UV-visible and IR spectroscopy [6].

The primary steps of the *o*-nitrobenzaldehyde photorearrangement into nitroso acid have been studied by means of time-resolved spectroscopy [4,5] where some controversial data on the nature of photoreactive excited electronic states were presented. To our knowledge no direct experimental observations, involving triplet or singlet excited states in the photochemical transformation of *o*-nitrobenzaldehyde, have been reported.

Because of the wide abundance of this type of photoreaction in chemistry, the fact that the details of the mechanism are still not completely understood, and its importance as a computer memory material, we have studied the photo-induced reaction mechanism of 1-nitro-2-naphthaldehyde (NNA), which undergoes an analogous photorearrangement to nitroso acid. In this paper we present data, obtained by means of time-resolved picosecond and nanosecond spectroscopy and several analytic measurements, which provide a rather complete understanding of the intermediates, final product, kinetics and mechanism of this photoreaction.

Based on the photoreaction mechanism of NNA, a novel photochromic material has been developed and successfully utilized for storing huge amounts of information inside a three-dimensional volume and accessing the stored information in parallel, at nanosecond transfer rates [10].

2. Experimental details

1-Nitro-2-naphthaldehyde (NNA) was synthesized according to the method described in Ref. [11]. All starting chemicals were Aldrich HPLC grade.

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The polymer materials were prepared by radical polymerization of methyl methacrylate solutions containing 10^{-1} M NNA, 10^{-4} M Rhodamine B base and 2×10^{-2} M 2,2'-azobis(2-methyl-propionitrile) initiator. The polymerization process was carried out at 50 °C for ~70 h. The polymer blocks were cut into 1 cm³ cubes and polished to $\lambda/5$.

The ground state absorption spectra were collected by a double beam Shimadzu UV160U spectrophotometer, and the IR spectra were recorded by means of a Nicolet 205 FTIR spectrometer. NMR spectra were recorded by means of a QE300 NMR spectrometer and mass spectra were recorded with a VG Analytical 7070E mass spectrometer.

The picosecond transient absorption spectra and kinetics were measured by the laser system described by us previously [12]. A single 35 ps, 355 nm third harmonic pulse, from a Quantel Nd:YAG laser, was used for the excitation of NNA solutions. The picosecond continuum used to detect the transient absorption spectra was generated by focusing the 532 nm or 1064 nm pulses into a cell containing a D₂O–H₂O mixture. The continuum pulse, after it passed through the volume of the sample cell, was dispersed by a monochromator and the spectrum recorded and analyzed by an OMA system. Changing the delay time between the excitation and probe pulses allowed us to record a complete histogram of the spectra of the transient species induced by the excitation pulse.

The nanosecond kinetics and spectra of the transients were measured by an experimental system utilizing a Continuum Surlite II Nd:YAG laser emitting 6 ns pulses at 1064 nm. The third harmonic, 355 nm, 3 mJ pulse was used for excitation of the sample solutions. The probe beam, generated either by a millisecond photoflash or a halogen projector lamp, was focused in the sample cell and then imaged, by a lens system on the entrance slit of a monochromator. The output of the monochromator was detected by a PMT (Hamamatsu R928) which was coupled to a digital Tektronix TDS 410A oscilloscope and computer. The same experimental system was used for both phosphorescence lifetime and transient spectra measurements for the nanosecond and longer time ranges.

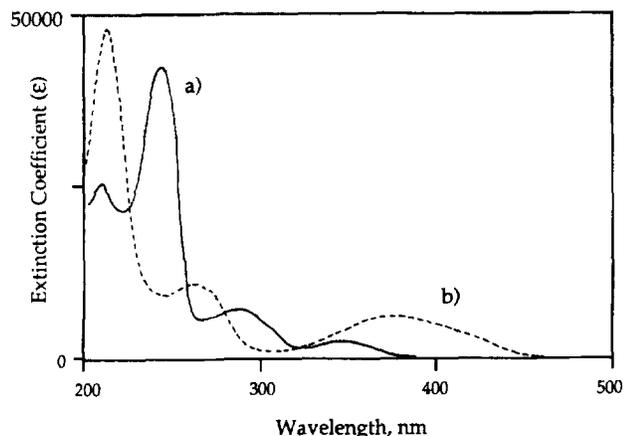


Fig. 1. Absorption spectra of (a) NNA and (b) nitroso acid in acetonitrile.

A 150 W Xe arc lamp (Oriel Research Arc Lamp Source) was used for continuous irradiation of the samples, using optical filters to select the appropriate wavelengths.

Low temperature experiments were conducted in a four side quartz optical cell placed in a liquid nitrogen quartz Dewar with optical windows. The low temperature solvents used were 3-methylpentane, methylcyclohexane and EPA.

The solutions were deaerated by several freeze–pump–thaw cycles and sealed under vacuum.

The method and experimental system for writing and reading information in three dimensions by means of two-photon absorption has been previously described in [10,13]. Therefore it will be presented, only briefly, in Section 5.

3. Results

3.1. Spectroscopic properties and photoreaction quantum yield

The absorption spectrum of NNA is shown in Fig. 1. Excitation of NNA with UV light induced the formation of the yellow nitroso acid which has its absorption maximum at 395 nm, see Fig. 1. To verify that the final product of the photochemical reaction of NNA is the nitroso acid, as is the case for *o*-nitrobenzaldehyde, we measured the IR, NMR and mass spectra of this product. A deaerated concentrated solution of NNA in cyclohexane was irradiated with UV light (150 W Xe lamp, $\lambda = 300$ –400 nm) and the precipitated product of this photoreaction was then collected, washed with solvent and dried. The IR spectrum of the product, Fig. 2, was found to exhibit the characteristic absorption bands of carboxylic acids. The broad band at 2800 cm^{-1} is due to the O–H group, and the sharp bands at 1700 cm^{-1} and at 1250 cm^{-1} are characteristic of the C=O and C–OH groups respectively. The ¹H-NMR and ¹³C-NMR spectra of the product exhibit characteristic peaks at $\delta 13.7$ and at $\delta 167$ respectively, due to the presence of COOH in the molecule. Similar peaks are observed for nitroso acid, produced by photolysis of *o*-nitrobenzaldehyde. The mass spectrum shows that the mass of the product is equal to 201.0426, which is exactly the mass of 1-nitroso-2-naphthalene carboxylic acid (C₁₁H₇NO₃). These data confirm that the photoreaction of NNA is strictly an intramolecular process of atom exchange between different molecular groups.

We found that the photorearrangement of NNA to nitroso acid is an irreversible process. We did not detect any back photoreaction when nitroso acid was excited at its long wavelength absorption band with $\lambda > 400$ nm. Prolonged irradiation of the nitroso acid, however, leads to photodecomposition. Because the nitroso acid is a relatively light stable compound, it was possible to measure its extinction coefficient rather accurately. The 10^{-4} M NNA solution in acetonitrile was irradiated with UV light (150 W Xe lamp, $\lambda = 300$ –400 nm) until no changes in the absorption spectra were observed. This implies that all of the NNA is completely

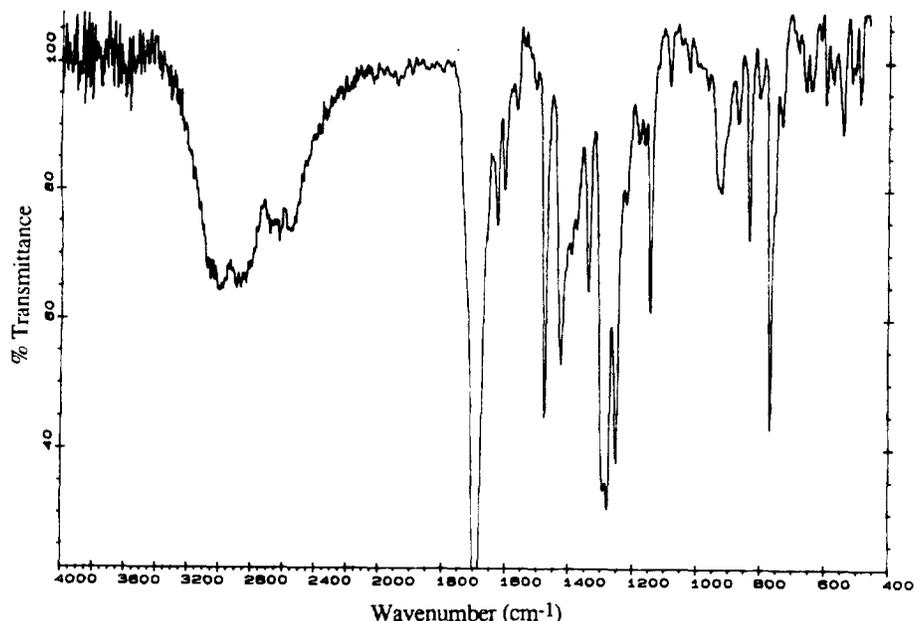


Fig. 2. IR spectrum of the NNA photoproduct.

Table 1

Solvent	Quantum yield
EPA	0.5; 0.1 ^a
acetonitrile	0.48
1,2-dichloroethane	0.49
3-methylpentane	0.50; 0.04 ^a
Me-cyclohexane	0.46; 0.04 ^a
cyclohexane	0.53

^a Measured at 77 K

transformed into nitroso acid and that the concentration of the photoinduced nitroso acid is equal to the initial concentration of NNA. The extinction coefficient of the nitroso acid was calculated from the ratio of the absorbances of nitroso acid and its precursor NNA, see Fig. 1.

We also measured the quantum yield of the phototransformation of NNA into nitroso acid, which is the ratio of the number of nitroso acid molecules formed during the light excitation process to the number of photons absorbed by NNA. A 10^{-3} M deaerated solution of NNA in different solvents (see Table 1) was placed in a 1 cm quartz optical cell and irradiated with 355 nm light, emitted by the third harmonic of a Surelite II Nd:YAG laser. The excitation light energy was maintained at ~ 7 mJ cm $^{-2}$. At this energy level the dependence of the accumulation rate of nitroso acid vs. energy was found to be linear. This linearity eliminated the possibility of non-linear photoprocesses as contributors to the observed photochemistry. The optical density of the solution at this wavelength is about 2, therefore, practically all the light is absorbed by the solution. The light intensity was measured by an Aberchrome 540 [14] chemical actinometer and also calculated using the energy, measured by a Molec-tron JD2000 joulemeter. Both measurements showed the

same result. The number of nitroso acid molecules was calculated from its absorption spectrum and extinction coefficient, measured for specific solvents. The measurements were conducted under conditions where the accumulation of nitroso acid had a linear dependence on excitation time. The quantum yields which we measured are summarized in Table 1. Our data show that the 0.5 quantum yield does not depend on solvent polarity, however at 77 K, the photochemical reaction of NNA occurs with a quantum yield of ~ 0.04 .

3.2. Transient absorption spectra and kinetics

When a solution of NNA was irradiated with a single 355 nm picosecond laser pulse, the formation of a transient species with the absorption spectrum shown in Fig. 3 was observed. The rate of formation of this, the only intermediate observed in our kinetics experiments, was practically as fast

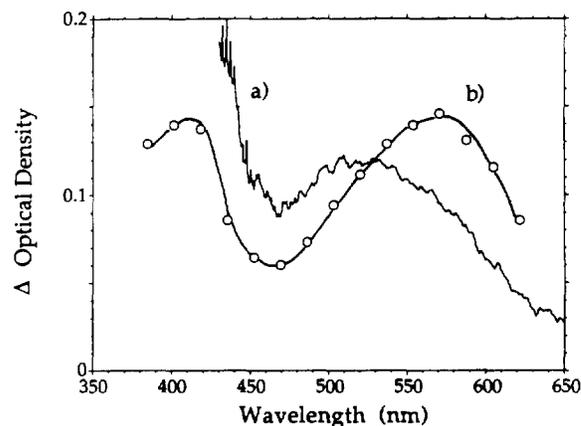


Fig. 3. Transient absorption spectra of (a) deaerated 4×10^{-4} M NNA solution in cyclohexane, 500 ps after excitation with 355 nm, 30 ps pulse, (b) in acetonitrile after excitation with 355 nm, 6 ns pulse.

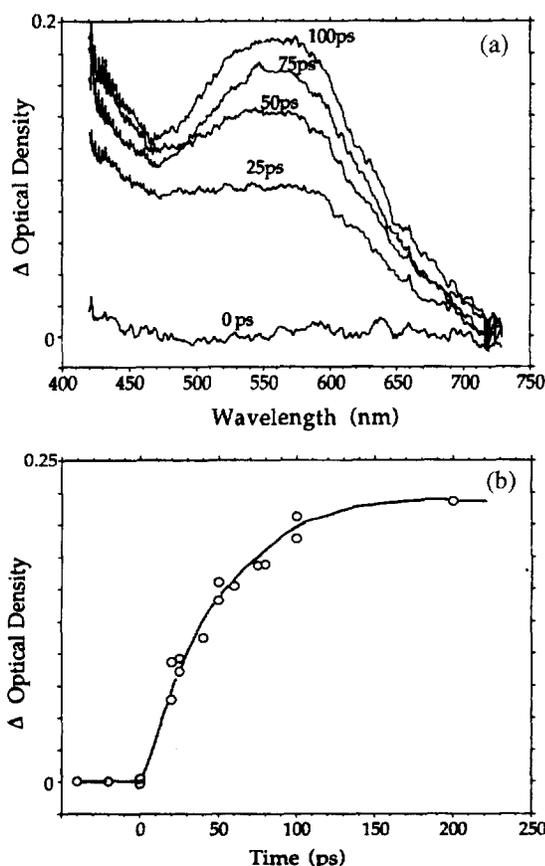


Fig. 4. (a) ΔA vs. λ and (b) accumulation kinetics of the transient, after excitation of deaerated 4×10^{-4} M NNA solution in 1,2-dichloroethane.

as the excitation pulse duration, $t_{\text{pulse}} \sim 40$ ps. Fig. 4 shows a plot of the optical density change, of the long wavelength absorption maximum of the transient, vs. time. The accumulation rate constant was measured to be $2 \times 10^{10} \text{ s}^{-1}$. Fig. 4(a) shows that the evolution of the triplet state spectrum follows the decay of the singlet state, proceeding via intersystem crossing. At shorter decay times, i.e. 25 ps, the spectra are composed of both $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$, while at later times, i.e. 75 ps, practically the whole spectrum is due only to the triplet state absorption.

The decay of the transient followed first-order kinetics and the observed lifetime of the transient was found to increase with increasing solvent polarity, Table 2. Also, the absorption spectra of the transient species experienced a red shift in the long wavelength band, with solvent polarity, as shown in Fig. 3. This indicates that the transient has a considerable dipole.

Unlike *o*-nitrobenzaldehyde [4], where the decay of the transient is strongly accelerated by the presence of water, we did not observe a significant change in the transient kinetics when a small amount of water was added to solutions of NNA. Instead, when a water–acetonitrile mixture was used as the solvent, the transient was found to be more stable (Table 2).

In oxygen saturated solutions the decay rate of the transient is faster than in deaerated solutions, as shown in Fig. 5. Oxygen is more effective in polar solvents, where the lifetime

Table 2

Solvent	k, s^{-1} (τ, ns) $\pm 10\%$ ^c
benzene ^a	2.0×10^7 ; (50)
1,2-dichloroethane ^a	6.7×10^6 ; (150)
<i>i</i> -PrOH ^a	5.0×10^6 ; (200)
CH ₃ CN ^a	3.1×10^6 ; (320)
CH ₃ CN + H ₂ O (1:1) ^a	1.6×10^6 ; (625)
EPA ^b	15.3; (65 ms)

^a Measured at 295 K.

^b Measured at 77 K.

^c Measured in deaerated solutions at 570 nm.

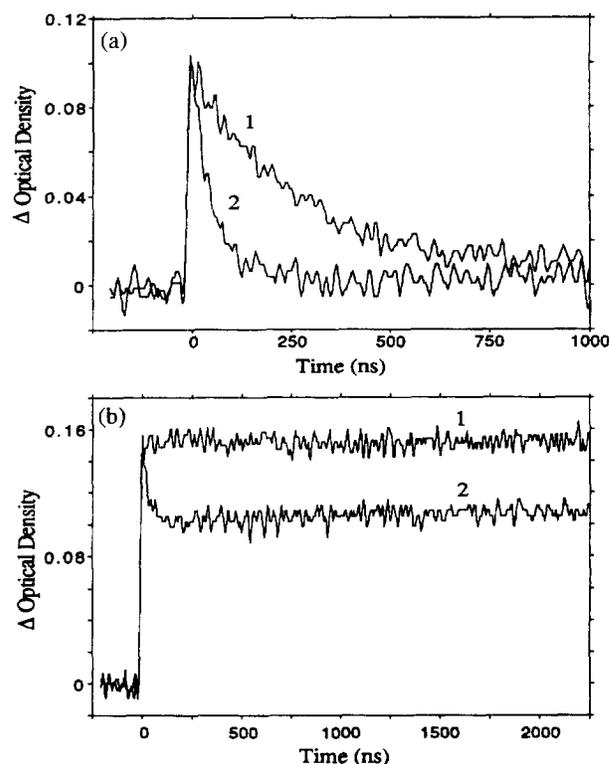


Fig. 5. Effect of oxygen on the transient kinetics of NNA in acetonitrile (conc. NNA 4×10^{-4} M): (a) measured at $\lambda = 570$ nm in deaerated (1) and oxygen saturated (2) solutions; (b) measured at $\lambda = 400$ nm in deaerated (1) and oxygen saturated (2) solutions.

of the transient is longer. In non-polar solvents, such as benzene, where the lifetime of the transient is about 50 ns, oxygen has practically no effect on the transient kinetics. This is expected because the reaction with oxygen is diffusion controlled. It should be noted that oxygen affects only the lifetime of the transient, while the intensity of the transient absorption remains the same in the presence and absence of oxygen. This is depicted in Fig. 5(a), where the rate of decay with O₂ is shown to be faster than without O₂. The quantum yield of the nitroso acid formation, measured by the transient absorption kinetics at 400 nm, where the nitroso acid has a strong absorption band, was found to decrease in the presence of oxygen, Fig. 5(b). At 1 ms after excitation when the fast transient has practically no measurable absorption, only the non-decaying

absorption of the stable nitroso acid is observed. The decrease in optical density in the presence of oxygen corresponds therefore to a decrease in the photoreaction quantum yield.

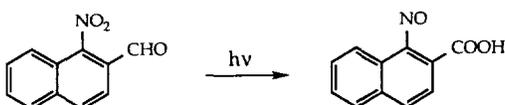
3.3. Low temperature experiments

Excitation, of NNA dispersed in EPA and *i*-PrOH matrices at 77 K, induced high intensity phosphorescence, which has the spectrum shown in Fig. 6(a). The decay of the phosphorescence intensity vs. time in EPA matrices is shown in Fig. 6(b), and the lifetime of the observed phosphorescence was estimated to be about 70 ms.

We also measured the transient absorption spectra and kinetics after excitation of NNA, with a 355 nm laser pulse, in glassy EPA and *i*-PrOH matrices at 77 K. The absorption spectrum of the transient, shown in Fig. 7(a), is very similar to that measured in liquid solutions at room temperature. The decay of this transient followed first-order kinetics with a lifetime of 65 ms, which is also the lifetime of the phosphorescence of NNA in EPA at 77 K.

4. Discussion

Our experimental data suggest that NNA, like its close analog *o*-nitrobenzaldehyde, undergoes photochemical rearrangement to the corresponding nitroso acid:



The quantum yield of this transformation was found to be rather insensitive to the nature of the solvent and excitation light wavelength (Table 1). This has been observed to be the case also for the photoreaction of *o*-nitrobenzaldehyde [4]. The lack of dependence of the reaction quantum yield on excitation light wavelength indicates that the photoreaction proceeds via the lowest electronic excited state. The reaction mechanism of *o*-nitrobenzaldehyde has been studied by several research groups [4,5], but no direct observations, which can prove the nature of the photoactive electronic excited state, were presented. Because the photoreaction quantum yield was decreased [4] by the addition of the triplet-state quencher *trans*-1,3-pentadiene, it was suggested that the photoreaction of *o*-nitrobenzaldehyde proceeds via a short-lived triplet excited state. Nevertheless, the authors of [5], who studied the photoreaction of *o*-nitrobenzaldehyde by means of time-resolved spectroscopy, found no evidence of triplet excited states involved in the photochemical reaction, and instead suggested that the photoreaction proceeds via the photoactive singlet excited state. Flash-photolysis studies of *o*-nitrobenzaldehyde [4,5] detected the only intermediate that has been observed during its phototransformation into nitroso acid.

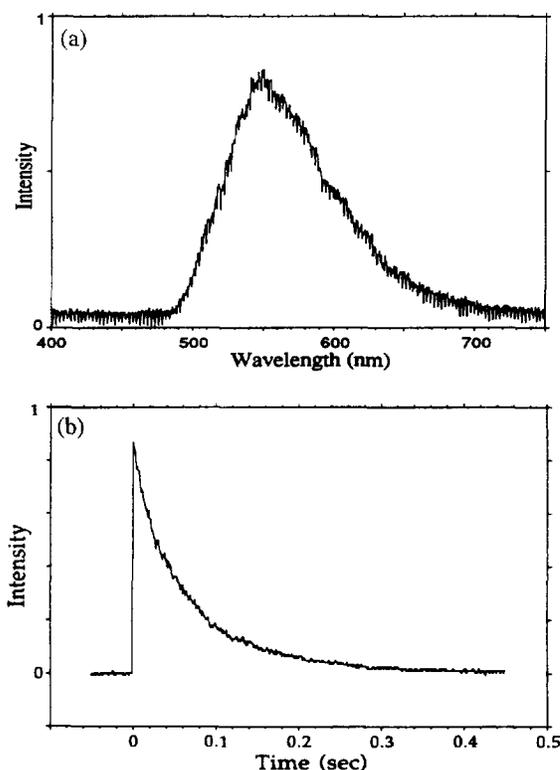


Fig. 6. (a) Phosphorescence spectrum and (b) phosphorescence decay kinetics of 4×10^{-4} M NNA in deaerated EPA at 77 K.

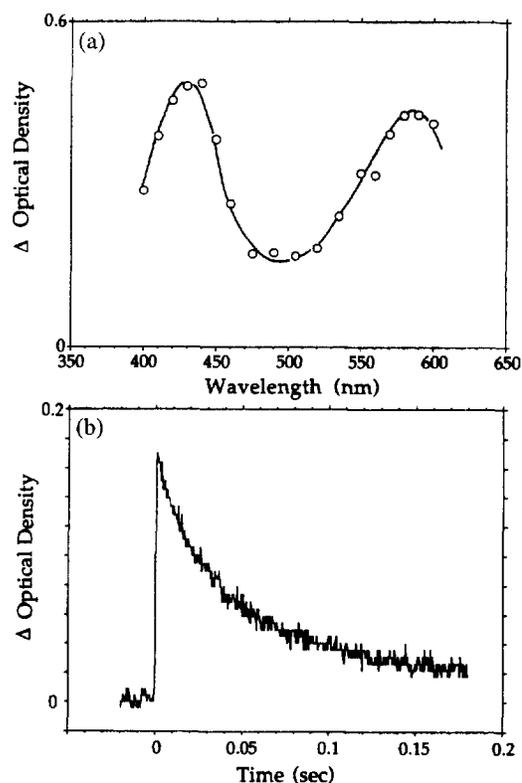
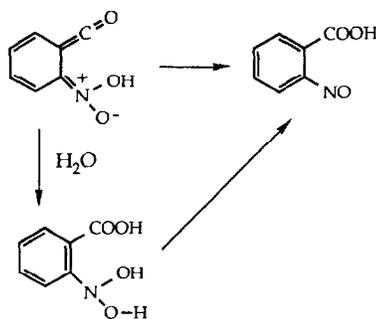


Fig. 7. (a) Transient absorption spectrum and (b) kinetics of NNA in EPA at 77 K.



This intermediate, assigned to a ketene structure, was found to be extremely sensitive to the presence of water, because water has been found to catalyze its transformation into nitroso acid [4,5]. The ketene intermediate in the photochemical reaction of *o*-nitrobenzaldehyde was also detected in matrix-isolation studies, at 10 K, by means of UV-visible and IR spectroscopy [6].

We also observed, as in *o*-nitrobenzaldehyde, one intermediate during photolysis of NNA. Its absorption spectra are shown in Fig. 3. Unlike *o*-nitrobenzaldehyde, the lifetime of the intermediate formed during photolysis of NNA was not affected by the presence of water but increased with increasing solvent polarity. These data are depicted in Table 2. These differences in the behavior of the intermediate observed, leads us to suggest that in the case of NNA the reactive intermediate is a triplet excited state rather than the ketene intermediate, which was observed in the photolysis of *o*-nitrobenzaldehyde.

As in the case of nitro- and formyl-substituted naphthalenes [15–20], excitation of NNA at 355 nm results in the population of the $^1n\pi^*$ state, ($\epsilon \sim 2200$). The absorption maximum of this band was found to red shift from 345 nm in polar acetonitrile to 348 nm in non-polar cyclohexane solutions, suggesting that this state has $^1n\pi^*$ character. There are also two $\pi\pi^*$ states in the UV area of 230 nm to 300 nm with $\epsilon_{245} = 42\,100$ and $\epsilon_{287} = 7400$. The excited $n\pi^*$ state relaxes, with a lifetime of 50 ps (Fig. 4), to a lower lying excited state which is assigned to a triplet state, $^3\pi\pi^*$, based on the data presented above. The intersystem crossing rate of $2 \times 10^{10} \text{ s}^{-1}$ is commensurate with an $^1n\pi^*$ initial level decaying into a $^3\pi\pi^*$ triplet state. This fast rate is responsible for a highly populated triplet state and consequently for the strong $T_1 \rightarrow T_0$ absorption observed with a maximum at $\sim 580 \text{ nm}$.

The location of the charge transfer (CT) bands plays a dominant role in the intersystem crossing (ISC) rate. In the case of NNA the CT band is expected to be in the higher energy region, as in 1-nitronaphthalene (e.g. 8.5 eV [21]), but contribute to the $^3\pi\pi^*$ character. This CT contribution again favors a fast $^1n\pi^* \rightarrow ^3\pi\pi^*$ rate. The measured 50 ps triplet formation time constant is slower than the 13 ps time constant observed for 1-nitronaphthalene because of the larger separation of the states found in NNA. Further support for the $^3\pi\pi^*$ assignment of the transient is the red shift which we observed of its long wavelength absorption band with increasing solvent polarity.

From the phosphorescence spectrum, Fig. 6(a), the location of the transient 0–0 band absorption was found to be 510 nm. ($19\,600 \text{ cm}^{-1}$) where the 1-nitronaphthalene CT, $^3\pi\pi^*$ band is also located [22]. This provides further support for the $^3\pi\pi^*$ assignment of the transient. Assignment to a $^3n\pi^*$ is not favored because of the large ST energy separation of $\sim 18\,000 \text{ cm}^{-1}$ (50 kcal) and the red shift observed with solvent polarity.

Stabilization of this triplet state by polar solvents suggests a considerable increase in the dipole moment of the triplet state. In polar solvents, such as acetonitrile and alcohols, where the lifetime of the observed triplet state is about 200–300 ns (see Table 2), we found that oxygen accelerates its decay rate, while the intensity of the signal due to triplet-triplet absorption at zero-time (right after the excitation with a 6 ns laser pulse) remains the same, Fig. 5. The decay rate constant of the triplet state in the presence of a triplet quencher, such as oxygen, may be represented as

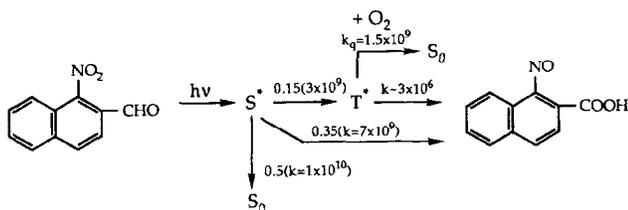
$$k = k_0 + k_q[\text{O}_2]$$

where k_0 is the rate constant in the absence of oxygen, k_q is the quenching constant and $[\text{O}_2]$ is the concentration of oxygen. In deaerated and oxygen saturated acetonitrile solutions the decay rate constants were measured and found to be equal to 3.1×10^6 and $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ respectively. The concentration of oxygen, in oxygen saturated solution, is about $9.5 \times 10^{-3} \text{ M}$ [15]. From these data, the triplet quenching constant was estimated to be $k_q \sim 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value corresponds to the triplet quenching by oxygen [23].

To establish further that the observed intermediate is the excited triplet state of NNA, we conducted experiments at 77 K, in EPA and *i*-PrOH matrices. The bright phosphorescence of the excited NNA molecules, dispersed in solid matrices at 77 K, was observed in the region of 520–580 nm, and is shown in Fig. 6(a). The triplet-triplet absorption spectrum, measured at 77 K (Fig. 7(a)), is found to be the same as the spectrum measured at room temperature. This fact suggests that the same intermediate is observed at both temperatures. The decay rate of the triplet state at 77 K, measured by the decrease in the triplet-triplet absorption intensity as a function of time, also corresponds to the phosphorescence decay rate, see Figs. 6(b) and 7(b). The quantum efficiency of the photochemical reaction at 77 K decreases by an order of magnitude compared with that measured at room temperature. These data are listed in Table 1. It should be noted that in non-polar matrices at 77 K, such as 3-methylpentane and methylcyclohexane, only weak phosphorescence was observed and the quantum efficiency of the photoprocess was found to be higher than in polar matrices. These data are also presented in Table 1.

Quenching of the photochemically active triplet state by oxygen leads to the decrease in the photoreaction quantum yield, observed in polar solvents, Fig. 5. In non-polar solvents, where the decay time of the triplet state is shorter than 50 ns, the effect of oxygen was not observed, because at that rate the concentration of oxygen was not enough to quench

the triplet state. Fig. 5(b) shows that in oxygen saturated acetonitrile solutions the photoreaction quantum yield was found to be 1.4 times less than the quantum yield in deaerated solutions. The lifetime of the triplet excited state was found to decrease by a factor of 4.6 under the same conditions, see Fig. 5(a). When the product of the photoreaction is formed exclusively via the triplet excited state, the quenching of this photoactive electronic excited state should also result in the decrease in the photoreaction quantum yield. The difference in the decrease in nitroso acid quantum yield and triplet excited state lifetime found in our experiments suggests that part of the product is formed via the singlet excited state. The total quantum yield of the photoreaction was measured to be 0.5, see Table 1. This suggests that an internal conversion deactivation process of the singlet excited state competes effectively with singlet to triplet intersystem crossing and the photoreaction. This is substantiated by the fact that no fluorescence was detected in NNA solutions. The formation rate constant of the triplet excited state, which corresponds to the decay constant of the singlet excited state, was measured to be $2 \times 10^{10} \text{ s}^{-1}$ (Fig. 4). These results prompt us to propose the following reaction scheme, quantum efficiencies and rate constants for the processes involved in the phototransformation of NNA:



We did not observe the ketene intermediate during photolysis of NNA, but the involvement of this product is suggested by analogy with the photoreaction of *o*-nitrobenzaldehyde, where the ketene transient was detected. Our failure to observe the ketene intermediate in the case of NNA may be due to its relatively low absorption intensity compared with the observed triplet–triplet absorption. The absorption spectra of the ketene and the triplet state are expected to overlap and consequently the ketene absorption spectrum may be masked.

5. Three-dimensional optical memory materials

The two forms of the molecule represent the 0 and 1 of the computer binary code. The original non-irradiated form corresponds to the zero of the binary code. When this molecule is excited it undergoes a photochemical transformation to a colored fluorescing form corresponding to the binary code 1. The forms corresponding to 0 and 1 in the binary code may be either reversible, whereupon they form a write/read/erase memory or if the reverse reaction is not possible, the materials may then be used in write only memory, ROM, devices.

Three-dimensional storage of information, i.e. writing inside the bulk rather than only on the surface, is achieved by a two-photon absorption process. We have described this method previously [10], therefore here we present briefly the salient points. Two pulsed beams intersect each other inside the bulk of the device as shown schematically in Fig. 8(a). Neither beam has enough energy, i.e. the wavelength is too long, to excite the molecule, however when the two beams intersect, inside the volume of the device, the sum of their energies is sufficient to populate the first allowed excited state. This is shown by means of an energy level diagram in Fig. 8(b). Subsequent photochemistry transforms the original molecule to the 'written' form corresponding to 1 in the binary code. The information is accessed by exciting the 'written' form to its first excited singlet state and recording its fluorescence by means of a CCD. Subsequently, the information is digitized and processed in a manner similar to that used to process the information of a magnetic disk. In addition to the fact that a huge amount of information may be stored, i.e. $10^{12} \text{ bits cm}^{-3}$, the information can be stored and accessed in parallel, i.e. a complete 100 Mb disk may be stored and accessed simultaneously, rather than by the normal bit at a time method.

The three-dimensional memory based on NNA is by design a ROM device, where information can be written once only but accessed many times. The process of making a memory device consists of dispersing *O*-nitronaphthaldehyde and Rhodamine B base in a 1 cm^3 PMMA polymer cube. Rhodamine B base corresponds to the 'write' form, 0 in the binary code. The cube is irradiated, simultaneously, with 532 nm and 1064 nm ps laser pulses shaped into a $8 \text{ mm}^2 \times 20 \mu\text{m}$

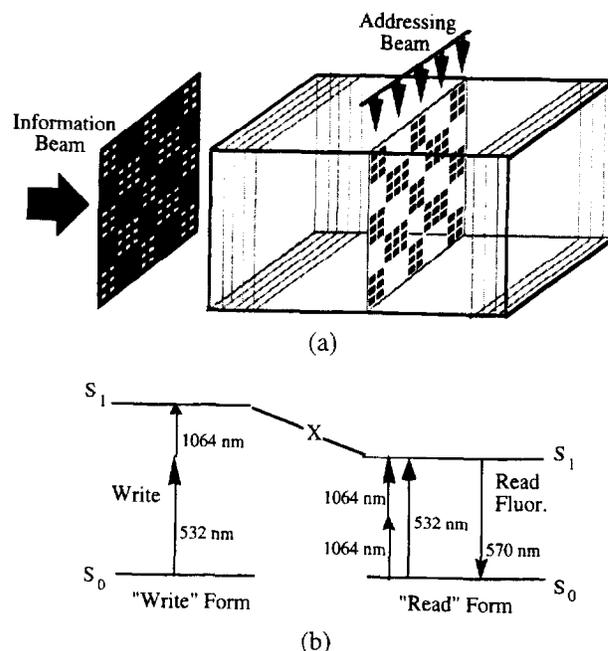
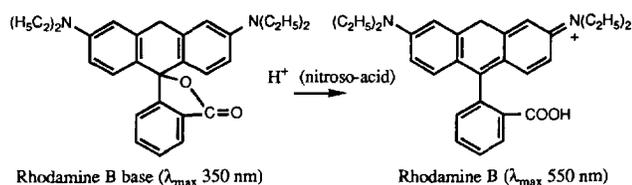


Fig. 8. (a) Optical path for storage and accessing all of the disk information in parallel. (b) Energy level diagram for writing and reading by the two-photon process.

thick plane beam. The 1064 nm information beam passes through an SLM (spatial light modulator) which contains the information to be stored, and propagates through the cube, Fig. 8(a). The 532 nm reference beam propagates also into the cube following an optical path perpendicular to that of the information beam. Where the two beams intersect light is absorbed, NNA generates nitroso acid, and photochemistry induces the Rhodamine B base to become Rhodamine B which is the 'read' form corresponding to 1 in the binary code.

Rhodamine B when excited fluoresces very strongly, making it a well suited form for accessing information



Reading is achieved by exciting a page with a 532 nm plane beam and recording the Rhodamine B fluorescence by means of a CCD. Using these materials and the two-photon method [10,12,13] described here briefly, we have been able to store in the bulk of a 1 cm³ cube and access in parallel more than 100 two-dimensional disks (pages) each containing 10 Mb/disk of information.

6. Conclusion

The phototransformation of NNA into nitroso acid is shown to proceed via both singlet ¹nπ* and triplet ³ππ* excited states. The quantum yield is rather insensitive to the polarity of the solvent and excitation light wavelength. The lifetime of the ³ππ* triplet state was found to increase with increasing solvent polarity and in highly polar solvents was long enough to allow the triplet state to be quenched by oxygen. The decrease in the photoreaction quantum yield in the presence of oxygen was also measured.

At low temperatures, 77 K, the photoreaction of NNA was found to proceed with considerably lower quantum yield, while a bright phosphorescence was detected and found to be the dominant deactivation channel of the triplet excited state. Based on our data and literature data available, a mechanism

for the phototransformation of 1-nitro-2-naphthaldehyde into nitroso acid is proposed. This molecular system forms the basis for a novel three-dimensional molecular computer memory device.

Acknowledgements

This work was supported in part by the United States Air Force, Rome Laboratory, under contract F-30602-93-C-0232 and F-30602-97-C-0029.

References

- [1] G. Ciamician, P. Silber, *Ber. Dtsch. Chem. Ges.*, 34 (1901) 2040.
- [2] A. Schonberg, *Preparative Organic Photochemistry*, Springer-Verlag, New York, 1968, pp. 267–270.
- [3] R.G.E. Morales, G.P. Jara, S. Cabrera, *Limnol. Oceanogr.*, 38 (3) (1993) 703.
- [4] M.V. George, J.C. Scaiano, *J. Phys. Chem.*, 84 (1980) 492.
- [5] R.W. Yip, D.K. Sharma, *Res. Chem. Intermed.*, 11 (1989) 109.
- [6] S. Kuberski, J.J. Gebicki, *Mol. Struct.*, 275 (1992) 105.
- [7] P. Mayo, S.T. Reid, *Quart. Rev.*, 15 (1961) 393.
- [8] R.W. Yip, D.K. Sharma, R. Giasson, D. Gravel, *J. Phys. Chem.*, 89 (1985) 5328.
- [9] H. Schupp, W.K. Wong, W. Schnabel, *J. Photochem.*, 36 (1987) 85.
- [10] A.S. Dvornikov, P.M. Rentzepis, *Opt. Commun.*, 136 (1997) 1.
- [11] M. Makosza, Z. Owczarczyk, *J. Org. Chem.*, 54 (1989) 5094.
- [12] A.S. Dvornikov, P.M. Rentzepis, *Res. Chem. Intermed.*, 22 (1996) 115.
- [13] A.S. Dvornikov, I. Cokgor, M. Wang, F.B. McCormick, S.E. Esener, P.M. Rentzepis, *IEEE CPMT A*, 20 (1997) 203.
- [14] H.G. Heller, J.R. Langan, *J. Chem. Soc. Perkin Trans. II*, (1981) 341.
- [15] J.G. Calvert, J.N. Pitts, *Photochemistry*, Wiley, New York, 1966, p. 369.
- [16] N.J. Turro, *Molecular Photochemistry*, W.A. Benjamin, New York, 1967, p. 15.
- [17] H.H. Jaffe, M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962, p. 213.
- [18] I. Itih, *Spectrochim. Acta A*, 52 (1996) 343.
- [19] M. Yagi, Y. Shioya, J. Higuchi, *J. Photochem. Photobiol. A: Chem.*, 62 (1991) 65.
- [20] L. Martins, M. Fernandes, T. Kemp, S. Formosinho, J. Branco, *J. Chem. Soc. Faraday Trans.*, 87 (1991) 3617.
- [21] F. Brogli, E. Heilbronner, T. Kobayashi, *Helv. Chim. Acta*, 55 (1972) 274.
- [22] H. Ohtani, T. Kobayashi, K. Suzuki, S. Nagakura, *Bull. Chem. Soc. Jpn.*, 53 (1980) 43.
- [23] S.L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973, pp. 59, 89.