

Latent photochromism (pseudothermochromism) and photofatigue of crystalline 2-(2',4'-dinitrobenzyl)pyridine

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ABSTRACT: Along with the metastable 2-(2',4'-dinitrophenylmethylidene)-1,2-dihydropyridine (**NH**) and the unstable 6-aci-nitro-2-nitro-5-(2'-pyridylmethylene)-1,3-cyclohexadiene (**OH**), the stable form of 2-(2',4'-dinitrobenzyl)pyridine (DNBP), **CH**, is photochemically converted into small amounts of 1,2-bis(2',4'-dinitrophenyl)-1,2-bis(2'-pyridyl)ethane, *trans*-bis[5-nitro-2-(pyridine-2-carbonyl)phenyl]diazene *N*-oxide, 6-nitro-3-(2'-pyridyl)-2,1-benzisoxazole and 3-nitropyrido[1,2-*b*]quinolin-6-ium-11-olate. The latent photochromism of DNBP, as shown by x-ray analysis of the structures of the side-products and ESR/IR measurements, is attributed to open-shell reactions that are initiated by hydrogen photoabstraction and subsequent creation of two monoradicals, **NH**[•] and **OH**[•]. Large amounts of the radicals (ca 50% **NH**[•] and 70% **OH**[•]) confined in the crystalline interior are persistent under ambient conditions. Through quasi-periodic reactions, the remaining radicals partially recover the ground-state isomers **CH**, **NH** and **OH**, or decay to the side-products, which results in crystalline photofatigue. Together with proton tunneling from the excited **CH**, the radical reactions represent dominant mechanism for the creation of **NH** and **OH** in the low-temperature regimes, but are successfully competed by the closed-shell reactions at higher temperatures. The precursor state, whose existence was assumed previously from transient absorption spectroscopy, may be identified as the radical **OH**[•]. The present work represents the first study of the photofatigue of a 2-(2',4'-dinitrobenzyl)pyridine compound and extends the 'classical' mechanism of the photochromic reactions of nitrobenzylpyridines with a set of open-shell radical reaction routes. Copyright © 2004 John Wiley & Sons, Ltd.

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KEYWORDS: 2-(2',4'-Dinitrobenzyl)pyridine; nitrobenzylpyridines; photochromic *ortho*-nitrobenzylpyridine; photochromism; photofatigue; radicals

INTRODUCTION

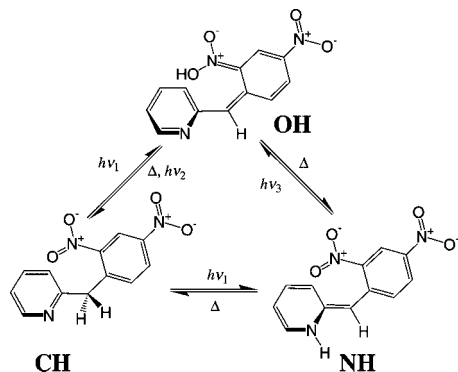
The scientific interest in photochromic compounds is driven by their potential application as phototriggers for electrical nano-circuits, photomodulators for non-linear optical materials and materials for photo-optical memory storage and switching devices.¹ Necessary requirements for the compounds in such applications are small structural perturbation during the photoreactions, preservation of the crystal integrity, stability of the colored forms, tunability of the yields and high resistance to undesirable side-reactions (photofatigue). A promising class of compounds that meet the first four of the above conditions are those similar to the photochromic 2-(2',4'-dinitrobenzyl)pyridines (DNBPs). The DNBPs have been used as phototrigger units in the caged compounds (for reviews,

all Ref. 2) and have also been proposed as efficient second-harmonic generation photomodulators.³

The collection of earlier studies has generally agreed upon a nitro-assisted proton transfer mechanism of the photochromic reactions, outlined in Scheme 1. When photoexcited, the otherwise stable **CH** forms isomerize to metastable blue-violet quinones/azamerocyanines **NH**, mainly via unstable aci-nitro tautomers **OH**.^{4,5} Surprisingly, apart from the application relevance of this photochromic system, and a few reports concerning residual yellow coloration,^{4,6} very little is known about its photofatigue. Long-term and/or intense irradiation of powdered or crystalline DNBP with UV-visible light at any temperature results in residual, unbleachable yellow-brownish coloration. The cyclability (the number of cycles needed for the blue absorbance to drop to 50% of the initial value) of powdered DNBP switched between the colorless and the blue form is $Z_{50} \approx 20$ (Fig. 1). The fatigue is accompanied by a decrease in several absorptions in the 1300–600 cm⁻¹ region, disappearance of a weak band at 980 cm⁻¹ and evolution of a single, unbleachable, weak band at 1020 cm⁻¹. A similar decrease in the photochromic efficiency is known for alkylnitrobenzenes in solution.⁷

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Scheme 1. The three-species mechanism of the photochromic proton transfer reactions in dinitrobenzylpyridines

Spectroscopic investigations have indicated that the actual mechanism of the photoreactions of DNBP is more complex than that shown in Scheme 1. First, at least two temperature regimes for the formation of both **NH** and **OH** exist: at higher temperatures (e.g. above ~ 160 K for **OH** and ~ 230 K for **NH** in the case of the parent compound DNBP) the photoproducts are created through thermally activated proton transfer. At lower temperatures, where the thermal proton transfer is forbidden, low-yield and nearly temperature-independent processes (probably proton tunneling from excited state) prevail.^{8,9} Second, the **OH** isomer in the solid DNBP evolves (on a microsecond time-scale) with delay relative to **NH**, which indicates a long-lived triplet state or an additional intermediate.⁸ Third, if DNBP dispersed in polymer matrices is flashed with UV radiation at cryogenic temperatures, it remains colorless, but develops the characteristic 600 nm **NH** band on warming in the dark. To explain the phenomenon, for which we propose here one of the terms *latent photochromism* or *pseudothermochromism*, Sousa and Loconti¹⁰ assumed the existence of a colorless 'dark intermediate' that decays to **NH**. Recently, Casalegno and co-workers^{11,12} characterized this precursor by transient absorption spectroscopy. It was found that the species, with a lifetime of about 10 μ s at room temperature

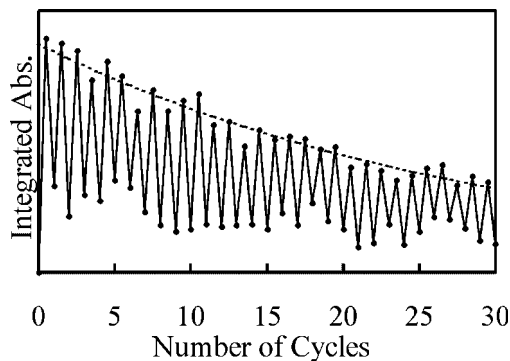


Figure 1. Time profile of the integrated absorbance of the 600 nm **NH** band upon switching between the colorless and the colored DNBP (coloration, 0.1 s flashes from Hg lamp, $\lambda < 440$ nm; bleaching, 1 min irradiation with Y-51-filtered output from Xe arc lamp, $\lambda = 500$ –800 nm)

in a polycrystalline matrix, absorbs at 335 nm and decays either to **OH** and then to **NH** and **CH**, or directly to **CH**.

Our motives for studying the photofatigue of DNBP were mainly based on the following two facts: (1) although much is known about the main photochromic reactions of DNBP, the side-reactions of this system have hardly been given any attention in the past, and (2) the several spectroscopic observations pointed out above could not be satisfactorily explained with Scheme 1. For a better understanding of the photochemistry of DNBP, therefore, one needs to look for information obtainable with other techniques, such as, in this case, structural and product analyses combined with ESR spectroscopy. In this work we characterized four side-products responsible for the photofatigue of DNBP and we show that all of the above experimental observations can be accounted for by two photochemically created radical intermediates. The present study, however, was not intended to give a complete and final decision on the reaction mechanism; rather, by obtaining proof for the existence of additional species, it was aimed to provide a direction in which the answers for the complicated photochemistry of DNBP should be sought.

RESULTS AND DISCUSSION

Photolysis of DNBP

The HPLC analysis of DNBP photolyzed with visible light from Xe lamp (400–800 nm) showed 13 photoproducts (Fig. 2). The composition of the photolyzates obtained from powdered bulk DNBP samples under various conditions was analyzed by preparative-scale TLC (for details on the irradiation conditions, see Experimental). From DNBP photolyzed at ambient temperature and at 275–278 K in air, nine and seven products were isolated, respectively, in addition to a dark, highly intractable material. Cryogenically irradiated DNBP samples, warmed to ambient temperature and then kept in the dark for several days, showed the same composition as the samples irradiated at ambient temperature. DNBP irradiated anaerobically at 275 K yielded smaller amounts of the yellow side-products and a higher concentration of the **NH** isomer than at other temperatures, which resulted in unusually dark blue coloration. Except for two components, DNBP irradiated in acetonitrile and in the solid state at 275 K afforded the same products, but greater amounts decomposed in the solution (73.2 vs 55.3%). In the presence of a triplet-quenching diene in acetonitrile, DNBP was largely consumed and decayed to as many as 18 products.

Photochemical effects on the crystal structure

In order to investigate the structural changes during the prolonged irradiation more directly, the effects of

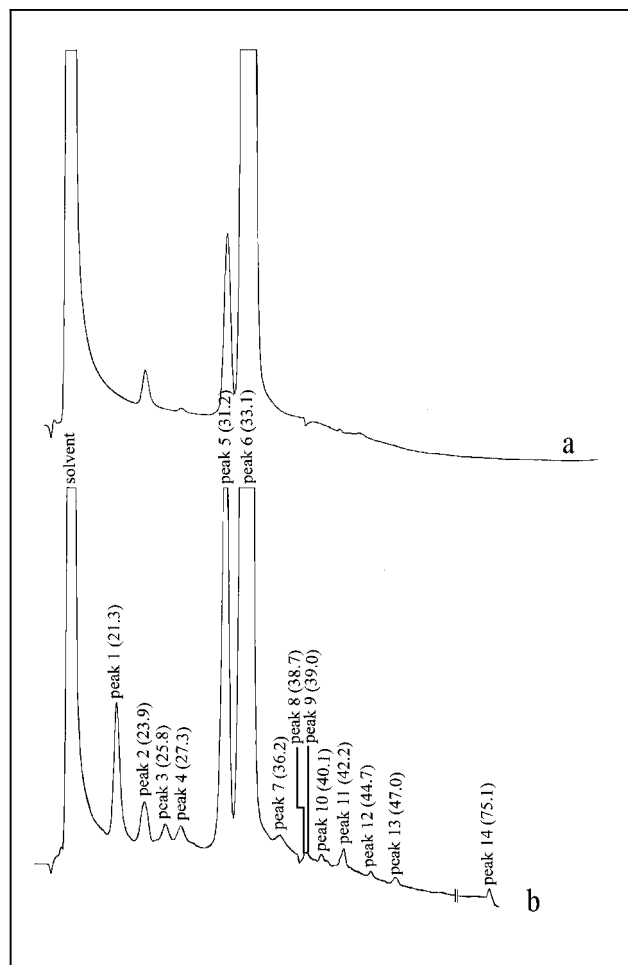


Figure 2. HPLC traces of DNBP (a) before and (b) after 296 h of irradiation with Xe arc lamp (400–800 nm). The retention times (in minutes) are given in parentheses

photoirradiation on the structure of DNBP were followed *in situ* by single-crystal x-ray structure analysis of the lattice constants and the thermal parameters of the *o*-nitro group at 250 K (Fig. 3). As expected from their conformational similarity,^{4,5} switching among CH, OH and NH resulted in small, albeit significant, changes but did not affect the long-range structural order of DNBP. However, prolonged irradiation of about 40 h resulted in notable structural changes: initial abrupt contraction of the cell (the cell volume decreased by 2.3% and the residual factor increased by 0.55%) and large expansion with increased mosaicity afterwards. Interestingly, standing in the dark led to partial recovery of the structural order of the brown crystal (the residual factor decreased by 3.99%). Similar changes were observed under argon. With the use of single-photon excitation, no secondary structure could be clearly discerned during the single-crystal measurements.

Characterization and crystal structures of the side-products

The time profile of the products of DNBP that was irradiated constantly during 10 days is presented in

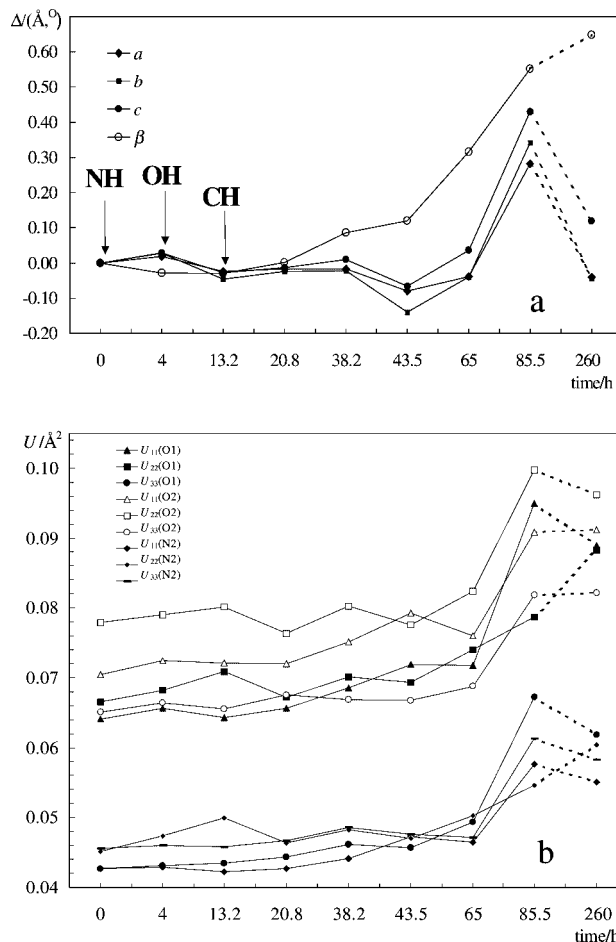


Figure 3. Change of the cell parameters (a) and the anisotropic displacement parameters (b) of a single crystal of DNBP irradiated in air. Before $t=0$, the colorless crystal was irradiated 0.25 h with $\lambda < 440$ nm (Hg lamp, filter UV-D33S) and the data were collected; the respective data are plotted at $t=0$. From $t=0$ the blue crystal was colored yellow by irradiation with 600 nm (λ_3) pulses for 0.67 h while collecting the data for 4 h; the resulting parameters are plotted at $t=4$ h. From $t=4$ h the yellow crystal was bleached with 400–440 nm radiation (λ_2) (Hg lamp, O-56 filter and Xe lamp, UV-D33S filter) and left in the dark. The data collected from the colorless crystal are plotted at $t=13.2$ h. Further irradiation was carried out with unfiltered output from an Xe lamp at $\lambda = 540$ –800 nm. Each point corresponds to the end of the data collection relative to $t=0$

Fig. 4. The plot shows an induction period, which was estimated from the change of the concentrations to about 25–50 h ($\sim 93\%$ DNBP remained), in agreement with the value obtained from the single-crystal study (~ 40 h). After the induction period, the concentrations of the products increased and decreased twice until the end of the irradiation, first within about 50–140 h and then within 140–240 h from the onset of irradiation. This indicated quasi-periodic reactions that repeat after about each 90–100 h of exposure. During each cycle DNBP decayed and was partially recovered from one product with a weight ratio of $\sim 12\%$ (peak 5 in Fig. 4) and four products with weight ratios varying between 0 and 4%

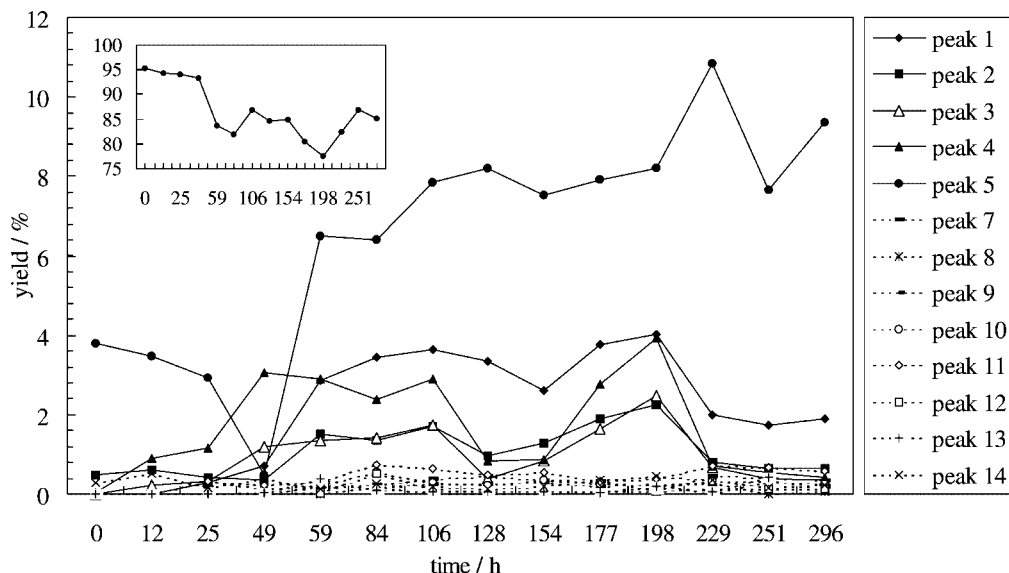


Figure 4. Time dependence of the composition of solid DNBP photolyzed with Xe lamp (400–800 nm) and analyzed by HPLC. The inset shows the variation of the remaining DNBP (the axes units are the same on both plots). Peaks identified with the standard addition method: peak 2, side product **2**; peak 4, side product **1**; peak 6, DNBP; peak 7, side product **3**; peak 12, side product **4**

(peaks 1–4), while a small amount was converted into several photoinactive products with relatively constant ratios of less than 1% (peaks 7–14). A thorough physico-chemical characterization of the products proved to be difficult owing to the small isolable quantities and their photoreactivity. Repeated recrystallizations afforded crystals from four stable products, namely 1,2-bis(2',4'-dinitrophenyl)-1,2-bis(2'-pyridyl)ethane (**1**), *trans*-bis[5-nitro-2-(pyridine-2-carbonyl)phenyl]diazene *N*-oxide (**2**), 6-nitro-3-(2'-pyridyl)-2,1-benzisoxazole (**3**) and 3-nitropyrido[1,2-*b*]quinolin-6-ium-11-olate (**4**). An additional amine product, 2-(4'-amino-2'-nitrobenzyl)pyridine, was obtained in the presence of triplet-quenching diene; the structure was identical with that of the same compound prepared chemically.¹³ The molecular structures of **1**–**4** as determined by x-ray diffraction are shown in Fig. 5; the relevant crystallographic data are listed in Table 1.

The molecule of **1** exists in the solid state in a *gauche* staggered conformation around the central C6–C18 bond with *anti*-oriented pyridyl and dinitrophenyl rings, which minimizes the steric repulsion. The central C6–C18 bond of 1.603(5) Å is very long to avoid the short contact within the molecule. However, the C17–C18–C19 [109.4(3)°] and C5–C6–C7 [109.8(3)°] angles are normal. The torsion angles of the two dinitrophenyl rings (C12–C7–C6–C18 and C24–C19–C18–C6) are 59.1(4)° and 62.0(5)°, respectively, whereas those of the two pyridyl rings (N1–C5–C6–C18 and N4–C17–C18–C6) are 42.1(5)° and 41.8(4)°, respectively.

The molecule of the dimer **2** is centrosymmetric with respect to the center of the azoxy bridge. The central N=N distance [1.241(5) Å] compares well with the mean value (1.24 Å) for uncoordinated dimeric *N*-unsubstituted *trans*-azobenzenes retrieved from the Cambridge Struc-

tural Database.¹⁴ The molecule of **3** is nearly planar. The angle between the pyridyl and benzisoxazole functions is 4.2(1)° and the nitro group rotates by 8.7(2)° around the C–N bond. The three condensed rings of **4** are coplanar, with slight deviation of the nitro group by 6.1(6)° from the common plane. The C–O and N=N bond lengths, 1.246(4) and 1.360(4) Å, are very similar to the values of the bromo derivative, 1.244(5) and 1.361(5) Å, respectively.¹⁵ The long C–O distance indicates single-bond character of the carbonyl bond and thus a significant contribution of the enolate form to the resonant structure of the molecule.

Possible intermediates and pathways to produce the side-products

The presence of the induction period (Fig. 4), the large number of side-products and their structures imply the existence of photoinduced radical species. The structure of the stable dimer **1**, the only characterized side-product with unoxidized benzylic carbons, clearly suggests the existence of a precursor monomer radical denoted **OH**• in Scheme 2. The most probable way for creation of **OH**• is abstraction of a single hydrogen atom from DNBP. A second radical denoted **NH**•, whose existence was confirmed by ESR spectroscopy (see below), could be obtained either by transfer of the remaining benzylic proton in **OH**• to the pyridyl nitrogen or by hydrogen abstraction from **NH** (Scheme 3). The present results thus support the assumptions of Kuindzhi *et al.*¹⁸ based on ESR measurements.

Products **1** and **2** indicate dimerization of **OH**• and **NH**•, while **3** and **4** suggest intramolecular cyclization. The quasi-periodic course of the photofatigue and the

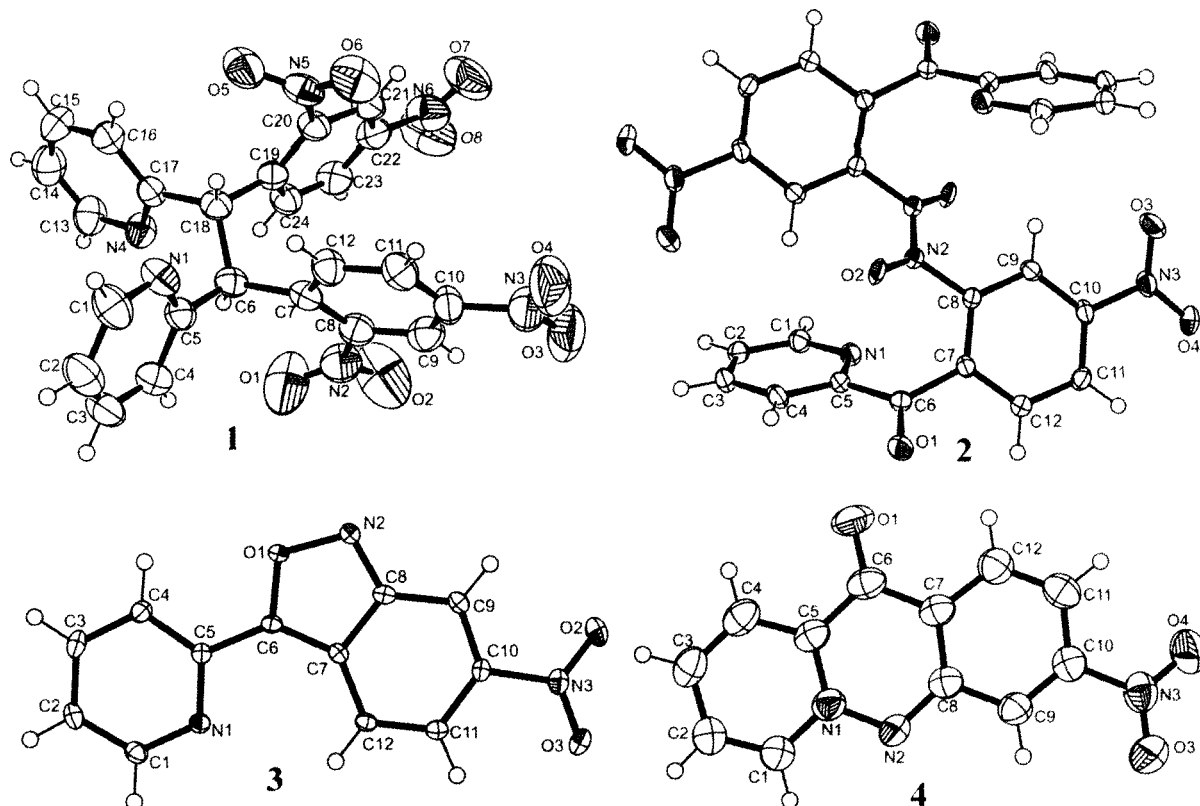


Figure 5. ORTEP diagrams (50% probability level) of the molecular structures of the photoproducts: (1) 1,2-bis(2',4'-dinitrophenyl)-1,2-bis(2'-pyridyl)ethane; (2) *trans*-bis[5-nitro-2-(pyridine-2-carbonyl)phenyl]diazene *N*-oxide (1:1 disordered over the center of the N=N bond); (3) 6-nitro-3-(2'-pyridyl)-2,1-benzisoxazole; (4) 3-nitropyrido[1,2-*b*]quinolin-6-ium-11-olate

anaerobic photolysis experiments indicate that eventual peroxide-mediated reactions are not the main source of the oxidized side-products 2–4. It seems unlikely that the product 4 is created from 3 pyrolytically, since such reaction requires very high temperatures.¹⁵ From the structures of the photoproducts and the literature data on photodecay of other nitro compounds,^{16,17} various mechanisms for the photofatigue of DNBP can be assumed (e.g. including diradicals or charged radical species). Elucidation of the exact reaction mechanism, however, would need further experimental and theoretical work. Extensive theoretical investigation of the potential energy surface for the main and the side reactions in DNBP is in progress and will be published elsewhere.

ESR spectra

To confirm the existence of the radical intermediates and to supplement the existing scarce data,¹⁸ the ESR spectra of DNBP were investigated. Powdered DNBP irradiated at 5 K (Fig. 6) developed weak, sharp resonance (324.351 mT, $g = 2.0046$) immediately after the irradiation with visible light from Xe lamp. As a result of the very small amount of long-lived radicals produced by the diffuse room light during sample preparation, the resonance at 324.351 mT is observable as a very weak signal

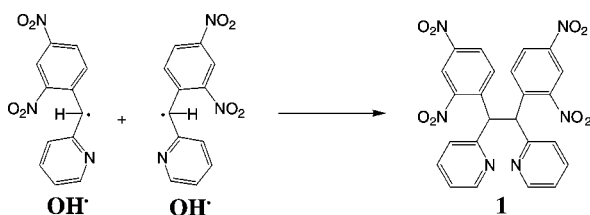
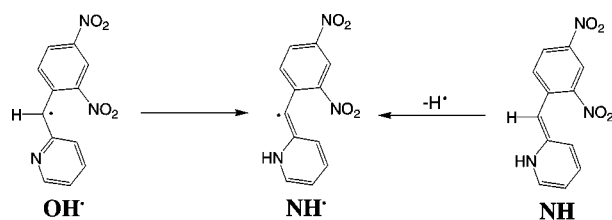
even in the non-irradiated sample. The additional broad, asymmetric signal that initially appears at 312.834 mT ($g = 2.0784$) remains unaffected by further irradiation and is probably due to a small amount of thermally unstable radicals of very short relaxation time produced at defects. Accordingly, it disappears immediately upon annealing at 20 K and can not be recovered by irradiation. Prolonged irradiation increased the resonance at 324.351 mT revealing overlapped singlet (fitted: 324.454 mT, $g = 2.0040$, $\Delta H_{pp} = 1.9$ mT) and doublet (322.596 and 326.697 mT, $g_{av} = 2.0029$, $D = 2.2$ mT) signals. The two signals intensified simultaneously with irradiation time and were stable indefinitely at 5 K. Upon warming to 300 K, 30% of the singlet and 50% of the doublet decayed with different rates (Fig. 7). The remaining radicals were stable in the dark for weeks, even in the presence of air.

Scattered reports on photoreactions of nitro aromatics were summarized by Ramamurthy and Venkatesan.¹⁹ The products, 2-nitrosobenzyl alcohols, were assumed to form through a diradical obtained by abstraction of the γ -hydrogen by the *o*-nitro group. Nitrosobenzyl alcohol is also obtained by partial decay of 2-nitrotoluene irradiated in solution.⁷ Instead, a structure of benzyl alcohol with an *o*-N(H)O $\cdot$ group was assigned to the radical species formed from several photoirradiated *o*-nitrobenzyl compounds.²⁰ In basic solutions, nitro aromatics

Table 1. Crystallographic data and experimental details for four side-products produced by the photolysis of 2-(2',4'-dinitrobenzyl)pyridine

Parameter	1	2 ^a	3	4
Empirical formula	C ₂₄ H ₁₆ N ₆ O ₈	C ₂₄ H ₁₄ N ₆ O ₇	C ₁₂ H ₇ N ₃ O ₃	C ₁₂ H ₉ N ₃ O ₃
Color	Colorless	Orange-red	Yellow	Red
Formula weight	516.43	498.42	241.21	259.22
Temperature (K)	296(2)	95(2)	95(2)	223(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> [−] 1	<i>P</i> [−] 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Diffractionmeter	SMART-CCD	SMART-CCD	SMART-CCD	R-AXIS RAPID
Unit cell dimensions	<i>a</i> = 9.1260(4) Å <i>b</i> = 10.9272(4) Å <i>c</i> = 13.8930(8) Å α = 101.437(2)° β = 107.156(3)° γ = 106.639(2)°	<i>a</i> = 6.1113(4) Å <i>b</i> = 9.8060(4) Å <i>c</i> = 10.1754(7) Å α = 63.007(2)° β = 87.333(2)° γ = 74.221(1)°	<i>a</i> = 10.7816(2) Å <i>b</i> = 3.7660(4) Å <i>c</i> = 25.2394(6) Å β = 98.728(1)°	<i>a</i> = 4.2493(1) Å <i>b</i> = 13.6055(7) Å <i>c</i> = 17.5911(1) Å β = 95.267(1)°
Volume (Å ³)	1206.35(10)	520.77(5)	1013.02(3)	1012.71(6)
<i>Z</i>	2	2	4	4
Density (calc.) (Mg m ^{−3})	1.422	1.589	1.582	1.596
Absorption coefficient (mm ^{−1})	0.110	0.118	0.118	0.119
<i>F</i> (000)	532	256	496	504
Crystal size (mm ³)	0.55 × 0.45 × 0.03	0.20 × 0.05 × 0.05	0.20 × 0.10 × 0.10	0.50 × 0.10 × 0.10
Theta range for data collection (°)	1.61 to 25.00	2.26 to 27.57	1.63 to 27.52	2.33 to 25.00
Index ranges	−7 ≤ <i>h</i> ≤ 10, −12 ≤ <i>k</i> ≤ 12 −16 ≤ <i>l</i> ≤ 16	−7 ≤ <i>h</i> ≤ 7 −12 ≤ <i>k</i> ≤ 12 −13 ≤ <i>h</i> ≤ 13	−13 ≤ <i>l</i> ≤ 13 −4 ≤ <i>k</i> ≤ 4 −32 ≤ <i>l</i> ≤ 32	−4 ≤ <i>h</i> ≤ 5 −15 ≤ <i>k</i> ≤ 16 −20 ≤ <i>l</i> ≤ 20
Reflections collected	6909	5219	9255	7367
Independent reflections	4155 [<i>R</i> (int) = 0.0486]	2359 [<i>R</i> (int) = 0.0501]	2303 [<i>R</i> (int) = 0.0633]	1751 [<i>R</i> (int) = 0.0825]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4155/0/345	2359/0/173	2303/0/163	1751/0/159
Goodness-of-fit on <i>F</i> ²	1.004	1.269	1.022	1.196
Final <i>R</i> indices	<i>R</i> ₁ = 0.0681 <i>wR</i> ₂ = 0.1462	<i>R</i> ₁ = 0.0630 <i>wR</i> ₂ = 0.1115	<i>R</i> ₁ = 0.0467 <i>wR</i> ₂ = 0.1102	<i>R</i> ₁ = 0.0728 <i>wR</i> ₂ = 0.1768
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1420, <i>wR</i> ₂ = 0.1844	<i>R</i> ₁ = 0.1446 <i>wR</i> ₂ = 0.1610	<i>R</i> ₁ = 0.0755 <i>wR</i> ₂ = 0.1248	<i>R</i> ₁ = 0.1123 <i>wR</i> ₂ = 0.2014
Largest diff. peak and hole (e Å ^{−3})	0.412/−0.249	0.579/−0.547	0.322/−0.317	0.315/−0.249

^a The molecule is centrosymmetric with respect to the center of the N=N bond.

**Scheme 2.** Dimerization of **OH•** to the side-product 1,2-bis(2',4'-dinitrophenyl)-1,2-bis(2'-pyridyl)ethane (**1**)**Scheme 3.** Possible routes for formation of **NH•** from **OH•** or **NH**

spontaneously produce radical anions.²¹ Consistent with the former assignment¹⁸ and the above ESR data on nitro aromatic compounds, the ESR spectra of photoirradiated DNBp confirm the creation of the **OH•** and **NH•** radicals that were assumed from the product analyses. The conformational similarity of the optimized radical structures [UB3LYP/6-31G(d) level, supplementary material, Table S1] with the molecular structure of **CH** in the crystal suggests that they can be produced and preserved in the crystalline lattice of **CH** without significant structural perturbation (Fig. 8). The spin isodensity surfaces calculated on the theoretical radical structures show that in both radicals the unpaired electrons are localized on the benzylic carbon atom.

Implications for the reaction mechanism

The above results confirm that the photofatigue of DNBp in the solid state (and probably in solution) is triggered by

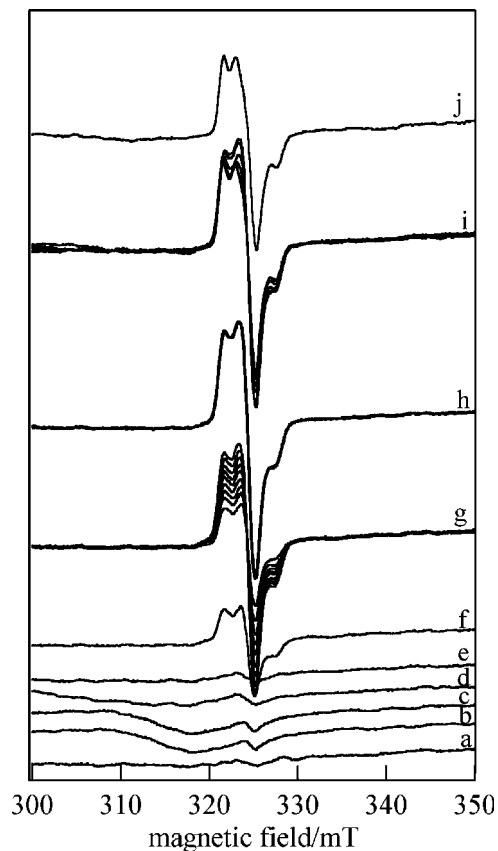


Figure 6. ESR spectra recorded from powdered DNBP. (a) Unirradiated, 5 K; (b) irradiated for 5 min with Xe lamp (400–800 nm), (c) irradiated for 15 min; (d) dark, heated to 20 K; (e) dark, cooled to 5 K; (f) irradiated for 60 min at 5 K; (g) irradiated for 75–195 min at 5 K; (h) dark, retained for 1 h at 5 K; (i) dark, heated from 5 to 250 K; (j) dark, room temperature; the spectrum remains unchanged for a long time in air

the creation of two radicals, ascribed to the structures $\text{NH}^\bullet$ and $\text{OH}^\bullet$. To investigate the reaction pathways that include the radicals, we monitored the evolution of NH and OH through the rapid-scan FTIR spectra of DNBP

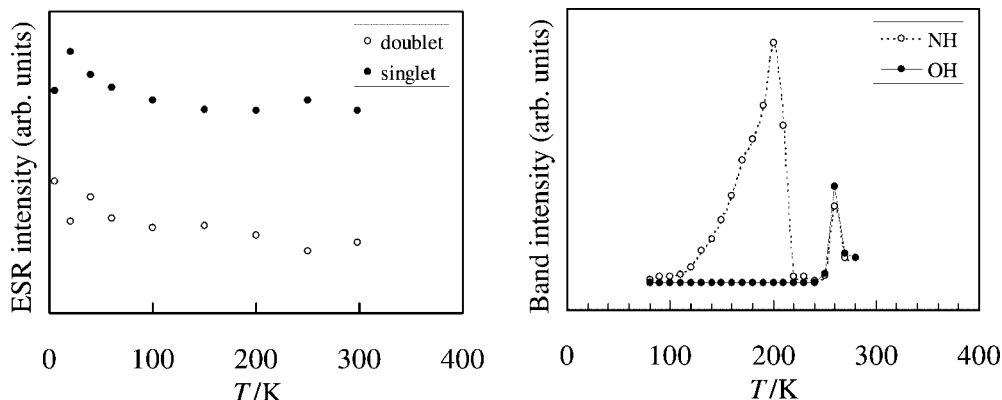


Figure 7. Thermal decay of the fitted intensities of the two ESR signals (left) and of the characteristic difference $\nu(\text{NH})$ and $\nu(\text{OH})$ bands (right) of photoirradiated DNBP. Irradiation conditions: Xe lamp through quartz windows (ESR) and high-pressure Hg lamp through quartz windows (IR). The intensity of the lowest points in the right-hand plot equals zero. The band intensities were not corrected for temperature effects

that was flashed with UV radiation at 80 K and then heated to room temperature in the dark (Fig. 9) (similar latent photochromism was also observed in the UV–visible–NIR spectra of single crystals of the *p*-azoxy dimer of DNBP). The temperature effects on the IR spectra were correlated with the respective ESR spectra (Fig. 7).

The difference IR bands, empirically assigned to the $\nu(\text{CH})$ (weak negative bands around 3010 cm^{-1}), $\nu(\text{NH})$ (complex band with submaxima at ca 3385 , 3238 and 3175 cm^{-1}) and $\nu(\text{OH})$ (3450 cm^{-1}) modes, respectively, were used as probes. The $\nu(\text{NH})$ mode of small amounts of NH in crystalline DNBP is usually observed as a very weak band at 3385 cm^{-1} and the $\nu(\text{ND})$ and $\nu(\text{OD})$ bands appear at 2507 and 2606 cm^{-1} , respectively. The appearance of two more components (3238 and 3175 cm^{-1}) besides the 3385 cm^{-1} $\nu(\text{NH})$ band (some of which may be due to $\text{NH}^\bullet$) remains unclear. A possible explanation may be that different conformer of NH is obtained by the radical thermal decay from that resulted by the proton transfer. The effects on the band intensities in Fig. 7 of concentration variations of NH and OH due to their decay during the experiment, the temperature effects and the ‘negative’ band at 3213 cm^{-1} were not accounted for.

After the sample had been flashed at 80 K with UV radiation, $\nu(\text{CH})$ modes appeared as weak negative bands, while only a very weak $\nu(\text{NH})$ band and no $\nu(\text{OH})$ bands could be observed. This indicated photodecay of CH , creation of a very small amount of NH and practically no significant amounts of OH . The ESR spectra, on the other hand, clearly suggest the creation of the radicals at any temperature within the range 5–300 K. It can be concluded, therefore, that at low temperature, photoexcited CH decays mainly to the radicals and small amounts of NH , probably through reaction(s) from its excited state.

The FTIR spectra indicate that upon warming in the dark the amount of NH initially increases and

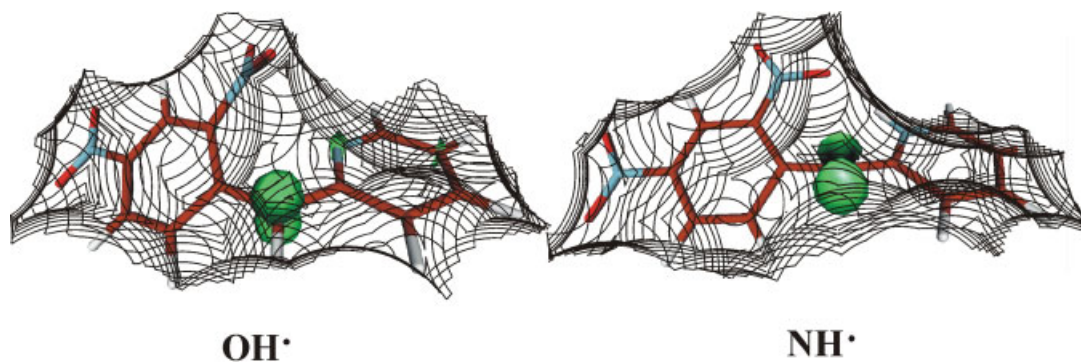


Figure 8. Theoretical [UB3LYP/6-31G(d)] structures of the radicals **OH•** and **NH•** and the respective spin isodensity surfaces co-plotted with the experimental cavities of **CH** molecules in crystalline DNBP. The cavities are represented as intersected surfaces of overlapping spheres at 1.2 Å from the respective van der Waals radii (C, 1.700; H, 1.200; N, 1.550; O, 1.520 Å). The contour lines represent steps of 0.2 Å. (For definition of the reaction cavity, see Refs 28 and 29) (This figure is available in colour online)

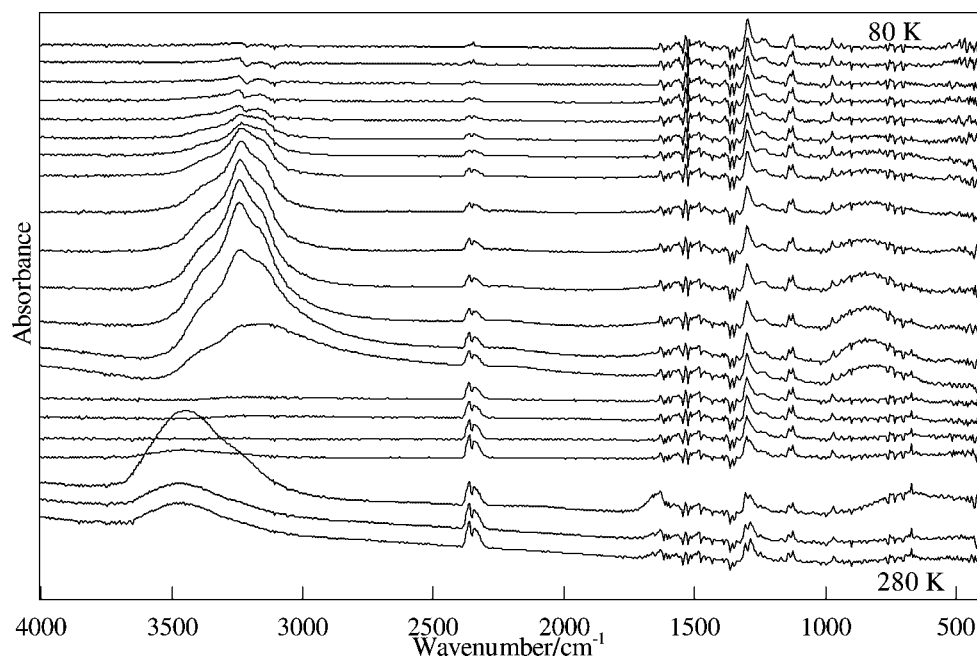


Figure 9. Difference rapid-scan FTIR spectra of DNBP irradiated (1 min) through the quartz windows of a low-temperature cell at 80 K and then warmed in the dark to ambient temperature. The spectra were recorded by heating at 10 K intervals; the temperature increases from the top spectrum downwards. The difference spectra were obtained by subtraction of the spectrum of the unirradiated sample from the respective spectra after irradiation at each temperature

subsequently decreases (Fig. 7, right plot). The temperature of the maximum integrated absorption of the **NH** band (190 K) corresponds well with the range 150–200 K where the doublet signal (**OH•**) reaches a local maximum and the singlet signal (**NH•**) is at a local minimum (Fig. 7, left plot). This supports the assumption that the **NH** form is created from the radical species. At 220 K, most of the **NH** produced thermally from the radicals decayed to **CH**, which is reflected in the disappearance of the $\nu(\text{NH})$ band (Fig. 7). Upon warming above 240 K, the $\nu(\text{OH})$ band appears, increases and subsequently decreases. This indicates that **OH** is thermally produced from the remaining radicals. The **OH** isomer reaches maximum concentration at 260 K. At higher temperatures it decays thermally to the metastable isomer **NH** (presence of an

overlapped shoulder around 3380 cm^{-1}) and the stable isomer **CH** (disappearance of the weak negative bands around 3010 cm^{-1}). On the basis of the above discussion, the **NH•** and **OH•** radicals can be identified as the long-lived ($>16\text{ h}$ at 77 K) intermediate whose existence was assumed previously¹⁰ and the extended reaction mechanism in Scheme 4 for the photoreactions in DNBP can be proposed.

Are the radicals identical with the precursor state?

The recent spectroscopic measurements of Casalegno and co-workers on DNBP in the crystalline state¹¹ and

(38–70 min), 100% EtOH, 1 mL/min⁻¹ (70–80 min)] and preparative [pump, L-6250; column, Chiralpak AD (Daisel Chem), sample, 5 mL] scales. After 296 h of irradiation, a total of 14 peaks were observed (denoted peaks 1–14 from lower retention times upwards in Fig. 2). The following peaks were identified with the products isolated by TLC: peak 2, **B5** (side-product 2); peak 3, **B7**; peak 4, side-product 1; peak 7, **A9** (side-product 3); peak 11, **A3**; peak 12, **A4** (side-product 4). Bulk samples were irradiated under a similar regime at 275–278 and 298 K and analyzed by preparative HPLC and TLC. In addition to the highly intractable dark brown material at $R_f = 0.0$ (**A0**, 8.7%), nine components were isolated by TLC, **A1**–**A9** (R_f , w): **A1** (0.02, 12.3%); **A2** (0.05, 3.3%); **A3** (0.08, 5.4%, red on TLC); **A4** (0.11, 6.4%, yellow on TLC); **A5** + **A6**, not separated (0.23, 8.4%); **A7** (0.35, 5.1%); **A8** (0.47, 44.7%, DNBP); **A9** (0.60, 5.6%, yellow on TLC). **A7** was identified from the analytical data as unreacted DNBP. **A5** and **A6** could not be separated satisfactorily; the structure of the azoxybenzene dimer was determined from a crystal obtained from their mixture. These two products gave the only result that was not readily reproducible: in several TLC experiments, either one or two components with very close R_f formed owing to secondary chemical reactions. The colorless **A5**, isolated by preparative HPLC, always yielded complex mixtures, which also contained **A6** and **A3**. The dimer 1,2-bis(2',4'-dinitrophenyl)-1,2-bis(2'-pyridyl)ethane (side product 1) was isolated as the first fraction with column chromatography (Al_2O_3 , gradual elution with CH_2Cl_2 in hexane) from the DNBP photolyzate that was kept in air. Secondary reactions proceeded in several other photoproducts. For the experiment at 275–278 K, DNBP powder (0.134 g) was placed on a cold plate and irradiated with filtered (Y-43) output from an Xe lamp for 11 days. At least seven components could be identified, with R_f values of 0.00, 0.01, 0.03 (yellowish), 0.06 (yellow), 0.40 (DNBP), 0.62 and 0.77. The products were extracted as described above.

Anaerobic solid-state photolysis. DNBP (44 mg) was sealed in a glass ampule under argon, attached to a cold plate (275 K) and irradiated with unfiltered output from Xe lamp for 10 days. Whereas on the upper side the substrate turned dark, the lower side turned intense blue. After exposure to air, the residue afforded at least seven products that were separated by TLC [Al_2O_3 /hexane–EtOAc (7:3)] with $R_f = 0.00$ (dark), 0.05 (red), 0.09 (yellow), 0.20, 0.41 (DNBP) and 0.64.

Aerobic solution-state photolysis. DNBP (29 mg) dissolved in anhydrous undegassed acetonitrile (6 mL, 99.8%; Aldrich SureSeal) was placed in quartz cuvettes on a cold plate at 275 K. During irradiation for 9 days, 4.8 mL of acetonitrile were added to refill the evaporated solvent. The acetonitrile was then evaporated at room temperature and the residue was analyzed by TLC

[Al_2O_3 /hexaneEtOAc (7:3)] as described for the solid DNBP. In addition to the dark residue at $R_f = 0.00$ (9.3%), nine components were isolated from the mixture (R_f , w): **B1** (0.01, 6.2%); **B2** (0.05, 8.2%); **B3** (0.11, 11.3%, yellow); **B4** (0.18, 9.3%); **B5** (0.22, 8.2%); **B6** (0.33, 4.1%); **B7** (0.37, 6.2%, yellow); **B8** (0.50, 26.8%, DNBP); **B9** (0.91, 10.3%).

Aerobic solution-state photolysis in presence of a triplet quencher. DNBP (7.4 mg) in anhydrous acetonitrile (6 mL, 99.8%; Aldrich SureSeal) with five drops of 2,5-dimethyl-2,4-hexadiene was placed in a quartz cuvette on a cold plate at 275 K. The solution when irradiated with unfiltered Xe lamp light turned yellow and then dark. The solvent was then evaporated and the residue was analyzed by TLC as described above. As many as 18 components, **C0**–**C17**, were isolated by preparative TLC with R_f values [Al_2O_3 /hexane–EtOAc (7:3)] of 0.00 (dark), 0.03, 0.06, 0.11 (yellow), 0.15, 0.21, 0.24 (red), 0.30 (yellow), 0.37 (yellowish), 0.41, 0.44 (yellow), 0.48 (yellow), 0.56 (yellow), 0.65 (yellow), 0.75, 0.78, 0.84 and 0.92.

Single-crystal photocrystallographic study. A Quanta-Ray MOPO-SL optical parametric oscillator pumped with a pulsed Quanta-Ray Nd:YAG laser was used as monochromatic source. High-pressure Hg and Xe arc lamps were used as polychromatic sources. The combined optical outputs were all focused on a single crystal of DNBP affixed on the goniometer head of the CCD diffractometer and data were collected at each stage of irradiation. The colorless crystal was irradiated during 0.25 h with $\lambda < 440$ nm (Hg lamp, UV-D33S filter) (λ_1) and the data were collected from the blue crystal. The respective data are represented as the point $t = 0$ in Fig. 3. At $t = 0$ the data collection was started together with the irradiation with 600 nm (λ_3) laser pulses for 0.67 h, whereupon the crystal turned yellow. After about 4 h the data collection was over; the respective data are plotted as the point $t = 4$ h. The yellow crystal was then bleached with 400–440 nm light (λ_2) (Hg lamp, O-56 filter and Xe lamp, UV-D33S filter), left in the dark for some time and the data were collected again; the respective parameters are plotted as the point $t = 13.2$ h. Further irradiation was carried out with unfiltered output from an Xe lamp at $\lambda = 540$ –800 nm. Each remaining point in Fig. 3 corresponds to the end of each data collection in respect to $t = 0$.

X-ray diffraction. X-ray data were collected either with a SMART-CCD diffractometer,²² equipped with the Rigaku liquid nitrogen cooling system, or with a Rigaku R-AXIS RAPID IP diffractometer.²³ The choice of the crystal size was limited by the small amount of the products available. The structures were solved by direct methods²⁴ and refined²⁵ on F^2 (Table 1). The non-H atoms were refined anisotropically and the aromatic

hydrogen atoms were included as riding bodies. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication No. CCDC 213691–213694.

ESR spectra. The ESR spectra from powdered DNBP were recorded on a JES-TE2000 spectrometer (Jeol) equipped with liquid He cryostat. The sample was irradiated with an Xe arc lamp through the quartz window.

IR spectra. The FTIR spectra were recorded in the rapid-scan mode from KBr pellets with an Excalibur FTS 3000 instrument (Bio-Rad). The samples were irradiated for 1 min with an unfiltered high-pressure Hg lamp through the double quartz windows of a temperature-controlled cell (Oxford Instruments) with double KSR5 windows for the probe beam. Conditions for spectral recording were sample/background 32/16, resolution 4 cm⁻¹, and interval 4000–400 cm⁻¹.

Theoretical calculations. All theoretical calculations were performed with the *Gaussian* 98 program suite²⁶ running on an SGI Origin2000 supercomputer. Ground-state models of isolated monomers geometrically close to the crystal **CH** structure were analytically optimized at the UB3LYP/6–31G(d) level.²⁷ The Cartesian coordinates of the optimized radical structures are deposited (Table S1).

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Supplementary material

The Cartesian coordinates of the theoretical structures of the two radicals (Table S1) are available on Wiley Interscience.

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