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Packing-dependent photochromism: the case of photoinduced intramolecular proton transfer in 6-(2′,4′-dinitrobenzyl)-2,2′-bipyridine

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A new photoactive monoclinic polymorph (γ-form) of 6-(2′,4′-dinitrobenzyl)-2,2′-bipyridine was obtained from an acetone–methanol solution. The crystal structure was compared with those of two polymorphs reported previously (photoactive orthorhombic α-form and photoinactive monoclinic β-form) and with structures of related nitrobenzylpyridines to explain the relation between the structure and photochromism. The comparison of the reaction cavities around the reactive pyridyl–benzyl–nitro fragment among the polymorphs and related nitrobenzylpyridines revealed that a crucial factor for photochromic activity is the rotational freedom of the *ortho*-nitro group in their crystals and its accessibility from the proton–donor and proton–acceptor sites. This is because the *ortho*-nitro group should rotate around the N—C bond to transfer a proton from the methylene group to the N atom of the pyridine ring.

1. Introduction

Polymorphism is very useful in probing the relationships between structures and their physical properties, as it provides an opportunity to compare the properties of the same molecule embedded in different crystalline environments (Bernstein, 2002). Particularly relevant (for example, for practical applications in the phonon-based data storage and processing) is the relationship between crystal packing and photochromism (Feringa, 2001). Recently, our research interest has been focused on the photochromic *ortho*-nitrobenzylpyridines (NBPs), which are very important but rather insufficiently studied photoreaction systems (Naumov *et al.*, 2002; Naumov & Ohashi, 2004*a*,*b*). The NBPs are probably one of the most exploited phototrigger units in the caged compounds (Corrie & Trentham, 1998; Toscano, 2001) for the controlled release of bioactive compounds and fluorescent dyes, and also have potentials for the photocontrol of non-linear optical properties (Houbrechts *et al.*, 1996).

The photochromism of the NBPs is mainly due to nitro-assisted proton transfer, *i.e.* intramolecular transfer of one benzylic proton in **CH** (benzyl form), which isomerizes to the blue metastable isomer **NH** (enamine form), through unstable isomer(s) **OH** (aci-nitro form), as shown in Fig. 1. Very small amounts of the photoinduced radicals in Fig. 1 account for additional, low-yield latent photochromism and photofatigue (Naumov & Ohashi, 2004*a*).

Several examples of non-photochromic crystalline NBPs have already been reported (*e.g.* Khatib *et al.*, 1997; Scherl *et al.*, 1996). Fast deexcitation through the $\pi-\pi$ stacking was

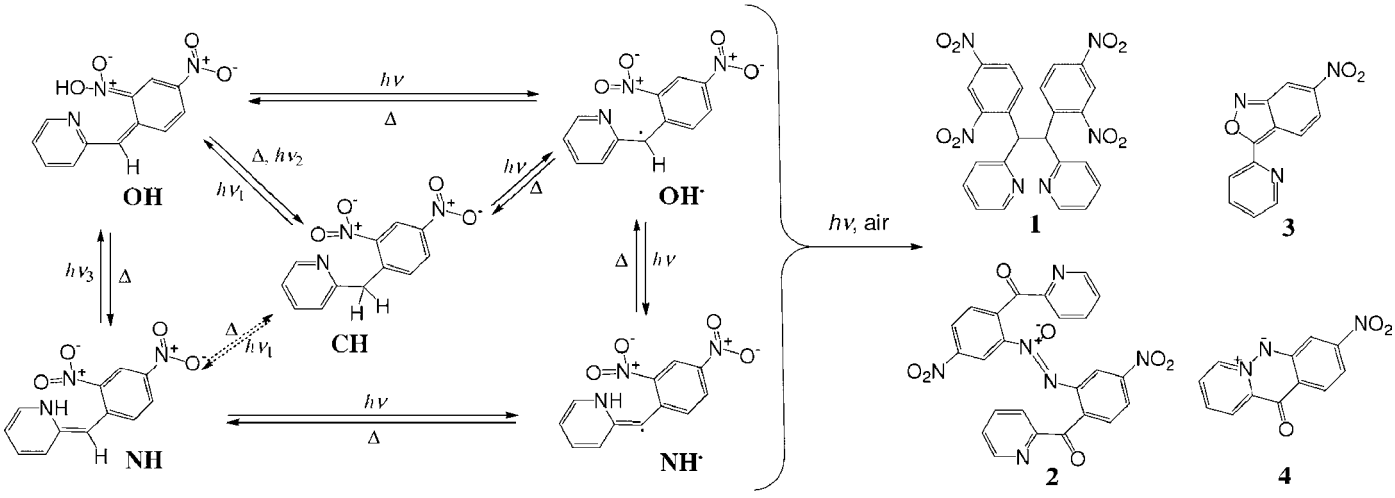

Figure 1
Reaction mechanism of the photoreactions of 2-(2′,4′-dinitrobenzyl)pyridine, including the closed- and open-shell species. The reactions denoted with broken arrows are characteristic for solutions.

proposed as a possible reason for their photoinactivity. However, the structural results (Naumov *et al.*, 2002) have indicated that the nitro group assists the proton transfer in NBPs. In addition, the theoretical results (Frank *et al.*, 1996, 1999) have shown that the involvement of the nitro group is important for the proton transfer in the ground-state thermal back-reaction **NH** ⇒ **CH**. On the basis of the results accumulated, it can be suggested that the photochromic activity of solid NBPs depends on the rotational freedom of the *ortho*-nitro group.

In order to examine the hypothesis more quantitatively, we searched for NBP polymorphs with different photochromic properties. Attempts to obtain other forms than the monoclinic $P2_1/c$ crystals of the parent compound 2-(2′,4′-dinitrobenzyl)pyridine from several solvents (acetone, benzene, hexane, thf, EtOAc) and their mixtures were unsuccessful. Therefore, the pyridyl ring was replaced with 2,2′-bipyridine and the resulting molecule, 6-(2′,4′-dinitrobenzyl)-2,2′-bipyridine (DNBBP), was chosen as a model compound. It was already reported that from ether–hexane mixtures DNBBP crystallizes in a photochromic orthorhombic form (α-form, space group $Pna2_1$), while from ethanol it crystallizes in a non-photochromic monoclinic form (β-form, space group $P2_1/c$; Eichen *et al.*, 1995; Scherl *et al.*, 1996). By recrystallizing from an acetone–methanol solution we succeeded in obtaining a new photochromic monoclinic polymorph, the γ-form. In this paper the crystal structure of the γ-form is reported and compared with the photochromic α-form and the non-photochromic β-form in order to clarify more quantitatively the relation between structure and photoactivity, which owes to the main, proton transfer reactions (those among **CH**, **OH** and **NH**).

2. Experimental

The precursor 6-bromo-2,2′-bipyridine was prepared by consecutive methylation, oxidation and bromination of 2,2′-bipyridine (the detailed synthetic procedures and analytical data have been deposited as supplementary material[1]). DNBBP was prepared by coupling the precursor with benzyl bromide according to the method reported previously (Scherl *et al.*, 1996). Colorless plate crystals of the α-form and long bladed crystals of the γ-form were obtained from ether–hexane and acetone–methanol solutions, respectively, by slow evaporation in the dark at ambient temperature.

The intensity data of the α- and γ-forms were collected on a Siemens SMART-CCD diffractometer equipped with the Rigaku liquid-nitrogen cooling system. The intensity data (Siemens, 1995) were corrected empirically for absorption effects (Sheldrick, 1996). The structures were solved by direct methods (Altomare *et al.*, 1994) and refined by full-matrix least-squares refinement on F^2 (Sheldrick, 1997*a*,*b*). The non-H atoms were refined anisotropically, the aromatic H atoms were included as riding bodies and the benzylic H atoms were located in the difference-Fourier map and refined (γ-form) or fixed at their expected positions (α-form). Additional experimental details are presented in Table 1.

3. Results and discussion

3.1. Crystal structures

The crystal of the γ-form obtained from an acetone–methanol solution belongs to the monoclinic crystal system, space group $P2_1/c$. The absence of phase transitions in the 78−362 K range was confirmed with differential scanning calorimetric measurements. In order to check for any temperature-induced structural changes, the structures of the α-form at 298 and 78 K were also redetermined. The crystal system and the space group $Pna2_1$ are consistent with the reported structure at 173 K (Scherl *et al.*, 1996). The crystal

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OG0001). Services for accessing these data are described at the back of the journal.

Table 1
Crystal data and experimental details for α-, β- and γ-forms of DNBBP.

The cell parameters of the β-form are listed for comparison purposes (Scherl *et al.*, 1996).

	α-form	γ-form	β-form
Crystal data			
Chemical formula	$C_{17}H_{12}N_4O_4$	$C_{17}H_{12}N_4O_4$	$C_{17}H_{12}N_4O_4$
M_r	336.31	336.31	336.31
Crystal setting, space group	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a (Å)	14.0059 (1)	20.8360 (3)	8.340 (3)
b (Å)	5.1399 (1)	5.27460 (10)	12.740 (4)
c (Å)	41.9853 (6)	14.0971 (2)	14.408 (4)
β (°)	–	104.4570 (10)	92.13 (2)
Volume (Å^3)	3022.48 (8)	1500.23 (4)	–
Z	8	4	–
D_x (Mg m^{-3})	1.478	1.489	–
Radiation type	Mo $K\alpha$	Mo $K\alpha$	–
No. of reflections for cell parameters	8192	8192	–
θ range (°)	1.94–27.46	1.01–27.60	–
μ (mm^{-1})	0.109	0.110	–
Temperature (K)	78 (2)	78 (2)	173
Crystal form, color	Block, colorless	Plate, colorless	–
F(000)	1392	696	–
Crystal size (mm^3)	0.35 × 0.10 × 0.05	0.40 × 0.25 × 0.05	–
Data collection			
Diffractometer	Siemens CCD	Siemens CCD	
Data collection method	ω scan	ω scan	–
Absorption correction	Empirical	Empirical	–
T_{min}	0.674	0.975	–
T_{max}	1.000	1.000	–
No. of measured, independent and observed reflections	19 857, 6678, 4589	100 984, 3445, 2934	–
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	–
R_{int}	0.080	0.048	–
θ_{max} (°)	27.5	27.6	–
Index ranges	$-15 \rightarrow h \rightarrow 18$	$-27 \rightarrow h \rightarrow 20$	–
	$-6 \rightarrow k \rightarrow 6$	$-6 \rightarrow k \rightarrow 6$	–
	$-47 \rightarrow l \rightarrow 54$	$-15 \rightarrow l \rightarrow 18$	–
Refinement			
Refienement on	F^2	F^2	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0640	R_1 = 0.0489	–
	wR_2 = 0.1564	wR_2 = 0.1413	–
R indices (all data)	R_1 = 0.1017	R_1 = 0.0573	–
	wR_2 = 0.1794	wR_2 = 0.1526	–
No. of reflections	6678	3445	–
No. of parameters	452	228	–
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	–
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	–
$(\Delta/\sigma)_{max}$	0.026	0.001	–
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.13, −0.27	0.40, −0.52	–
Extinction method	*SHELXL*	–	–
Extinction coefficient	0.0104 (11)	–	–

Computer programs used: *SMART* and *SAINT* (Siemens, 1995), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *ORTEP*II (Johnson, 1976).

data for the α- and γ-forms at 78 K are listed in Table 1, together with the cell dimensions of the β-form at 173 K. If the a and c axes of the γ-form are switched, the c axis length of the α-form is twice that of the γ-form. The structural difference between the α- and γ-forms was confirmed from the systematic absences and the simulated powder diffraction patterns. On the other hand, there is no apparent relation between the cell dimensions of the γ- and β-forms, although the same space group is assigned to both polymorphs.

The molecular structure of the γ-form with the atom labelling, shown in Fig. 2(*a*), is very similar but not identical to the molecular structure of the α-form. As shown in Fig. 2(*b*), the molecular structure of the β-form is very different from that of the γ-form. The molecular parameters in the three structures are compared in Table 2. The *ortho*-nitro group and the bipyridyl nitrogen N1 in the α- and γ-forms are positioned on the same side of the plane in the methylene bridge (C5—C6—C7). The interplanar angle between the phenyl ring and the pyridyl ring including N1 in the γ-form [50.93 (5)°] is smaller than those of the two crystallographically independent molecules in the α-form [56.7 (2) and 58.4 (2)°] and that of the β-form (65.1°). The smaller angle results in shorter contact

Table 2
Selected intramolecular parameters of the three forms of DNBBP.

The atom labels refer to Fig. 1. The values for the β-form were extracted from the deposited structure and the corresponding e.s.d's were unavailable.

	Polymorph		
	α-form	β-form	γ-form
Photochromism	Yes	No	Yes
Solvent	Ether–hexane	Ethanol	Acetone–methanol
T (K)	78	173	78
ρ_{calc} (g cm^{-3})	1.478	1.460	1.489
d(N1---O1) (Å)	3.210 (5) 3.177 (5)	4.004 (6)	3.056 (2)
d(N1---C6) (Å)	2.459 (6) 2.451 (6)	2.431	2.452 (2)
d(C6---O1) (Å)	2.887 (6) 2.873 (6)	2.764	2.854 (2)
d(H61---O1) (Å)	2.339 2.342	2.380	2.469 (2)
d(H61---N1) (Å)	2.905 2.913	3.348	2.978 (2)
∠(C6—H61---N1) (°)	106.8 107.9	25.5	113.9 (1)
∠(C6—H61---O1) (°)	47.7 48.8	99.6	57.3(1)
Ortho-nitro–phenyl angle (°)	35.7 (5) 37.1 (5)	21.8	35.5 (1)
Phenyl–pyridyl angle (°)	58.4 (2) 56.7 (2)	65.1	51.1 (1)

between the *ortho*-nitrobenzyl group and the pyridyl fragment. Consequently, the N1—O1 distance of the γ-form is the shortest among the three forms, as shown in Table 2.

The conformation of the non-photochromic β-form is significantly different from those of the photochromic α- and γ-forms. The *ortho*-nitro group and the bipyridyl nitrogen N1 are positioned on the opposite side of the methylene bridge plane and the ring interplanar angle is larger. Correspondingly, the *ortho*-nitro group is remote from the pyridyl acceptor [N1---O1 4.004 (6) Å].

The crystal structures of the α- and γ-forms are similar to each other, as shown in Fig. 3. Both crystals feature 'sandwich'-like structures composed of double dinitrophenyl and bipyridyl layers parallel to the *a* and *c* axes in the α- and γ-forms, respectively. Within each dinitrophenyl double layer the molecules interact with two- and three-centered C—H···O(nitro) hydrogen bonds, while within each bipyridyl layer they are held together with C—H···N(pyridyl) hydrogen bonds and van der Waals contacts.

The crystal structure of the β-form is significantly different from those of the α- and γ-forms. There is partial stacking between the bipyridine and the dinitrophenyl rings.

3.2. Photochromic properties

The γ-form is colourless at ambient temperature under light from a neon lamp, but turns violet almost immediately when it is flashed with UV radiation (λ < 360 nm, 0.1 s). The violet absorption of the γ-form is completely bleachable in about 12 h in the dark at 298 K. Owing to partial decay, however, several minutes of exposure to direct UV radiation brings a permanent red coloration and incomplete recovery of **CH**.

As shown in Fig. 4, the UV–vis spectra of the colorless **CH** isomers of the γ- and α-forms are practically identical, but the spectra of their photocolored species are distinctively different. The spectra of the α-form indicate that only a very small amount of **CH** decays, showing two new bands, at 483 and 620 nm, assigned to **OH** and **NH**, respectively, by comparison with similar compounds (Scherl *et al.*, 1996). On the contrary, the spectra of the γ-form show a significant decrease of **CH** and the appearance of a strong absorption continuum in the 200–800 nm region, a part of which is unbleachable and can be prescribed to photofatigue products.

Since the photochromic γ- and α-forms have very similar conformations while the non-photochromic β-form has a different conformation, it is clear that the molecular structure is relevant to the photochromism. The *ortho*-nitro group of the DNBBP molecule in the β-form is placed far from the pyridyl nitrogen N1. Therefore, this distance should be an important factor for photochromic activity if we assume that the nitro group abstracts the proton from the methylene group and delivers it to the pyridyl nitrogen. Even if the very short-lived **OH** isomer is formed in the β-form by photoexcitation, it cannot decay to the **NH** isomer since the acid–nitro group cannot transfer the proton to the pyridyl nitrogen. Consequently, the β-form is not photochromic under UV radiation. The difference in absorption spectra and stability of the photoinduced products between the γ- and α-forms can be attributed to the fine details of the molecular structures, such as the value of the interplanar angle as given in Table 2.

3.3. Reaction cavity

The above discussion suggests that the ability of the nitro group to abstract a proton from the proton donor (the benzylic carbon C6) and to bring it to the proton acceptor (the pyridyl nitrogen N1), *i.e.* the rotational freedom of the nitro group in the crystal, is one of the decisive factors for the photochromic activity. The steric requirements for the rotation of the nitro group were investigated by means of the reaction cavity concept, since it already proved successful in explaining the large number of solid-state processes at little computer cost (Ohashi *et al.*, 1981; Ohashi, 1988). Therefore, the reac-

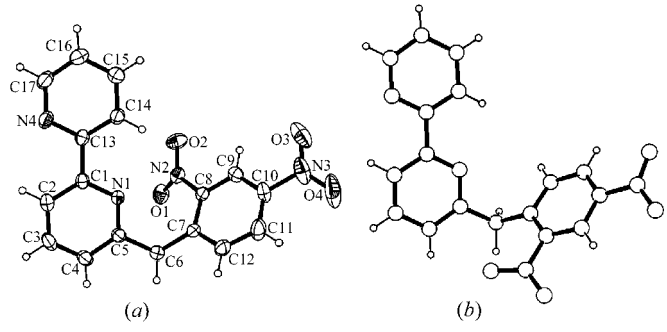

Figure 2
(*a*) *ORTEP* diagram of the molecular structure of the γ-form at 78 K with atom labelling. The ellipsoids are drawn at the 70% probability level. The α-form has a very similar molecular structure. (*b*) The molecular structure of the β-form at 173 K from the reported data (Scherl *et al.*, 1996).

Table 3
Calculated reaction cavity volumes for photochromic and non-photochromic nitrobenzylpyridines.

Compound	CSD refcode or reference	Solid-state photochromism	T (K)	V (Å^3)
DNBP	(This work)	Yes	78	21.60
6-Me-DNBP†	Unpublished data	Yes	78	19.73
3-Me-DNBP†‡	RIGHUK	Yes	343	24.31
3-Me-DNBP†‡	RIGHUK01	Yes	295	22.63
4-Me-DNBP†	TOYYAH	Yes	295	24.54
α-DNBBP	(This work)	Yes	78	20.16
			78	20.62
γ-DNBBP	(This work)	Yes	78	21.31
β-DNBBP	ZOGQAN	No	173	17.34
NH_2-NBP§	Unpublished data	No	78	13.49
DNBP dimer¶	Naumov & Ohashi (2004*a*)	No	296	16.56
				17.15

† The position of the methyl group refers to the pyridyl ring. ‡ Low- and high-temperature polymorphs of the same compound. § 2-(4′-Amino-2′-nitrobenzyl)pyridine. ¶ 1,2-Bis(2′,4′-dinitrophenyl)-1,2-bis(2′-pyridyl)ethane [(1) in Fig. 1].

tion cavity around the reactive pyridyl–benzyl–nitro fragment [N1—C5—C6(H_2)—C7—C8—NO_2] was calculated for each form. The decision to use the whole fragment in the calculations instead of the nitro group only was based on the understanding that both the rotational freedom *and* the ability of the nitro group to transfer the proton to the nitrogen acceptor are crucial factors for the creation of the blue **NH**, and thus for photochromic activity. Even if the proton is abstracted and the short-lived aci–nitro isomer **OH** is formed, if the distance to the acceptor (the pyridyl nitrogen) is large and there are no fast solid-state dynamical processes (*e.g.* ring flipping), **OH** will not be able to decay to the long-lived **NH** and hence the compound will not be photoactive. Therefore, the void space required for the entire reaction is expected to afford a more adequate representation of its steric requirements than the space available for the nitro rotation only.

Fig. 5 shows the reaction cavities for the reactive fragment in the three forms. The two crystallographically independent molecules in the α-form, *a* and *b*, have the volumes 20.16 and 20.63 Å^3, respectively. The cavity in the γ-form (21.31 Å^3) is nearly the same size and shape as those of the two molecules in the α-form, as well as with that of 2-(2′,4′-dinitrobenzyl)pyridine (21.60 Å^3), which is also photochromic in the solid state. On the other hand, the *ortho*-nitro group of the non-photochromic β-form is confined to narrower space (17.34 Å^3) than those of the photochromic α- and γ-forms and 2-(2′,4′-dinitrobenzyl)pyridine. An analogous explanation holds for the polymorphism-dependent photoactivity of 2-(2′,4′-dinitrobenzyl)-3-methylpyridine (Schmidt *et al.*, 1999).

The cavity of 2-(2′,4′-dinitrobenzyl)pyridine at 77 K is shown in Fig. 5(*e*). The shape and the large volume (21.60 Å^3) of the cavity suggest that almost unhindered rotation (or, at least, enhanced torsion) of the nitro group is possible around the C(phenyl)—N(nitro) bond. By rotating, the nitro group is able to approach both the proton donor and acceptor. It can be concluded that the photochromic activity of the NBPs in

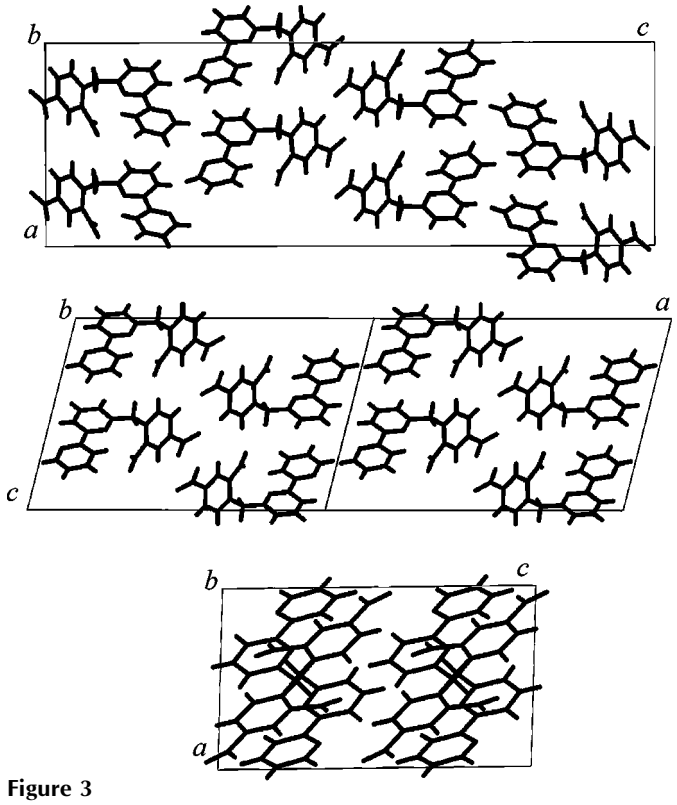

Figure 3
Crystal structures of (*a*) the photochromic α-form, (*b*) the photochromic γ-form and (*c*) the non-photochromic β-form, viewed along the *b* axis.

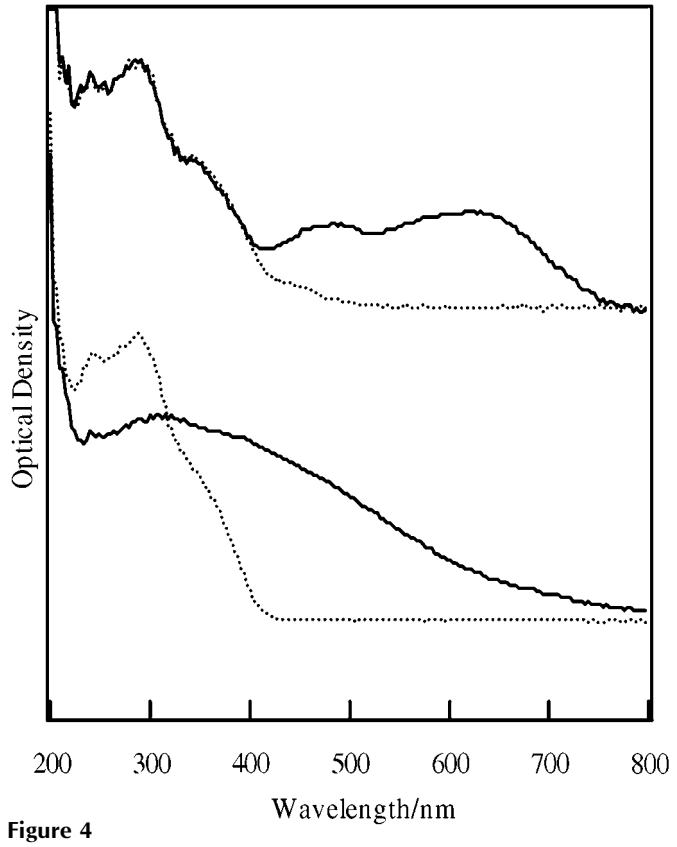

Figure 4
UV–vis spectra of the α-form (upper) and the γ-form (lower) in KBr discs recorded before (dotted curves) and after (solid curves) short exposure to UV light from a high-pressure Hg lamp.

the solid state depends strongly on the rotational freedom of the *ortho*-nitro group.

In order to generalize the relationship between the size of the reaction cavity and the photoactivity, the reaction cavities of NBP crystals whose structures were determined by X-ray diffraction or retrieved from the literature were calculated. Some selected values are listed in Table 3. The values for the non-photochromic crystals are about or less than 17 Å^3. The smallest reaction cavity was found in the photoinactive 2-(4′-amino-2′-nitrobenzyl)pyridine, 13.49 Å^3 at 78 K (Naumov & Ohashi, 2004*a*). The temperature effects on the reaction cavity volume were also considered. Typically, the reaction volumes increase by 2.9 and 2.1 Å^3 for DNBP and γ-DNBBP, respectively, on increasing the temperature from 78 to 298 K. Even if the contraction of 3 Å^3 is supposed upon cooling to 78 K for the three photochromic entries RIGHUK, RIGHUK01 and TOYYAH in Table 3, the resulting values will be still larger than those of the non-photochromic entries.

4. Summary

A new photochromic polymorph of 6-(2′,4′-dinitrobenzyl)-2,2′-bipyridine (γ-form) was obtained from an acetone–methanol solution. The molecular conformation and the crystal packing of the γ-form are similar to those of the photochromic α-form, but are very different from those of the non-photochromic β-form. The *ortho*-nitro groups of the molecules in the α- and γ-forms are proximate to the pyridyl nitrogen N1, whereas in the β-form the *ortho*-nitro group is remote from N1. This suggests that the ability of the nitro group to abstract a proton from the proton donor (the benzylic carbon C6) and to deliver it to the proton acceptor (the pyridyl nitrogen N1), *i.e.* its rotational freedom in the crystal, is one of the decisive factors for the photochromic activity.

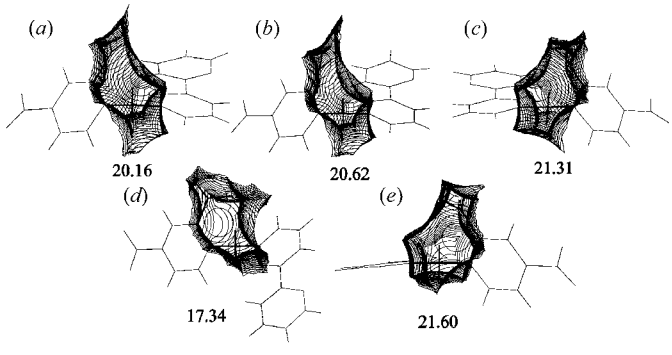

Figure 5
Plot of the reaction cavities around the reactive $NCC(H)_2CCNO_2$ backbone (in bold) in (*a*) and (*b*) the α-form, (*c*) the γ-form, (*d*) the β-form and (*e*) 2-(2′,4′-dinitrobenzyl)pyridine, viewed parallel to the plane of the benzylic bridge. The cavities are represented as surfaces of the spheres from the surrounding atoms of the neighbouring atoms, the radius of each sphere being greater by 1.2 Å than the van der Waals radius for the atom (C: 1.700, H: 1.200, N: 1.550, O: 1.520 Å). The contour lines represent steps of 0.1 Å. Each number represents the cavity volume (Å^3).

The steric requirements for the rotation of the nitro group in the crystalline lattice were investigated semi-quantitatively within the reaction cavity concept by calculating the reaction cavity around the reactive pyridyl–benzyl–nitro fragment in each form. The size of the cavities of the photochromic α- and γ-forms is significantly larger than that of the non-photochromic β-form. This indicates that the rotational freedom of the *ortho*-nitro group is the most important factor for the photochromism. At the same time, the strong dependence of the photochromism on the rotational ability of the nitro group provides additional support for the proposed nitro-assisted proton transfer mechanism.

At the present stage, it seems difficult to generalize in a straightforward way to all NBPs the structural (geometric and steric) criteria for photochromism derived from three polymorphs of a single compound. This is due to the presence, besides the proton transfer, of open-shell reactions (Fig. 1) that may result in low-yield latent photochromism, even in cases of unfavorable geometry for proton transfer. This important fact has not been considered in the previous attempts of structure–reactivity correlations (as an example, for an exceptional case whose photochromic activity might be due to latent photochromism, see Khatib *et al.*, 1997).

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