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Effects of Crystal Packing on Photoinduced Proton-Transfer Processes of 2,4-Dinitrobenzylpyridine Derivatives

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Abstract

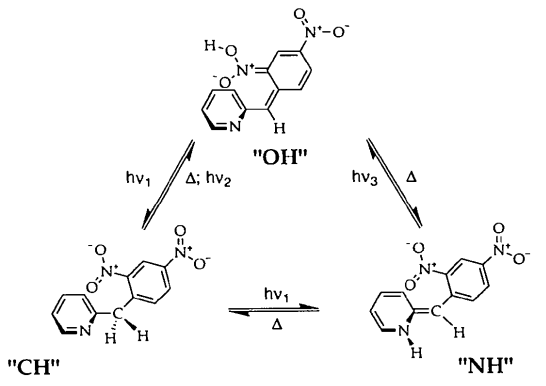
Photoinduced and thermally activated proton-transfer processes taking place in crystals of 2-(2,4-dinitrobenzyl)pyridine and some of its derivatives are highly sensitive to molecular packing. Small differences in the way the molecules are packed in the crystal are found to dominate molecular properties in controlling the photoactivity of the different phototautomers, leading, for example, to photoactive or photoinert systems. Three compounds, 2-(2,4-dinitrobenzyl)-4-methylpyridine, 1-(2,4-dinitrophenyl)-1-(2-pyridine)ethane and 4′-(2,4-dinitrobenzyl)-4-methyl-2,2′-bipyridine, having different photochemical properties, were prepared and their crystal structures characterized by means of X-ray analysis. In the photoinert crystals the 2,4-dinitrophenyl group is π-stacked with other aromatic rings of neighboring molecules. This arrangement may open some deactivation channels to the excited state which are faster than the proton-transfer process, leading to photoinert crystals. The absence of π-stacking between the chromophore and other aromatic rings leads to photoactive systems. An O atom of the *o*-nitro group is the only basic atom that is systematically found to interact with the abstracted proton. It seems that this atom is responsible for the photoinduced proton abstraction of the benzylic H atom, while the role of the N atom of the pyridine ring in the proton-abstraction process is mainly inductive.

1. Introduction

Photoinduced and thermally activated inter- and intramolecular transformations provide the means to control the physical properties of molecular and supramolecular species such as catenanes (Vögtle, Müller, Müller, Bauer & Rissanen, 1993), host molecules (Willner, Marx & Eichen, 1992; Willner, Eichen, Doron & Marx, 1992; Würthner & Rebek, 1995), biological materials (Willner & Rubin, 1996; Osterhelt, Bräuchle & Hampp, 1991), polymeric films and membranes (Willner, Sussan & Rubin, 1991; Mamada, Tanaka, Kungwatchakun & Irie, 1990; Irie & Iga, 1986; Drain, Cristensen & Mauzerall, 1989), glasses and supercooled melts (Khatib, Poplawski & Eichen, 1997), and crystals (Eichen *et al.*, 1995; Scherl *et al.*, 1996). The development of such tunable materials is an important step towards the control of processes at the molecular level.

Induced proton-transfer (PT) and proton-mediated electron-transfer processes are of particular interest to this field since they present a number of unique properties (Bell, 1973; Jeffrey & Saenger, 1991; Kosower & Huppert, 1986; Philips, 1973; Porter, 1967; Weller, 1961): (*a*) Tautomerization processes in protonic systems do not necessarily require large structural reorganization and therefore can take place in the solid state, be it amorphous or crystalline, even at very low temperatures. (*b*) Proton-transfer processes are among the fastest reactions competing with most of the nonreversible parasitic processes and thus often lead to fatigue-resistant switch systems. (*c*) Proton-transfer reactions can be thermo-, photo-, electro- and even piezo-induced, ensuring a wide scope of potential applications for such systems. (*d*) Protonic systems may be designed to self-assemble into large and well defined supramolecular assemblies where the monomers are interconnected *via* hydrogen bonds and other noncovalent interactions.

One of the most interesting solid-state photoactive proton-transfer processes is the photoinduced proton transfer taking place in crystals of 2-(2,4-dinitrobenzyl)pyridine [α-DNBP (1) (Chichibabin, Kuindzhi & Benewolenskaja, 1925)] and some of its derivatives. Previous reports referred to the question of the reaction path and concluded that the transfer is intramolecular on the basis of the crystal structure of (1) (Seff & Trueblood, 1968). Detailed optical spectroscopic characterization of 2-(2,4-dinitrobenzyl)pyridine and some of its derivatives in the crystalline state (Sixl & Warta, 1985; Eichen *et al.*, 1995; Scherl *et al.*, 1996) have led to the proton-transfer mechanism outlined in Scheme I. The nature of the excited states responsible for the photoactivity of nitroaromatic compounds, especially in the crystalline state, is characterized only in some cases (Döpp, 1975; Dürr & Bouas-Laurant, 1990, and references therein; Sarma & Desiraju, 1985).



(I)

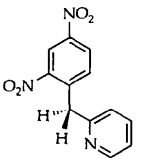
However, not all the 2-(2,4-dinitrobenzyl)pyridine derivatives are photoactive. Some of the molecules prepared in recent years, such as 2-(2,4-dinitrobenzyl)phenanthroline, were reported to be photoinert (Scherl *et al.*, 1996). Another DNBP derivative, 6-(2,4-dinitrobenzyl)-2,2′-bipyridine, forms two different polymorphs, one photochromic and the other photoinert (Eichen *et al.*, 1995). This example emphasizes the strong influence of the differences in the supramolecular interactions found in the different crystals on their photochemical properties.

In similar cases, such as in the case of salicylideneaniline and its derivatives, the differences in the photochemical properties observed for the various crystals was correlated with the differences in the free volume available in the crystal lattice (Schmidt, 1976; Aldoshin & Chue, 1994, and references therein). Salicylideneanilines crystallize in two different packing patterns: (i) Crystals with aromatic rings tightly π-stacked together. In this type of packing the molecules are planar and densely packed. These crystals are photoinert and generally thermochromic. (ii) Less densely packed crystals where the aromatic rings are not π-stacked. In this type of packing the molecules are not planar and therefore less densely packed. These crystals are photoactive and the phototautomers are not always thermally accessible.

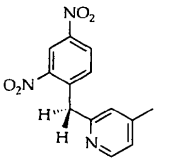
It was therefore suggested that the differences in photoactivity originate from the differences in the free volume of the crystals. This suggestion was based, in part, on the lack of any D/H isotope effect for the photocoloration reaction (Cohen, Schmidt & Flavian, 1964), indicating that the process is not merely a simple proton-transfer reaction, but rather an important skeletal reorganization associated with a proton-transfer process.

In the case of 2-(2,4-dinitrobenzyl)pyridine and its derivatives, a high primary isotope effect was reported (Eichen *et al.*, 1995; Scherl *et al.*, 1996), indicating a process that requires only little structural reorganization. Furthermore, no evident correlation between the crystal density and photoactivity could be drawn on the basis of the known structures. The molecule contains one sp^3 carbon connecting the two aromatic rings and therefore may not be planarized. Based on previously reported crystal structures of 2,4-dinitrobenzylpyridine derivatives and on the observation that the photoinduced proton-transfer process is a true bulk effect and is not restricted to defect sites (Scherl *et al.*, 1996), two alternative approaches were proposed for the rationalization of the differences between photoactive and photoinert systems: (i) close-contact π–π interactions between the 2,4-dinitrobenzyl chromophore of one molecule and other neighboring aromatic rings exist only in photoinert crystals. On the other hand, in the photoactive crystals the 2,4-dinitrobenzyl chromophore is relatively isolated and with no close inter-ring contacts to any other aromatic ring. It was suggested that in structures where the 2,4-dinitrobenzyl chromophore is tightly stacked with aromatic systems of neighboring molecules, deactivation pathways that are faster than proton transfer may be envisaged due to stronger electronic coupling between the excited chromophore and other π-systems. These new deactivation routes may lead to photoinert crystals. This argument may be backed by many examples from the salicylideneaniline series (Schmidt, 1976; Aldoshin & Chue, 1994, and references therein; Kawato, Koyama, Kanatomi, Yonatani & Matsushita, 1994; Kawato, Koyama, Kanatomi, Tagawa & Iga, 1994; Hoshino, Inabe, Mitani & Maruyama, 1988), where tight molecular arrangement due to π-stacking results with a lack of photoactivity. Fig. 1 presents the molecular arrangement found in (*a*) the photoactive and (*b*) the photoinert phase of the 6-(2,4-dinitrobenzyl)-2,2′-bipyridine system (Eichen *et al.*, 1995) as an example for the different packing patterns found in 2,4-dinitrobenzylpyridine derivatives. (ii) The photoinduced proton-transfer process involves the abstraction of a carbon-bound proton. This implies a relatively high activation barrier for the process. Therefore, this reaction may require a significant activation of the benzylic proton by both the O atom of the *o*-nitro group and the N atom of the pyridine group. According to previously reported crystal structures, all the photoactive systems have both the O atom of the *o*-nitro group and the N atom of the pyridine ring interacting with the same benzylic proton and situated on the same side of the molecule. It was suggested that this arrangement allows the lowering of the barrier for the proton abstraction by forming some kind of a low energy path to deprotonation (Scherl *et al.*, 1996). In all known photoinert structures, at least one of these two requirements is not fulfilled. For example, Fig. 2 presents the different molecular conformations found in (i) the photoactive and (ii) the photoinert phases of the 6-(2,4-dinitrobenzyl)-2,2′-bipyridine system (Eichen *et al.*, 1995). It is evident that in the photoinert structure the two basic atoms interact with different H atoms, in contrast to the photoinert structure where the two basic groups interact with the same benzylic H atom.

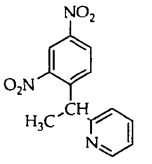
In order to better understand the structural factors controlling the photoactivity of this class of compound, three compounds: 4-methyl-2-(2,4-dinitrobenzyl)pyridine (2), 1-(2-pyridine)-1-(2,4-dinitrophenyl)ethane (3) and 4-methyl-4′-(2,4-dinitrobenzyl)-2,2′-bipyridine (4), having different photochemical proton-transfer responses, were prepared and their crystal structure determined by X-ray analysis.



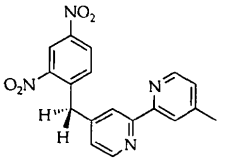
(1)



(2)



(3)



(4)

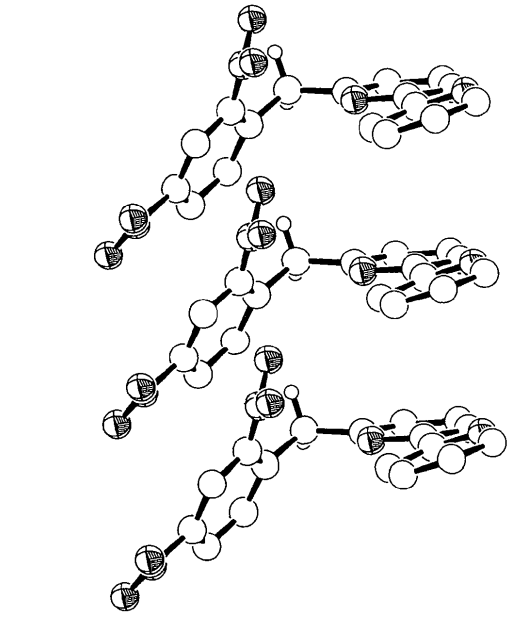
2. Experimental

2.1. *Crystal growth*

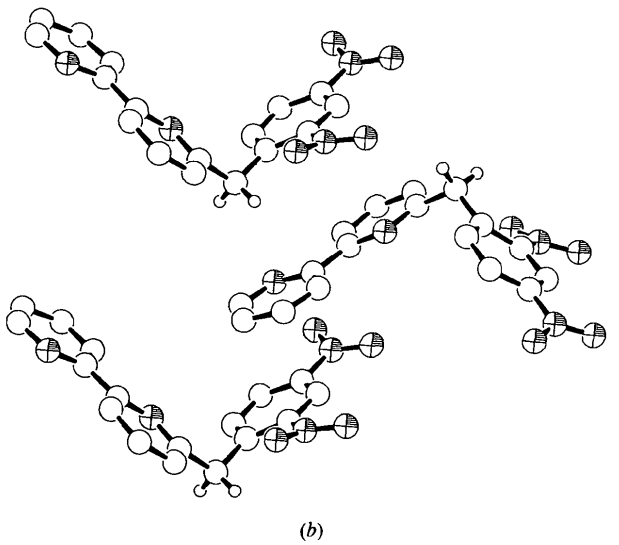
The synthesis of (2), (3) and (4) is reported elsewhere [(2) and (3): Khatib & Eichen (1997); (4): Corval, Kuldova, Trommsdorff, Eichen & Lehn (1997)]. Crystals of (2), (3) and (4) were obtained by recrystallization from absolute ethanol after careful purification by means of flash chromatography (alumina/dichloromethane:hexane mixtures).

2.2. *Data collection and refinement*

All X-ray diffraction data were collected at room temperature on a Philips PW 1100 four-circle computer-controlled diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.7107 Å) with $\omega/2\theta$ scans (scan width: 1.2°, scan rate: 3° min^{-1}). Unit-cell parameters were determined by a least-squares fitting of the setting angles of 25 centered reflections in the range 2.2 < θ



(*a*)



(*b*)

Fig. 1. A schematic representation of the molecular arrangement of 6-(2,4-dinitrobenzyl)-2,2′-bipyridine in (*a*) the photoactive and (*b*) the photoinert phases (Eichen *et al.*, 1995).

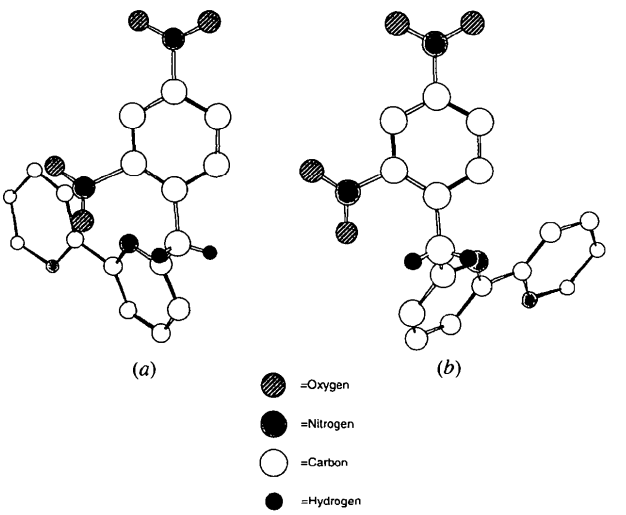


Fig. 2. A schematic representation of the molecular conformations of 6-(2,4-dinitrobenzyl)-2,2′-bipyridine found in (*a*) the photoactive and (*b*) the photoinert phases (Eichen *et al.*, 1995).

Table 1. *Experimental details*

	(2)	(3)	(4)
Crystal data			
Chemical formula	$C_{13}H_{11}N_3O_4$	$C_{13}H_{11}N_3O_4$	$C_{18}H_{14}N_4O_4$
Chemical formula weight	273.25	273.5	350.33
Cell setting	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	11.210 (3)	10.214 (3)	9.941 (3)
b (Å)	15.181 (4)	13.221 (4)	11.195 (3)
c (Å)	7.734 (2)	10.068 (3)	15.463 (5)
α (°)		92.12 (3)	
β (°)	102.75 (3)	105.29 (3)	102.29 (3)
γ (°)		89.55 (3)	
V (Å^3)	1283.7 (6)	1310.6 (7)	1681.4 (9)
Z	4	4	4
D_x (Mg m^{-3})	1.414	1.385	1.384
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71070	0.71070	0.71070
No. of reflections for cell parameters	25	25	25
θ range (°)	2.2–11.3	2.5–11.7	2.7–11.2
μ (mm^{-1})	0.108	0.105	0.101
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form	Triangular wedges	Plate	Plate
Crystal size (mm)	1.33 × 0.78 × 0.65	0.78 × 0.4 × 0.2	0.36 × 0.32 × 0.13
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Philips PW 1100 four-circle	Philips PW 1100 four-circle	Philips PW 1100 four-circle
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None	None
No. of measured reflections	1776	3649	2425
No. of independent reflections	1665	3414	2332
No. of observed reflections	1458	2011	1441
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0644	0.0301	0.0347
θ_{max} (°)	23.93	22.50	23.00
Range of h, k, l	$0 \rightarrow h \rightarrow 11$	$-12 \rightarrow h \rightarrow 11$	$-10 \rightarrow h \rightarrow 10$
	$0 \rightarrow k \rightarrow 17$	$-15 \rightarrow k \rightarrow 15$	$0 \rightarrow k \rightarrow 12$
	$-8 \rightarrow l \rightarrow 8$	$0 \rightarrow l \rightarrow 11$	$0 \rightarrow l \rightarrow 16$
No. of standard reflections	3	3	3
Frequency of standard reflections (min)	120	120	120
Intensity decay (%)	25	4	1.4
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0566	0.0640	0.0575
$wR(F^2)$	0.2130	0.2129	0.1723
S	1.262	1.183	1.108
No. of reflections used in refinement	1659	3312	2323
No. of parameters used	226	449	291
H-atom treatment	Isotropic	Isotropic	Isotropic
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1023P)^2 + 0.9019P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 0.9773P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0105P)^2 + 1.1033P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.038	−0.040	0.030
$\Delta\rho_{max}$ (e Å^{-3})	0.437	0.143	0.228
$\Delta\rho_{min}$ (e Å^{-3})	−0.457	−0.210	−0.163
Extinction method	*SHELXL*93 (Sheldrick, 1993)	None	None
Extinction coefficient	0.0754 (117)	–	–
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	Philips PW 1100/20 (Philips, 1973)	Philips PW 1100/20 (Philips, 1973)	Philips PW 1100/20 (Philips, 1973)
Cell refinement	Philips PW 1100/20 (Philips, 1973)	Philips PW 1100/20 (Philips, 1973)	Philips PW 1100/20 (Philips, 1973)
Data reduction	*PROCN* (Philips, 1973)	*PROCN* (Philips, 1973)	*PROCN* (Philips, 1973)
Structure solution	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)	*SHELXS*86 (Sheldrick, 1990)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)

< 11.5°. The intensities of three standard reflections were measured every 120 min during the data collection. Decays of 25, 4 and 1.4% were observed for (2), (3) and (4), respectively. A decay correction was applied only for (2). All non-H atoms were found by direct methods and refined anisotropically. H atoms were found using a difference-Fourier map and refined isotropically. All experimental details are summarized in Table 1.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
2-(2,4-Dinitrobenzyl)-4-methylpyridine (2)				
C1	0.2951 (4)	0.5585 (3)	0.4277 (5)	0.0582 (12)
C2	0.3437 (4)	0.4916 (3)	0.5374 (5)	0.0545 (11)
C3	0.3610 (3)	0.4101 (3)	0.4675 (5)	0.0504 (10)
C4	0.3284 (3)	0.4030 (3)	0.2848 (5)	0.0504 (10)
C5	0.2816 (3)	0.4737 (2)	0.1820 (5)	0.0434 (10)
C6	0.2501 (4)	0.4639 (3)	−0.0177 (5)	0.0528 (11)
C7	0.1793 (3)	0.5377 (2)	−0.1216 (4)	0.0435 (10)
C8	0.0617 (4)	0.5209 (3)	−0.2231 (5)	0.0511 (11)
C9	−0.0066 (4)	0.5845 (3)	−0.3265 (5)	0.0529 (11)
C10	0.0401 (3)	0.6679 (2)	−0.3263 (5)	0.0470 (10)
C11	0.1528 (3)	0.6899 (2)	−0.2251 (5)	0.0455 (10)
C12	0.2203 (3)	0.6243 (2)	−0.1276 (4)	0.0416 (9)
C13	0.4117 (6)	0.3343 (4)	0.5848 (8)	0.078 (2)
N1	0.2620 (3)	0.5516 (2)	0.2499 (4)	0.0537 (9)
N2	0.3423 (3)	0.6502 (2)	−0.0277 (4)	0.0494 (9)
N3	−0.0319 (3)	0.7365 (3)	−0.4355 (5)	0.0633 (10)
O2	0.3525 (3)	0.7219 (2)	0.0468 (4)	0.0660 (9)
O1	0.4273 (3)	0.6001 (2)	−0.0256 (4)	0.0730 (10)
O3	0.0004 (3)	0.8125 (2)	−0.4087 (5)	0.0830 (11)
O4	−0.1179 (4)	0.7132 (3)	−0.5517 (6)	0.1046 (14)
1-(2,4-Dinitrophenyl)-1-(2-pyridine)ethane (3)				
C1*A*	−0.0752 (6)	0.6362 (5)	0.2579 (7)	0.080 (2)
C2*A*	−0.0643 (6)	0.6754 (5)	0.3871 (7)	0.082 (2)
C3*A*	0.0503 (7)	0.6528 (5)	0.4878 (7)	0.088 (2)
C4*A*	0.1481 (7)	0.5934 (5)	0.4526 (6)	0.078 (2)
C5*A*	0.1283 (4)	0.5557 (3)	0.3182 (5)	0.0530 (12)
C6*A*	0.2312 (5)	0.4869 (4)	0.2750 (5)	0.0578 (13)
C7*A*	0.2920 (4)	0.5365 (3)	0.1698 (4)	0.0501 (11)
C8*A*	0.2216 (5)	0.5381 (4)	0.0314 (5)	0.0664 (14)
C9*A*	0.2695 (6)	0.5836 (4)	−0.0680 (6)	0.0688 (15)
C10*A*	0.3952 (5)	0.6276 (4)	−0.0294 (5)	0.0621 (13)
C11*A*	0.4748 (5)	0.6269 (4)	0.1041 (5)	0.0566 (13)
C12*A*	0.4191 (4)	0.5830 (3)	0.2005 (4)	0.0510 (12)
C13*A*	0.1652 (7)	0.3834 (5)	0.2201 (8)	0.081 (2)
N1*A*	0.0171 (4)	0.5767 (3)	0.2201 (4)	0.0669 (11)
N2*A*	0.5083 (5)	0.5862 (3)	0.3447 (5)	0.0722 (12)
N3*A*	0.4511 (6)	0.6782 (4)	−0.1335 (5)	0.0846 (14)
O1*A*	0.4561 (4)	0.6106 (3)	0.4380 (4)	0.0933 (13)
O2*A*	0.6278 (4)	0.5676 (3)	0.3584 (4)	0.1059 (14)
O3*A*	0.5666 (5)	0.7113 (3)	−0.0964 (5)	0.109 (2)
O4*A*	0.3758 (6)	0.6870 (4)	−0.2478 (5)	0.141 (2)
C1*B*	0.7386 (10)	0.1482 (5)	−0.0795 (7)	0.094 (2)
C2*B*	0.8658 (13)	0.1877 (5)	−0.0676 (11)	0.115 (3)
C3*B*	0.9684 (11)	0.1627 (7)	0.0419 (11)	0.120 (3)
C4*B*	0.9422 (7)	0.1002 (6)	0.1371 (8)	0.092 (2)
C5*B*	0.8122 (5)	0.0628 (4)	0.1209 (5)	0.0627 (13)
C6*B*	0.7785 (5)	−0.0090 (4)	0.2223 (5)	0.0586 (13)
C7*B*	0.6771 (4)	0.0389 (3)	0.2937 (4)	0.0524 (12)
C8*B*	0.5383 (5)	0.0377 (4)	0.2264 (5)	0.0618 (13)
C9*B*	0.4422 (6)	0.0780 (4)	0.2868 (6)	0.070 (2)
C10*B*	0.4825 (5)	0.1224 (4)	0.4168 (6)	0.0608 (13)
C11*B*	0.6157 (6)	0.1258 (4)	0.4878 (6)	0.0623 (14)
C12*B*	0.7109 (5)	0.0850 (4)	0.4253 (5)	0.0573 (12)
C13*B*	0.7282 (8)	−0.1107 (5)	0.1491 (7)	0.077 (2)
N1*B*	0.7098 (4)	0.0869 (3)	0.0138 (4)	0.0731 (12)
N2*B*	0.8536 (5)	0.0920 (4)	0.5095 (5)	0.0796 (13)
N3*B*	0.3792 (6)	0.1648 (4)	0.4832 (6)	0.0837 (14)
O1*B*	0.9429 (4)	0.1068 (3)	0.4526 (4)	0.1003 (14)
O2*B*	0.8726 (4)	0.0842 (4)	0.6347 (4)	0.120 (2)
O3*B*	0.4179 (5)	0.1944 (3)	0.6045 (5)	0.1030 (14)
O4*B*	0.2615 (5)	0.1644 (4)	0.4153 (6)	0.126 (2)
4′-(2,4-Dinitrobenzyl)-4-methyl-2,2′-bipyridine (4)				
C1	0.1499 (6)	−0.0740 (5)	0.9356 (4)	0.106 (2)
C2	0.1938 (5)	−0.0037 (4)	1.0079 (3)	0.0857 (14)
C3	0.2974 (4)	0.0783 (3)	1.0057 (2)	0.0655 (10)
C4	0.3483 (4)	0.0809 (4)	0.9294 (3)	0.0695 (11)
C5	0.2990 (4)	0.0061 (4)	0.8596 (3)	0.0653 (10)
C6	0.3554 (5)	0.1558 (5)	1.0851 (3)	0.0828 (14)
C7	0.2479 (4)	0.2142 (3)	1.1274 (2)	0.0603 (10)
C8	0.2335 (5)	0.1737 (4)	1.2094 (3)	0.0759 (12)
C9	0.1353 (5)	0.2179 (4)	1.2518 (3)	0.0792 (13)
C10	0.0496 (4)	0.3057 (4)	1.2101 (3)	0.0692 (11)
C11	0.0577 (4)	0.3493 (4)	1.1286 (3)	0.0685 (11)
C12	0.1571 (4)	0.3021 (3)	1.0890 (2)	0.0588 (10)
C13	0.3578 (4)	0.0051 (4)	0.7788 (3)	0.0678 (11)
C14	0.5167 (5)	0.0830 (5)	0.7070 (4)	0.0913 (15)
C15	0.4823 (6)	0.0021 (5)	0.6389 (4)	0.095 (2)
C16	0.3781 (5)	−0.0789 (5)	0.6390 (3)	0.0866 (14)
C17	0.3157 (5)	−0.0758 (4)	0.7116 (3)	0.0778 (12)
C18	0.3322 (10)	−0.1678 (9)	0.5654 (5)	0.131 (3)
N1	0.1987 (4)	−0.0724 (3)	0.8618 (2)	0.0889 (11)
N2	0.1622 (5)	0.3518 (3)	1.0013 (2)	0.0874 (11)
N3	−0.0562 (5)	0.3541 (4)	1.2540 (4)	0.1095 (15)
N4	0.4579 (3)	0.0860 (3)	0.7775 (2)	0.0791 (10)
O1	0.2687 (4)	0.3503 (3)	0.9751 (2)	0.1192 (13)
O2	0.0522 (5)	0.3881 (4)	0.9573 (2)	0.147 (2)
O3	−0.1429 (5)	0.4199 (4)	1.2100 (4)	0.158 (2)
O4	−0.0528 (5)	0.3265 (4)	1.3299 (3)	0.152 (2)

Table 3. *Significant intramolecular dimensions* (Å,°)*

Crystal	(2)	(3*A*)†	(3*B*)†	(4)
Pyridine–phenyl (°)	56.9 (4)	115.1 (4)	114.8 (4)	87.8 (4)
Pyridine–pyridine (°)	–	–	–	5.9 (5)
o-Nitrophenyl (°)	41.7 (4)	44.4 (4)	35.7 (4)	28.1 (4)
p-Nitrophenyl (°)	15.3 (4)	7.1 (4)	6.3 (4)	9.4 (4)
N2—H61 (Å)*	2.86 (6)	2.68 (6)	2.67 (6)	2.98 (6)
	[2.88 (6)]	[2.66 (6)]	[2.64 (6)]	[2.98 (6)]
N2—H61—C6 (°)	89.3 (3)	104 (3)	104 (3)	83.5 (3)
	[86.8 (3)]	[100 (3)]	[102 (3)]	[81.8 (3)]
N2···H62 (Å)	>3.5	–	–	>3.5
O1—H61 (Å)	2.35 (7)	2.47 (7)	2.38 (7)	2.41 (6)
	[2.34 (7)]	[2.42 (7)]	[2.33 (7)]	[2.41 (6)]
O1—H61—C6 (°)	112 (3)	111 (3)	113 (3)	103 (3)
	[109 (3)]	[107 (3)]	[109 (3)]	[101 (3)]
O1—H62 (Å)	>3.5	–	–	>3.5
N1—H61 (Å)	2.95 (7)	3.17 (6)	3.22 (6)	>3.5
	[3.05 (7)]	[3.31 (6)]	[3.35 (6)]	[>3.5]
N1—H61—C6 (°)	50 (2)	30 (3)	28 (3)	–
	[47 (3)]	[29 (3)]	[27 (3)]	–
N1—C5—C6—H61 (°)	107 (3)	−172 (3)	175 (3)	–
	[107 (7)]	[−171 (7)]	[174 (7)]	

* The second value (in square brackets) represents the data after recalculation of the distances and angles using the average C—H distance of 1.083 Å, as was measured by neutron diffraction for C—H···*X* systems. † H61 = H6.

3. Results and discussion

Final atomic coordinates and equivalent isotropic displacement parameters for the studied crystals are presented in Table 2, selected intramolecular bond lengths and angles in Table 3 and selected intermolecular parameters in Table 4.*

The molecular conformation of the three molecules is similar to the structures observed for several other 2,4-dinitrobenzylpyridine derivatives. The two nitro groups deviate from the mean plane of the phenyl ring and one of the O atoms of the *o*-nitro group interacting with one

* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: DE0002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Significant intermolecular dimensions* (Å, °)*

Crystal		(2)	(3A)	(3B)	(4)
Phenyl–phenyl	Symmetry	–	$1-x, 1-y, -z$	$1-x, -y, 1-z$	–
	Distance (Å)	–	4.309 (6)	4.298 (6)	–
	Angle (°)	–	0.0	0.0	–
Phenyl–pyridine	Symmetry	–	–	–	$x, \frac{1}{2}-y, z-\frac{1}{2}$†
	Distance (Å)	–	–	–	3.734 (6)†
	Angle (°)	–	–	–	3.9 (3)†
Pyridyl–pyridine	Symmetry	$1-x, 1-y, 1-z$	–	–	–
	Distance (Å)	4.340 (6)	–	–	–
	Angle (°)	0.0	–	–	–
O1—H61	Symmetry	$1-x, 1-y, -z$	–	–	–
	Distance (Å)	2.82 (6) [2.77 (6)]	–	–	–
	Angle (°)	146 (3) [142 (3)]	–	–	–
O2—H61	Symmetry	–	$1-x, 1-y, 1-z$	$2-x, -y, 1-z$	–
	Distance (Å)	–	2.88 (8) [2.74 (8)]	2.79 (7) [2.70 (7)]	–
	Angle (°)	–	147 (3) [147 (3)]	150 (3) [150 (3)]	–
N4···H62	Symmetry	–	–	–	$1-x, -y, 2-z$
	Distance (Å)	–	–	–	2.75 (6) [2.65 (6)]
	Angle (°)	–	–	–	160 (4) [161 (4)]

* The second value (in square brackets) presents the data after recalculation of the distances and angles using the average C—H distance of 1.083 Å as was measured by neutron diffraction for C—H···*X* systems. † Refers to the distal pyridine ring.

of the benzylic H atoms. The dominant intermolecular interactions are the intermolecular π–π stacking between the various ring systems and hydrogen bonds (Bernstein, Etter & Leiserowitz, 1994, and references therein; Sharma & Desiraju, 1994; Sharma, Panneerselvam, Pilati & Desiraju, 1993; Desiraju, 1991) formed between the benzylic protons and neighboring basic moieties such as O and N atoms.

3.1. *2-(2,4-Dinitrobenzyl)-4-methylpyridine (2)*

The molecular structure and atom labeling of 2-(2,4-dinitrobenzyl)-4-methylpyridine (2) and its arrangement in the unit cell are presented in Figs. 3 and 4, respectively. Crystals of (2) are monoclinic, space group $P2_1/c$, with four molecules in the asymmetric unit. The planes of the *o*-nitro and *p*-nitro groups are twisted by 41.7 (4) and 15.3 (4)°, respectively, from the phenyl ring plane. The mean plane of the pyridine ring is twisted from the mean plane of the phenyl ring by 56.9 (4)°, so that the *o*-nitro group and the N1 atom of the pyridine moiety are positioned on the same side of the molecule. The O1 atom of the *o*-nitro group and the N atom of the pyridine ring interact with the same benzylic hydrogen, H61, d(O···H) = 2.35 (7) Å [2.34 (7) Å*], with O1···H61—C6 = 112 (3)° [109 (3)°], and d(N···H) = 2.95 (7) Å [3.05 (7) Å], with N1···H61—C6 = 50 (2)° [47 (3)°]. The torsion angle between the carbon–nitrogen C5—N1 bond and the carbon–hydrogen C6—H61 bond is N1—C5—C6—H61 = 107 (3)°. The shortest inter-ring distance is found between the pyridine ring and another pyridine ring from a neighboring molecule related by the $1-x$, $1-y$, $1-z$ symmetry operation, d(center–center) = 4.340 (6) Å. This inter-ring separation reflects the absence of any significant π–π interactions between the two moieties. Similarly, the dinitrophenyl moiety is relatively isolated with no close intermolecular contacts to any other aromatic ring. The closest ring to the dinitrophenyl group is the pyridine ring of the molecule related by the $+x$, $+y$, $1+z$ symmetry operation, d(center–center) = 4.728 (6) Å, which is twisted by 56.9 (4)° from the mean plane of the phenyl ring. The O1 atom of the *o*-nitro group interacts with the benzylic H61 atom of the molecule related by the $1-x$, $1-y$, $-z$ symmetry operation, d(O···H) = 2.82 (6) Å [2.77 (6) Å], O1···H61—C6 = 146 (3)° [142 (3)°].

The molecular structure and supramolecular arrangement of the molecules in this crystal are in agreement with the two proposed models dealing with the origins of the photoactivity of DNBP systems. The crystals of 2-(2,4-dinitrobenzyl)-4-methylpyridine are indeed photochromic and develop a deep blue color upon exposure to near-UV light.

A monotonic decay of 25% in the intensity of the standard reflections was observed during data collection, reflecting some type of interaction between the

* X-ray and neutron diffraction measurements yield different C—H bond lengths. Therefore, the distances and angles of the C—H···*X* systems are given as measured by X-ray diffraction and compared with the same parameters (the values in brackets) calculated using standard neutron diffraction C—H distances in C—H···*X* systems (*X* = N, O; 1.083 Å).

X-ray beam and the crystal. Interestingly, this decay is reversible. The intensity of the standard reflections is almost completely recovered within 3 d. This effect is currently being studied in order to uncover its origin.

3.2. *1-(2,4-Dinitrophenyl)-1-(2-pyridine)ethane (3)*

The molecular structure and atom labeling of 1-(2,4-dinitrophenyl)-1-(2-pyridine)ethane (3) and its arrangement in the unit cell are presented in Figs. 5 and 6, respectively. Crystals of (3) are triclinic, space group $P\bar{1}$, with four molecules in the unit cell. There are two (*A* and *B*) pairs of symmetrically nonequivalent molecules in the unit cell. The molecule is chiral and each one of the two enantiomers is represented by two slightly different conformers in the unit cell. The main structural and environmental differences between the *A* and *B* conformers are listed in Tables 3 and 4, respectively. The planes of the *o*- and *p*-nitro groups are twisted about the mean plane of the phenyl ring by 44.4 (4) and 7.1 (4)°, respectively, for the *A* molecule and 35.7 (4) and 6.3 (4)°, respectively, for molecule *B*. The angle between the mean planes of the pyridine and phenyl rings is 115.1 (4) and 114.8 (4)° for molecules *A* and *B*, respectively. Thus, the *o*-nitro group and the N atom of the pyridine moiety are situated at opposite sides of the molecule both in *A* and *B* conformers. Consequently, solely the O1 atom of the *o*-nitro group is within interaction distance and orientation to the benzylic H6 atom, d(O···H) = 2.47 (7) [2.42 (7)] and 2.38 (7) Å [2.33 (7) Å], O1···H6—C6 = 111 (3) [107 (3)] and 113 (3)° [109 (3)°] for molecules *A* and *B*, respectively. The lone pair of the N1 atom of the pyridine ring is pointing towards the methyl group and is close to being in an *anti* position to the benzylic H6 atom, N1—C5—C6—H6 = −172 (3) [−171 (7)] and N1—C5—C6—H6 = −175 (3)° [−174 (7)°] for molecules *A* and *B*, respectively. The distance from the N1 atom of the pyridine ring to the same proton is d(N···H) = 3.17 (6) [3.31 (6)] and 3.22 (6) Å [3.35 (6) Å], N1···H6—C6 = 30 (3) [29 (3)] and N1···H6—C6 = 28 (3)° [27 (3)°] for molecules *A* and *B*, respectively. No close-contact π–π interactions are found in the crystal lattice. The shortest intermolecular inter-ring distances are found between the phenyl rings and other phenyl rings from neighboring molecules related by the $1-x, 1-y, -z$ (*A*) and $1-x, -y, 1-z$ (*B*) symmetry operations. The center-to-center distances between the rings [d(center–center) = 4.309 (6) and 4.298 (6) Å for molecules *A* and *B*, respectively] indicate the absence of any close-contact π–π interactions between the two. Similarly, the pyridine moieties are situated far apart from one another and from the phenyl rings. The O2 atoms of the *o*-nitro groups interact with the benzylic H6 atoms of the molecules related by the

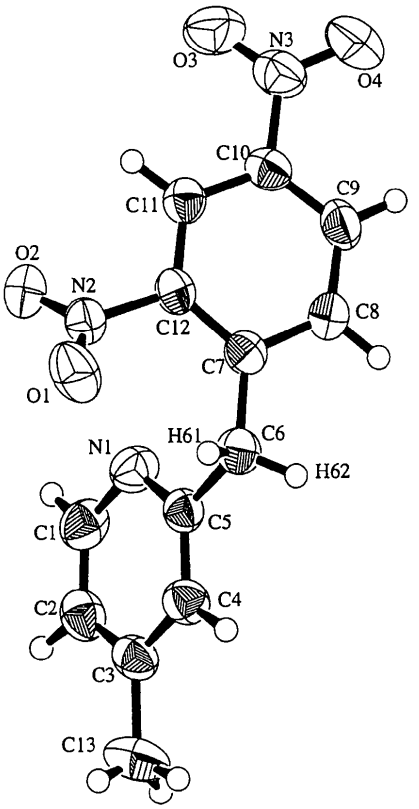


Fig. 3. The molecular structure and atom-labeling scheme of 2-(2,4-dinitrobenzyl)-4-methylpyridine (2).

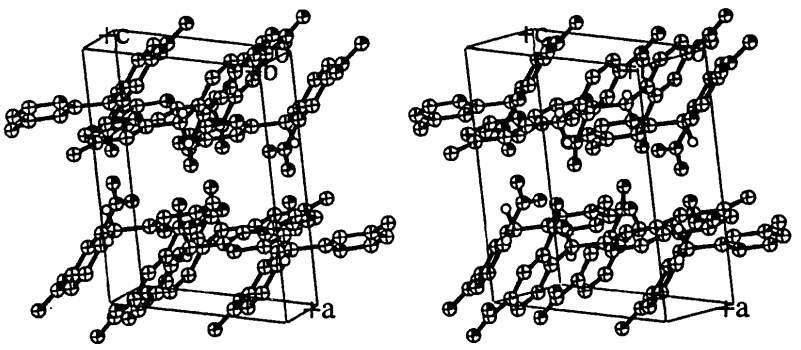


Fig. 4. A stereoscopic view of the arrangement of 2-(2,4-dinitrobenzyl)-4-methylpyridine (2) in the unit cell.

$1-x, 1-y, 1-z$ (*A*) and $2-x, -y, 1-z$ (*B*) symmetry operations, d(O···H) = 2.88 (8) [2.74 (8)] and 2.79 (7) Å [2.70 (7) Å], with O2···H6—C6 = 147 (3) [147 (3)] and 150 (3)° [150 (3)°] for molecules *A* and *B*, respectively.

According to model (ii) presented above, this crystal was expected to be photoinert as only the *o*-nitro group is interacting with the photolabile benzylic proton. However, the crystals were found to be photoactive, developing a deep blue color upon exposure to near-UV light. It is therefore evident that the role of the N atom of the pyridine ring in the proton-abstraction process is mainly inductive and its interaction with the benzylic proton is not essential for the excited state proton abstraction to occur.

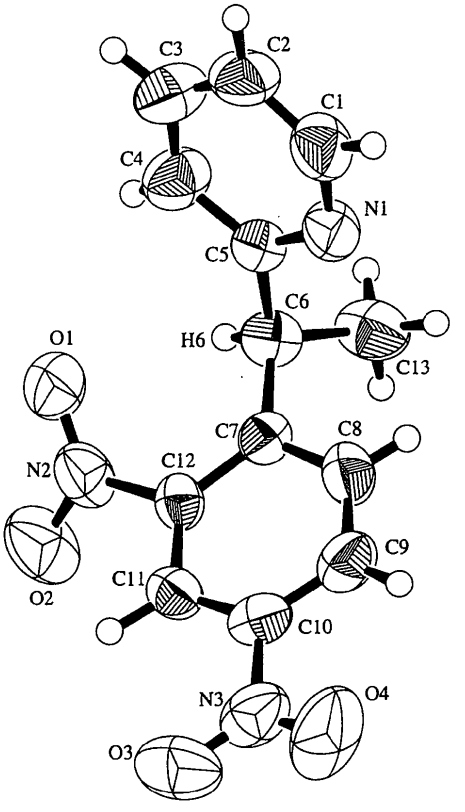


Fig. 5. The molecular structure and atom-labeling scheme of 1-(2,4-dinitrophenyl)-1-(2-pyridine)ethane (3).

3.3. *4′-(2,4-Dinitrobenzyl)-4-methyl-2,2′-bipyridine (4)*

The molecular structure and atom labeling of 4′-(2,4-dinitrobenzyl)-4-methyl-2,2′-bipyridine (4) and the unit-cell content of crystals of (4) are presented in Figs. 7 and 8, respectively. Crystals of (4) are monoclinic, space group $P2_1/c$, with four molecules in the asymmetric unit. The planes of the *o*- and *p*-nitro groups are twisted by 28.1 (4) and 9.4 (4)°, respectively, from the mean plane of the phenyl ring. The interplanar angle between the phenyl ring and the proximal pyridine ring is 87.8 (4)°. The interplanar angle between the two pyridine rings is 5.9 (5)°. In this case, close contact between the N1 atom of the proximal pyridine ring and the benzylic H61 atom is topologically impossible. The O1 atom of the *o*-nitro group interacts with the benzylic H61 atom, d(O···H) = 2.41 (6) Å [2.41 (6) Å], with an angle of O1···H61—C6 = 103 (3)° [101 (3)°]. The distal pyridine ring is almost coplanar with the dinitrophenyl ring of a neighboring molecule related by the $x, \frac{1}{2}-y, z-\frac{1}{2}$ symmetry operation. The angle between the mean planes of 3.9 (3)° and the center-to-center distance of 3.734 (6) Å reflects the existence of a π–π interaction between these two rings. No other pair of aromatic rings exhibit close π–π interactions in this crystal.

The N4 atom of the distal pyridine ring interacts with the benzylic H62 atom of the molecule related by the $1-x, -y, 2-z$ symmetry operation, d(N···H) = 2.75 (6) Å [2.65 (6) Å], with an angle of N4···H62—C6 = 160 (4)° [161 (4)°].

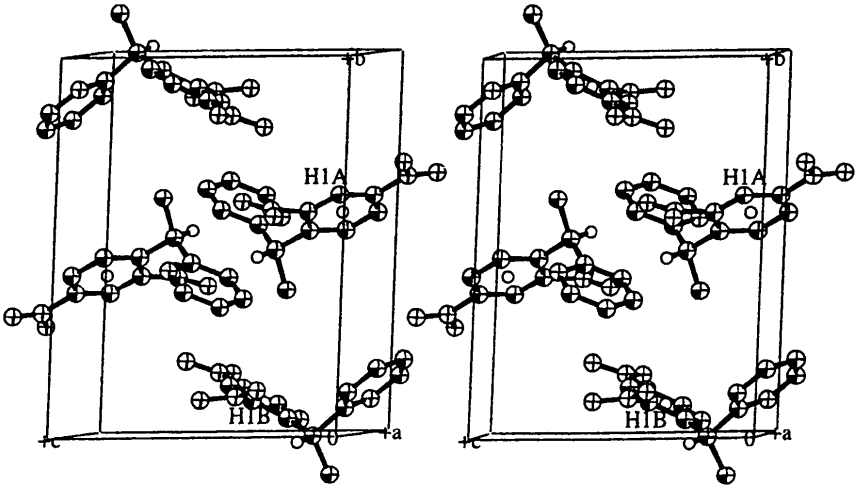


Fig. 6. A stereoscopic view of the arrangement of 1-(2,4-dinitrophenyl)-1-(2-pyridine)ethane (3) in the unit cell. Molecules *A* and *B* are labeled as H1*A* and H1*B*.

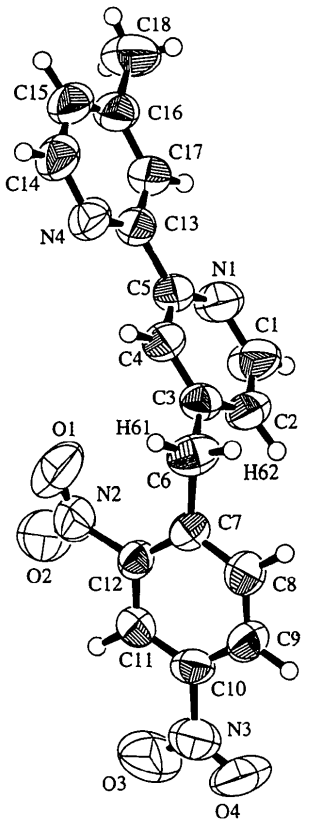


Fig. 7. The molecular structure and atom-labeling scheme of 4′-(2,4-dinitrobenzyl)-4-methyl-2,2′-bipyridine (4).

As stated above, it is topologically impossible to photoinduce a direct transfer of the benzylic proton to the nitrogen of the proximal pyridine ring of the same molecule. On the other hand, according to the arrangement of the basic groups around the abstracted proton, the 'CH' → 'OH' proton-transfer process (see Scheme I) is still theoretically feasible. However, the crystals were found to be photoinert and did not exhibit any photoactivity at the temperature spectrum range 325–77 K and 400–800 nm, respectively. This implies that the close-contact π–π interactions inhibit the proton-transfer process, probably by opening some new deactivation routes which are faster than the proton transfer.

4. Conclusions

Photoinduced and thermally activated proton-transfer processes are known to take place in single crystals of dinitrobenzyl pyridine derivatives. Recent reports have concluded that this effect is a true bulk effect and is not restricted to defect sites. Therefore, a correlation between the crystalline structure and the proton-transfer properties may be drawn. Previous attempts to correlate the photoactivity of α-DNBP and its derivatives with the properties of the molecular structure and crystal packing have led to the conclusion that the process is intramolecular (Seff & Trueblood, 1968) and that two different alternative models exist for the origins of the photoactivity (Eichen *et al.*, 1995; Scherl *et al.*, 1996). Model (i) suggests that close-contact π–π interactions

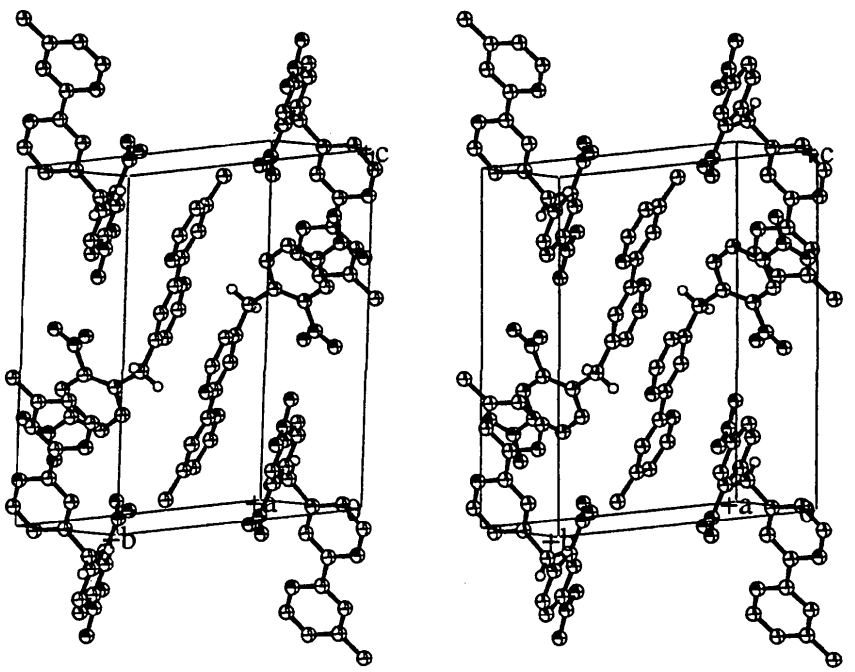


Fig. 8. A stereoscopic view of the arrangement of 4′-(2,4-dinitrobenzyl)-4-methyl-2,2′-bipyridine (4) in the unit cell.

between the 2,4-dinitrobenzyl group and other aromatic rings open some deactivation routes to the excited state that are faster than the proton-transfer process and model (ii) suggests that the abstraction of the benzylic proton requires its activation by both the *o*-nitro group and the N atom of the pyridine ring, in order to generate the substantial electrostatic potential needed for the proton-abstraction process.

The molecular structure and crystal packing in the crystal of 2-(2,4-dinitrobenzyl)-4-methylpyridine (2) is such that both the *o*-nitro group and the pyridine nitrogen are situated at the same side of the molecule. These two atoms interact with the same benzylic proton. On the other hand, the dinitrophenyl moiety is free from any close-contact π–π interactions. Therefore, this system is in agreement with the two models. However, in 1-(2,4-dinitrophenyl)-1-(2-pyridine)ethane (3) the torsion angle N1—C5—C6—H6*A* shows that the lone pair N atom of the pyridine ring is pointing towards the methyl group. Thus, this nitrogen is too far from the benzylic hydrogen and cannot contribute to the abstraction of the proton. This implies that, in contrast to model (ii), the role of the nitrogen of the pyridine ring in the proton-abstraction process is mainly inductive and its interaction with the benzylic proton is not essential for the excited-state proton abstraction to occur. In the case of 4′-(2,4-dinitrobenzyl)-4-methyl-2,2′-bipyridine (4) the pyridine nitrogen is situated in a *para* position relative to the benzylic carbon and therefore cannot interact with any of the benzylic protons. On the other hand, as the effect of this nitrogen is mainly inductive, 4′-(2,4-dinitrobenzyl)-4-methyl-2,2′-bipyridine (4) should still be photoactive through the 'CH' → 'OH' path. However, this crystal is found to be photoinert. This observation, together with the observation that the dinitrophenyl group is π-stacked with the distal pyridine ring of a neighboring molecule, agrees with model (i).

The findings that photoinert systems are related to π–π interactions that control the packing of the molecules in the crystal are in agreement with many previously reported salicylideneaniline crystalline systems. However, it seems that at least for the 2,4-dinitrobenzylpyridine family, the free volume argument is inconsistent with the observed spectroscopic and kinetic data. In this type of system only the π–π interactions of the 2,4-dinitrophenyl ring with other aromatic rings lead to photoinert systems, while π–π interactions between pyridine rings can be found in photoactive and photoinert systems. It is therefore suggested that the difference between photoactive and photoinert systems originate from the difference in the deactivation pathways that are available to the electronic excited states. π–π interactions between the chromophore (2,4-dinitrophenyl ring) and other aromatic rings allow fast deactivation of the electronic excited state *via* energy or electron transfer. Alternatively, π–π interactions between the chromophore and other aromatic rings can induce a change in the relative population of the different excited states, leading to inactive excited species. In the absence of these fast deactivation channels, proton transfer may take place. Several new 2,4-dinitrobenzylpyridine derivatives are currently being prepared and characterized by means of optical spectroscopy and X-ray analysis in order to further clarify this point.

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