# Triplet Sensitized Laser Flash Photolysis of BNN3, Caged Nitric Oxide

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The excited triplet state of *N,N'*-dimethyl-*N,N'*-dinitroso-*p*-phenylenediamine (BNN3, $\lambda_{max}$: 299 nm), caged nitric oxide ($E_T$: 230 kJ mol$^{-1}$), was found to readily undergo N–N bond homolysis to release NO. This suggests that by covalently binding a triplet sensitizing chromophore, e.g., biacetyl, to BNN3 *N*-methyl group, its NO photoreleasing light can be switched from UV to visible, less cytotoxic light, such as 425 nm.

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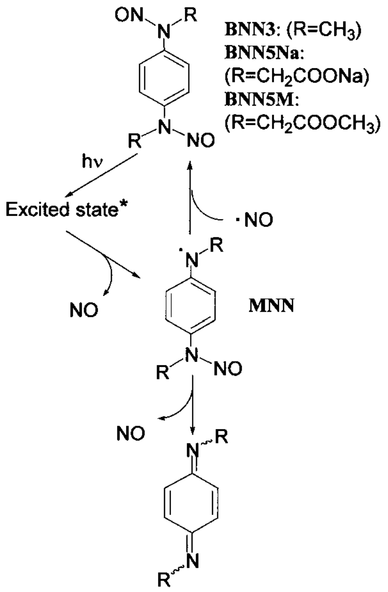
Endogenous nitric oxide (NO) synthesized *in vivo* by NO synthase is an important signaling molecule.[1] High-performance caged NO, itself biologically inert, extrudes NO upon photoirradiation, and should provide useful information on the role of NO. Bis-*N*-nitroso-*p*-phenylenediamine derivatives (BNN) have been reported for this use.[2,3] Photochemical NO release by BNN consists of two processes (Scheme 1).

We proposed that direct photolytic N–N bond homolysis of BNN3 ($\lambda_{max}$ 299 nm; ε: 14,100 mol$^{-1}$dm$^3$cm$^{-1}$) occurred from an excited singlet state based on the observation that the NO-forming quantum yield ($\Phi_{NO}$) was hardly affected by air.[2] If the intermediary MNN-NO radical pair (Scheme 1) in a solvent cage is in a singlet state, substantial recombination in the solvent cage should occur to regenerate BNN, reducing $\Phi_{NO}$.[4] Using 3,3,4,4-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) as an NO quencher,[5] however, $\Phi_{NO}$ of BNN3 photolysis was found to be 2.[2] Such quantitative NO formation in BNN photolysis suggests that initial N–N bond homolysis occurs from an excited triplet state, yielding a triplet MNN-NO radical pair whose fastest reaction path involves diffusion from the solvent cage rather than recombination.



**Scheme 1.** BNN photochemical processes.

We studied the laser flash photolysis of BNN3 in the presence of three triplet sensitizers, biacetyl, Michler's ketone, and benzil, at 295 K.

When a BNN3 benzene solution was irradiated with a 308 nm laser pulse (20 ns width), absorption due to MNN3 radicals ($\lambda_{max}$ 390 nm) occurred within a duration of the laser pulse (Figure 1). Similarly, on biacetyl sensitization with 425 nm laser pulse, BNN3 yielded a transient absorption at 390 nm. The spectrum recorded at 2 μs after the laser shot is identical to that of MNN3 in direct photolysis with 308 nm light (Figure 1).[6] Decay curves of transient absorptions generated by direct and triplet sensitized photolysis of BNN3 in Figure 1 inset also demonstrate that both photolysis generate the same transient species, MNN3. Such very efficient MNN3 radical formation by triplet sensitization shows that the triplet excited state of BNN3 readily undergoes N–N bond homolysis. The energy transfer rate ($k_q$) from the triplet-excited state of biacetyl to BNN3 was estimated to be 5.8 × 10$^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ from apparent pseudo-first-order rate constants determined by the rising curve of MNN radicals at 405 nm at different BNN3 concentrations.[7] Michler's ketone-sensitized photolysis also proceeded smoothly, yielding MNN3. $k_q$ for quenching the excited triplet state of Michler's ketone was determined to be 7.60 × 10$^9$ mol$^{-1}$ dm$^3$ s$^{-1}$ from T–T absorption decay of Michler's ketone at 700 nm generated by 390 nm laser light at different BNN3 concentrations. These bimolecular energy transfer rates are almost at the diffusion limit, suggesting that the triplet-state energy ($E_T$) of BNN3 is lower than $E_T$ of Michler's ketone,[8] 260 kJ mol$^{-1}$, and

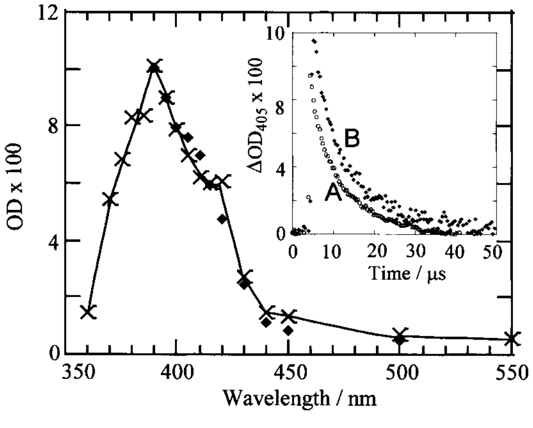


**Figure 1.** Transient MNN radical spectra. Cross: BNN3 alone irradiated with 308 nm laser light, $[BNN]_0$ = 0.12 mmol dm$^{-3}$. Closed lozenge: Biacetyl sensitized photolysis with 425 nm laser light, $[BNN]_0$ = 0.978 mmol dm$^{-3}$; [biacetyl] = 23.7 mmol dm$^{-3}$. Inset: Time courses of 405 nm absorbance due to MNN radical. A, $[BNN3]_0$ = 0.10 mmol dm$^{-3}$ alone; B, $[BNN3]_0$ = 0.10 mmol dm$^{-3}$; $[Biacetyl]_0$ = 23.7 mmol dm$^{-3}$.

biacetyl,[8] 236 kJ $mol^{-1}$, within Sandros formalism.[9]

To estimate the BNN3 triplet state energy more precisely, triplet sensitized photolysis of BNN3 at a 425 nm laser pulse was studied using benzil ($E_T$ = 223 kJ $mol^{-1}$) as a sensitizer. The decay curve of the T–T absorption of benzil was monitored at 500 nm at varying concentrations of BNN3. $k_q$ for quenching the excited triplet state of benzil with BNN3 was determined to be $4.91 \times 10^8$ $mol^{-1}dm^3s^{-1}$. Assuming a diffusion limit of $10^{10}$ $mol^{-1}dm^3s^{-1}$, $\Delta E_T$ was estimated from the Sandros' equation for endothermic energy transfer to be 7.3 kJ $mol^{-1}$. $E_T$ of BNN3 in benzene is thus estimated to be 230 kJ $mol^{-1}$ and is much greater than the bond dissociation energy, 170 kJ $mol^{-1}$, reported for the usual N-N bond.

$$k_q = k_{diff}\,[\exp(-\Delta E_T/RT)/\{1 + \exp(-\Delta E_T/RT)\}]$$

The major pathway of direct photolysis of usual mono-*N*-nitroso compounds is conformational change around the N–N bond, i.e., anti–syn isomerization, not NO-forming pathways.[10] Summarizing previous[2,3,8] and present studies, although N–N bond scission from the excited singlet state of BNN cannot be completely eliminated, we surmise that (1) the excited singlet state of BNN3 formed in direct photolysis may undergoes intersystem crossing, yielding the excited triplet state of BNN3, whose N–O bond splits quantitatively and (2) these two photochemical events occur quantitatively within a few nanoseconds. Similar interheteroatom bond homolysis in direct photolysis of 4-methylthiobenzoyl peroxide has been reported, i.e., the excited singlet state of peroxide undergoes fast intersystem crossing and subsequemt O–O bond homolysis from the triplet state.[11]

The triplet mechanism for direct BNN3 photolysis is in accord with PTIO trapping of 2 mol of NO from the photolysis of 1 mol BNN3 with 308 nm light.[2] This triplet mechanism is the advantage of BNN reagents to accomplish quantitative NO photorelease. These observations suggest that the light for NO photorelease of BNN reagents can be switched from UV to visible, less toxic light by introducing a suitable triplet-sensitizing chromophore in BNN, e.g., binding the biacetyl chromophore at *N*-methyl group of BNN3. NO can then be released by irradiating with 425 nm light due to intramolecular triplet sensitization by biacetyl chromophore.

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## References and Notes

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