

# An intermolecular hydrogen transfer process inducing triplet biradical photochromism of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine in the solid state

Aleksandra Lewanowicz<sup>a,\*</sup>, Roman Gancarz<sup>b</sup>

<sup>a</sup> Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wybrzeże S. Wyspiańskiego 27, PL 50-370 Wrocław, Poland

<sup>b</sup> Medical Chemistry and Microbiology Group, Chemistry Department, Wrocław University of Technology, Wybrzeże S. Wyspiańskiego 27, PL 50-370 Wrocław, Poland

Received 28 June 2007; received in revised form 31 October 2007; accepted 14 November 2007

Available online 23 November 2007

## Abstract

An intermolecular hydrogen transport process, as a source of photochromism in a crystal, was identified in 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (DHP). The photochromic form of that compound, dark violet in color, according to EPR measurements is triplet biradical in nature. According to photoluminescence measurements, the lowest excited triplet state ( $T_1$ ) as well as the excited singlet state ( $S_1$ ) of the DHP molecule is of  $\pi, \pi^*$  type. Two active non-symmetrical biradical forms, absorbing at 400 nm and 550 nm, are proposed connected with a hydrogen transfer process created by transformation of the forms on mutual terms ('hydrogen cascade'). Optical generation of the photochromic form was followed by steady-state UV–vis spectroscopy. The rate constants are equal to  $k_{400} = 4.36 \pm 0.17 \times 10^{-3} \text{ s}^{-1}$  and  $k_{550} = 5.87 \pm 0.56 \times 10^{-4} \text{ s}^{-1}$ , respectively. The values of energy of activation of these two parallel processes obtained by analysis of non-isothermal kinetics of the bleaching process are equal to 10.96 kJ/mol and 31.2 kJ/mol, respectively. The IR spectra together with EPR measurements as well as X-ray structural analysis and calculations on the semi-empirical AM1 level method seem to support the intermolecular hydrogen transfer chain process.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** 1-Methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine; Intermolecular hydrogen transfer; Triplet biradical; IR spectra; Photochromism; Photoluminescence

## 1. Introduction

Investigations of the photochemical properties of organic photochromic materials have a long history because of their potential applications in different areas of technology, science and human life [1]. In modern magnetochemistry preparation of high-spin organic molecules and investigation of their structure are the main research topic at this moment. So, reinforcing interest in magnetic materials with bi- and polyradical fragments as elements of hierarchic structures, opens a new field of application for systems with optically generated bulk magnetic properties ('molecular magnets') [2–5].

In 2000, Tanaka and Toda announced a novel photochromism of biindenylidene based on the formation of triplet biradicals in the crystal [6,7]. So, coexistence of photomagnetism and pho-

tochromism, a new feature of organic materials, may lead to preparation of a novel, well-defined magnetic-type compound.

Our previous work on the optical properties of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (Fig. 1) showed that this compound also exhibits certain photo-magnetic properties [8–10].

DHP belongs to the class of photochromic materials. For substituted 1,4-dihydropyridines a photochromism was observed in different environments [11–14]. The original form of DHP, a representative compound for that group, is transparent in the visible range. Irradiation of that material in the UV absorption range, within the  $S_1 \leftarrow S_0$  transition, yields a new colored species characterized by absorption bands in the visible range. This phenomenon was also observed both in the solid state and in solution [10,15–17].

The colored form of DHP in the solid state is very stable (days: in the crystal; a year: in a solid matrix) [18]. The bleaching process might be realized in two possible ways: spontaneously – in the crystal, in the dark in a long-lasting process as mentioned

\* Corresponding author. Tel.: +48 713203924; fax: +48 713203364.  
E-mail address: [aleksandra.lewanowicz@pwr.wroc.pl](mailto:aleksandra.lewanowicz@pwr.wroc.pl) (A. Lewanowicz).

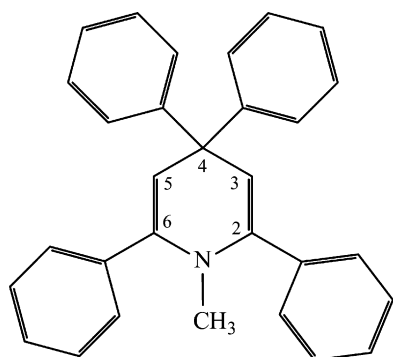


Fig. 1. Molecular formula of 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine, DHP.

above, or as a thermally driven reaction [19,20]. Concerning the mechanism of the DHP photochromic process there is general agreement that more than one reactive center is responsible for that property. There is no consensus on the structure of the photocolored species of DHP or on details of the photo and thermally initiated reaction pathways [11–13,21,22]. In spite of the negative results of EPR measurements, two biradical structures as intermediates are included in the photoreaction scheme proposed in [11]. However, they did not confirm the presence of such colored biradicals [11]. Additionally, the results of IR spectroscopy and NMR measurements were also negative from the point of view of detection of the 1,4-dihydropyridine photochromic species. However, the formation of intermediate(s) containing a cyclopropyl moiety at an early stage of the photo-process was observed [21]. A monoradical recombination cycle as one of the steps in the reaction path explaining the photochemical activity of DHP is proposed in [10]. The process following the excitation of the original form seems to be formation of a radical rather than a purely intramolecular rearrangement process. In this model, breaking of one of the C(4)–phenyl bonds (cf. Fig. 1) and formation of the radicals opens the possibility for recombination, resulting in the re-formation of the original molecule. The possibility of generation of a biradical structure is not discussed.

The aim of the present work is to identify the photochromic form of DHP and determine the reaction path. Modifying our earlier model [8,17], we have focused on the first steps of the photochemical reaction following illumination of the material under study. We carried out UV–vis absorption as well as steady-state IR spectra and EPR measurements of different forms of DHP in the solid state. Using the isothermal as well as the non-isothermal technique, the parameters of the kinetics were determined. The results of thermally driven measurements were analyzed according to the method presented in [23]. Molecular packing of crystalline DHP as well as possible intermolecular contacts were re-analyzed. The experimental data were supported by theoretical considerations on a semi-empirical level by the AM1 method. Two non-symmetrical biradical structures derived from DHP were proposed and discussed. Their mutual transformation is due to an intermolecular hydrogen transfer process. The scheme of the reaction path is proposed. The consequence of that reaction for observed photo-magnetic properties

of DHP is also discussed. The energy value and nature of the lowest excited singlet and triplet states of the DHP molecule were identified, based on analysis of low-temperature photoluminescence spectra.

## 2. Experimental

DHP crystals were illuminated using a high-pressure HBO 200 lamp with a band pass filter allowing irradiation with the wavelength corresponding to the UV absorption band of the compound. The transmission range of the filter covered essentially the 313-nm emission of the lamp. However, the transmittance of the filter at shorter wavelengths, down to 290 nm was found to be very small, though not negligible. The exposure time ranged between 1 and  $1.2 \times 10^4$  s. The optically generated photochromic form of DHP reported here was obtained from direct UV–vis experiments. Crystallites of DHP were mixed with KBr (ca. 1:400), ground and compressed at  $p = 2 \times 10^7$  Pa. The kinetics of the non-isothermal bleaching reaction in polycrystalline DHP in a KBr matrix, mounted in a temperature-controlled sample holder was determined spectrophotometrically by following the decay of the absorbance on the band peaked at 550 nm. Time-dependent evolution of absorption bands was measured with a Shimadzu UV-2101PC spectrophotometer. The IR steady-state spectra of DHP in the crystalline state were registered using a Perkin Elmer System 2000 FTIR with Multiscope system in reflection mode. Low-temperature photoluminescence measurements were carried out on a HITACHI F-4500 Fluorescence Spectrophotometer. An Oxford Instruments DN1704 cryostat was mounted inside the HITACHI spectrophotometer. The temperature of the sample, in a quartz tube, was reduced rapidly to 120 K, and then was slowly cooled down to 77 K.

## 3. Results and discussion

### 3.1. Optical generation of the photochromic form and thermal bleaching in the solid state

The absorption spectra of the polycrystalline DHP in both stable and colored forms (corrected due to scattering) are shown in Fig. 2. As seen in the figure, the low-energy absorption band of the stable form of DHP, which peaks at  $34\,000\text{ cm}^{-1}$ , has a low-energy tail extending to ca.  $28\,000\text{ cm}^{-1}$ . Illumination of the colorless samples with 313 nm light results in the appearance of two new absorption bands in the visible region; the DHP crystal becomes violet. This color change was also observed when the crystal was exposed to the sunlight for a few minutes.

Analysis of the UV–vis absorption spectrum of samples containing the colored form, performed with the Marquard–Levenberg method assuming Gaussian shapes of the bands, reveals the presence of three peaks centered at  $34\,050\text{ cm}^{-1}$ ,  $24\,800\text{ cm}^{-1}$ , and  $17\,920\text{ cm}^{-1}$ , the ratios of their integral intensities amounting approximately to 31:1:6 [18].

Optical generation of the photochromic form and the isothermal kinetics of each entity responsible for the color of the crystal were studied by analysis of the evolution with time of the absorption band(s) in the visible spectral range. Collections

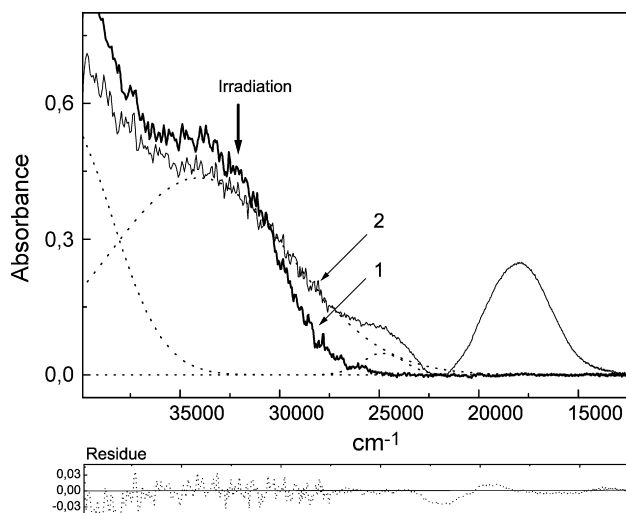


Fig. 2. Absorption spectra of polycrystalline DHP in a KBr matrix at ambient temperature: original form (1), and the sample after 180 min of irradiation (2). The arrow indicates the energy of the light quanta. The deconvoluted bands are also shown.

of some time-dependent long-wavelength sections of the spectra measured by irradiation in the range of  $10^1$  to  $10^4$  s are shown in Fig. 3. Unfortunately, a very noisy signal centered at 400 nm (Fig. 3), appears after illumination. We experienced some problems with correct setting of the baselines because of the background scattering. Despite this inconvenience we registered small but distinct growth of absorbance as the time of illumination was increased; the changes of absorbance were larger than the inaccuracy in the absorbance.

The experiments performed for DHP in solution have demonstrated that the bleaching reaction is of the first-order [8]. For generation of the colored form we also adopted first-order kinetics. Time-dependent changes of absorbance were related to the changes of concentration of the colored form using the equations resulting from the Lambert–Beer law:  $(n/n_0) = (A_\infty - A)/(A_\infty - A_0)$ , where  $A$ ,  $A_0$ ,  $A_\infty$  denote momentary absorbance and absorbances at  $t=0$  and  $t \rightarrow \infty$ . The rate

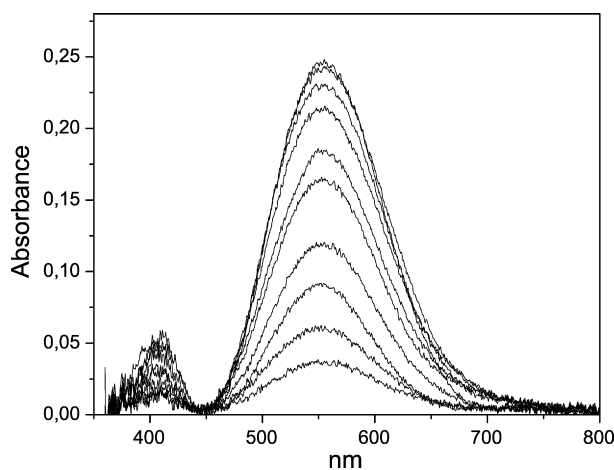


Fig. 3. Time-dependent evolution of UV absorption spectra of DHP in a KBr matrix;  $T=295$  K, UV exposure using HBO 200 lamp with 313 nm filter; illumination time  $10^1$  to  $10^4$  s (from bottom to top).

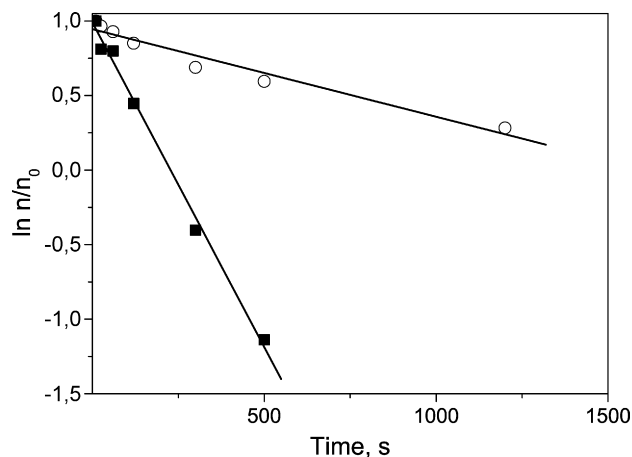


Fig. 4. First-order isothermal kinetics of generation of the colored forms of DHP monitored at absorption bands centered at 400 nm (full square) and 550 nm (open circle);  $T=295$  K,  $\lambda_{\text{irr}}=313$  nm.

constant was determined from the slope of the time dependence of the reactant concentration, plotted in semi-logarithmic coordinates. Fig. 4 shows the results of monitoring the absorption bands that appear at 400 nm and 550 nm after illumination of the solid sample.

The values of the rate constants of the photocoloration processes are equal to  $k_{550} = 5.87 \pm 0.56 \times 10^{-4} \text{ s}^{-1}$  and  $k_{400} = 4.36 \pm 0.17 \times 10^{-3} \text{ s}^{-1}$  for the high- and low-intensity absorption bands, respectively. Two such different values indicate independent processes, which are active at the beginning of generation of the colored forms. Most probably, more than a single process is connected with the entities characterized by the 400 nm absorption band, especially over a long-time scale. Unfortunately, because of the procedure used, only the first time period of sample coloration ('fast behavior') could be taken into account.

Having in mind the poor reversibility of the photochromic system under study, the non-isothermal technique was employed. The method essentially consists in measuring the kinetic response of the sample upon linearly increasing its temperature. In only one experimental run was the extraction of Arrhenius parameters possible. Therefore, we used the elegant methodology offered in the series of papers [23] to estimate the energy of activation of the DHP bleaching reaction.

Briefly, the basic equation for the temperature dependence of concentration of reactant is the following:

$$n = n_0 \exp \left( -\frac{\nu}{\beta} \int_{T_0}^T \exp \left( -\frac{E_a}{RT} \right) dT \right) \quad (1)$$

where  $n$ ,  $n_0$  denote momentary concentration and concentration at  $t=0$ ,  $\nu$ , frequency factor, and  $\beta$ ,  $E_a$ ,  $R$  and  $T$  denote heating rate, activation energy, Boltzmann constant and temperature, respectively. If  $E_a \gg RT$  and  $T > T_0$ , the Eq. (1) can be approximated to

$$n = n_0 \exp \left[ -\frac{\nu RT^2}{\beta E_a} \exp \left( -\frac{E_a}{RT} \right) \right]. \quad (2)$$

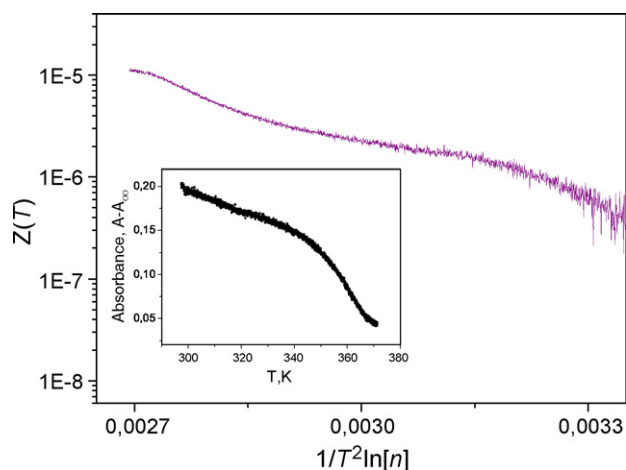


Fig. 5. Non-isothermal kinetics: the result of transformations of the kinetics data according to the Eqs. (2) and (3), and plotted in Arrhenius coordinates. *Inset*: Non-isothermal measurements of absorbance decay of polycrystalline DHP in a KBr matrix monitored at 550 nm with heating rate ca. 0.25 K/min.

The absorbance changes were converted into concentrations according to the Lambert–Beer law, as mentioned above. Additionally, a new function defined as

$$Z(T) = T^{-2} \ln \frac{n_0}{n} \quad (3)$$

in combination with Eq. (2) should be able to obtain the activation energy from the rectilinear portion of the plot of  $Z(T)$  versus  $1/T$ . The experimental results were transformed according to the procedure presented above (Fig. 5). Two processes characterized by different activation energy were estimated in the 320–360 K range of temperature. These values are 31.20 kJ/mol and 10.96 kJ/mol for the high- and low-temperature processes, respectively.

The activation energy of the high-temperature process in the 340–360 K temperature range can be assigned to 2,4-bridge formation of the decay product. Almost the same value was obtained from the isothermal method for a DHP polycrystalline sample deposited in an MgO matrix [9]. According to theoretical predictions the activation energy, equal to 40 kJ/mol, has been attributed to the reaction between the non-biradical forms, resulting from phenyl migration, and the 2,4-bridged form [10,17].

We have related the activation energy of the low-temperature process, in the 320–340 K temperature range, estimated as 10.96 kJ/mol, to reactions of biradicals (cf. Section 3.3).

### 3.2. The IR spectrum of DHP in the solid state

Figs. 6–9 show the IR as well as the differential spectra of colorless and colored forms of DHP. Prominent differences in fundamental vibration frequency together with intensity changes were seen only in the 3400–2500  $\text{cm}^{-1}$  range. In the IR as well as in the differential spectra of the photochromic form one can find two new fundamental vibration frequencies at  $\sim 2852 \text{ cm}^{-1}$  and  $\sim 2922 \text{ cm}^{-1}$  (Figs. 6 and 7). Their relative integral intensities with relation to the stretching fundamental vibration frequency  $\nu_{\text{CH}_2} = 3051.8 \text{ cm}^{-1}$  were 0.226 and 0.428, respectively.

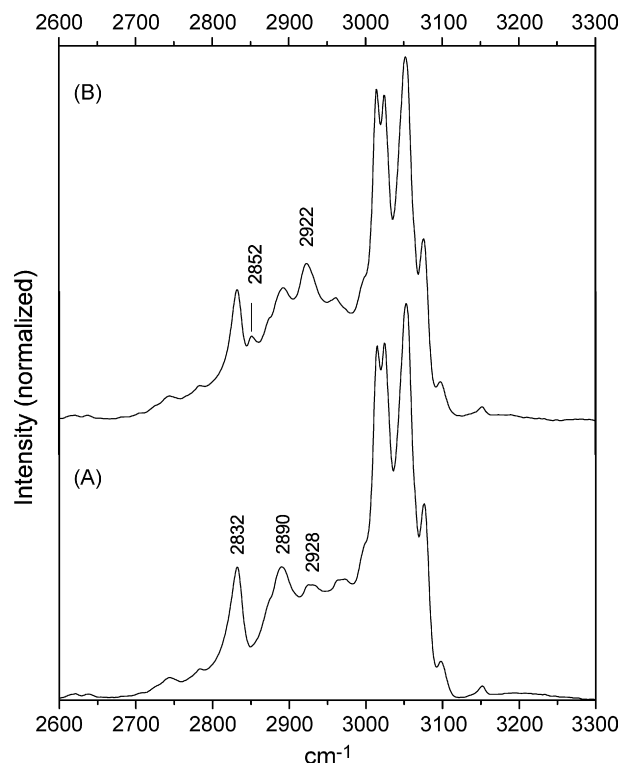


Fig. 6. The 3400–2500  $\text{cm}^{-1}$  range of IR spectra (normalized) of DHP original (colorless) stable form (A) and colored form (B).

The observed frequency values correspond to the well-known fundamentals of the  $\text{CH}_2$  group. However, the  $\text{CH}_2$  group does not exist in the basic molecular structure of DHP (cf. Fig. 1). Thus we postulate that the new IR bands identified are due to a newly created photochromic form having the structure discussed in Section 3.3 (cf. the structure proposed in Fig. 11).

The violet DHP crystal turned to russet-yellow, after multiple irradiation  $\leftrightarrow$  thermal bleaching cycles. The IR spectrum of the sample was congested, mostly because of products of side reactions (Fig. 8). For that reason the spectra were difficult to

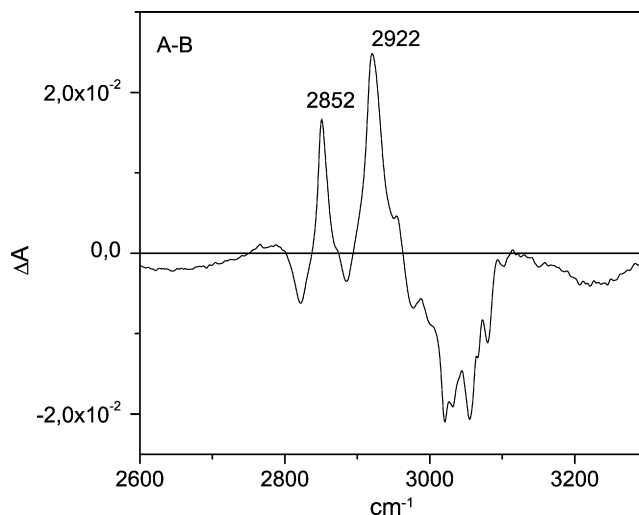


Fig. 7. The differential IR spectrum of colorless – photochromic form of DHP solid sample in 3400–2500  $\text{cm}^{-1}$  range.

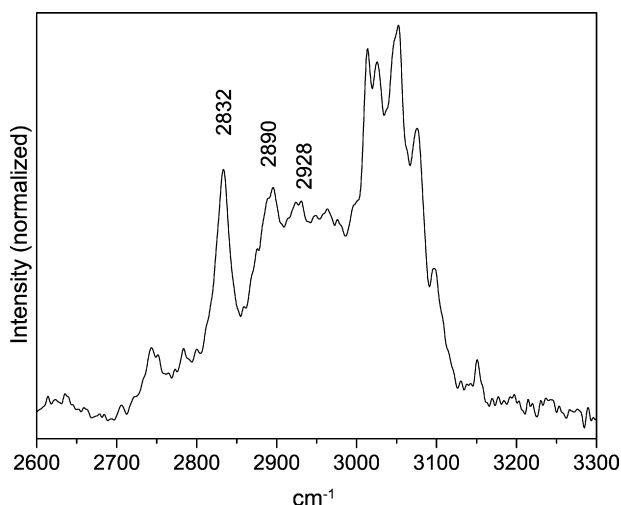


Fig. 8. The 3400–2500  $\text{cm}^{-1}$  range of the IR spectrum (normalized) of a sample of russet-yellowish crystalline DHP (in a KBr matrix) after multiple irradiation  $\leftrightarrow$  bleaching cycles.

interpret. However, the 3400–2500  $\text{cm}^{-1}$ -range of the spectrum discussed seems to be well resolved. The spectral pattern of the IR spectrum is similar but non-identical to that of the original form of the DHP sample (cf. Figs. 6 and 8). In detail, in the CH stretching range the fundamental vibration frequency of 2852  $\text{cm}^{-1}$  has disappeared. In the IR differential spectrum we observe two separated bands with maxima at 3024  $\text{cm}^{-1}$  and 3056  $\text{cm}^{-1}$ , the latter with a positive sign, and weak fundamental vibration frequency signals at 2938  $\text{cm}^{-1}$  and 2904  $\text{cm}^{-1}$ , respectively (Fig. 9).

These values correspond well to the cyclopropyl fragment identified in the vibrational spectra of bicyclo[2.1.0]pentane

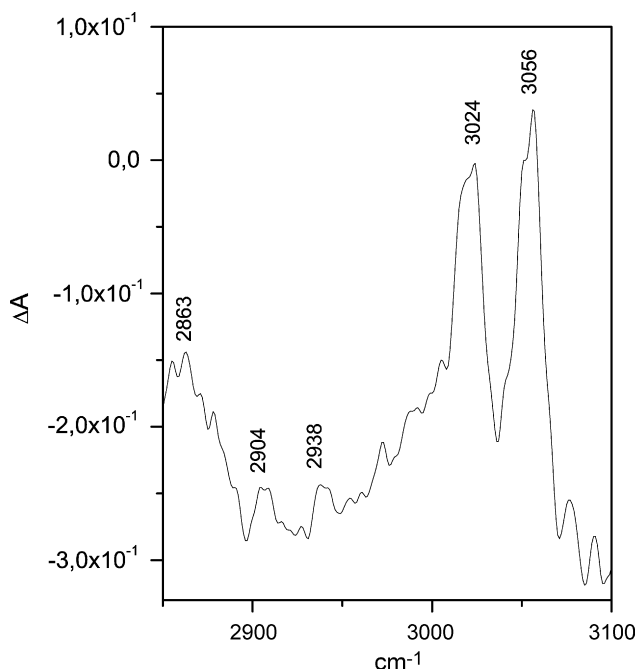


Fig. 9. The IR differential spectrum of original-thermally bleaching product of side reaction.

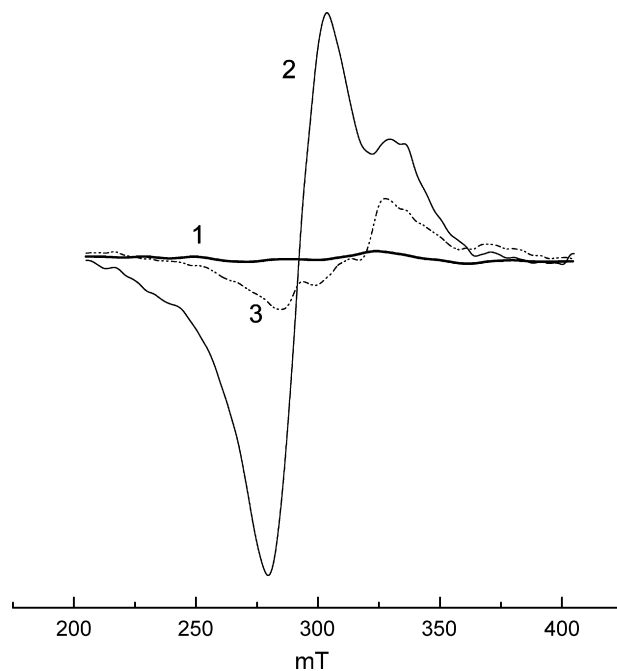


Fig. 10. EPR signals of DHP in the solid state: (1), original stable form; (2), colored (dark-violet) form; after irradiation with  $\lambda_{\text{exc}} = 365 \text{ nm}$  and  $t = 30 \text{ min}$ ; (3), sample after annealing at 400 K during 30 min.

[24,25]. In the molecule under study it can be related to the 2,4-bridged DHP product, which possesses a cyclopropyl moiety (cf. Fig. 12). The fact that the photochromic form resulting from the thermally driven reaction is converted to contain a cyclopropyl moiety was theoretically predicted in our earlier papers. In particular, the results of calculations showed the possibility of 2,4-bridge formation, associated with the energy barrier equal to 40 kJ/mol [8,17].

### 3.3. Biradicals and hydrogen transfer chain structure

The results of EPR measurements of different forms of DHP crystal are shown in Fig. 10. The violet crystal gave an EPR signal without hyperfine structure, which is assignable to a triplet biradical. The EPR lines are broad as a result of interaction of the two electrons with unpaired spin, and asymmetric due to the difference in  $g$ -factor of the two radical sites. The effective  $g$ -value equals to 2.0167 ( $B = 334.6 \text{ mT}$ ) and 2.2939 ( $B = 294.2 \text{ mT}$ ). The intensity of the EPR signal diminished after annealing the sample at a high temperature (400 K).

Taking into consideration the stability of the newly created structure, the presence of a  $\text{CH}_2$  group and preservation of the quinoid ring structure, we postulate the presence of two stable, weakly coupled structures denoted as A and B in Fig. 11.

The structure of non-symmetrical triplet biradical forms of DHP is in agreement with the experimental results mentioned above. According to calculations on the semi-empirical AM1 level, the B structure with well-separated radical centers is lower in energy than the A structure, with two radical centers located inside the same phenyl ring. The absorption of the former one, labeled as ‘photochromic’, has a maximum at 700 nm, while the latter one with absorption maximum at 300 nm, is closer to the

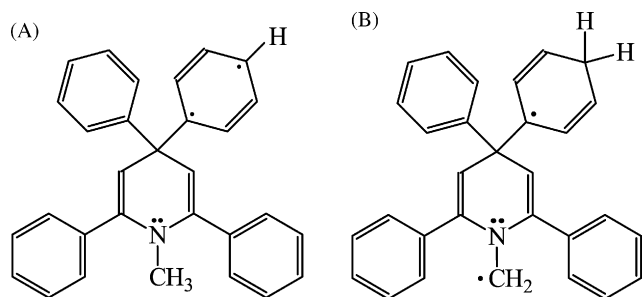


Fig. 11. Proposed photogenerated biradical structures active in the first step of photoreaction.

first absorption band of the original form of DHP. In the colored form the two radical centers are located on different fragments of the molecule: the methylene (former methyl) moiety being attached to the nitrogen atom and on the carbon atom in the phenyl ring attached to position 4 of the central pyridine ring (cf. Fig. 11). The large separation in that form, enforced by molecular non-planarity, warrants low-spin coupling and leads to the triplet biradical isomer of DHP. The proposed biradical structures and intermolecular hydrogen transfer chain process are presented in Fig. 12.

The postulated intermolecular hydrogen atom transfer is not in contradiction with the geometry of interacting molecules in the solid state. According to the results of X-ray structural analysis, such hydrogen transfer is possible, as the intermolecular C...H distance between the reacting centers equals  $d = 3.4 \text{ \AA}$ . ORTEPIII visualization of neighboring DHP molecules engaged in the hydrogen atom transfer process is shown in Fig. 13.

The photochemical reaction that starts on the crystal surface proceeds by an intermolecular ‘hydrogen cascade’  $[-\text{CH}_3 \cdots \text{C}_{\text{Ar}}-\text{CH}_3 \cdots \text{C}_{\text{Ar}}-]$  (Fig. 13). However, structural imperfections, e.g. ‘single effect of defects’ in the crystal lattice

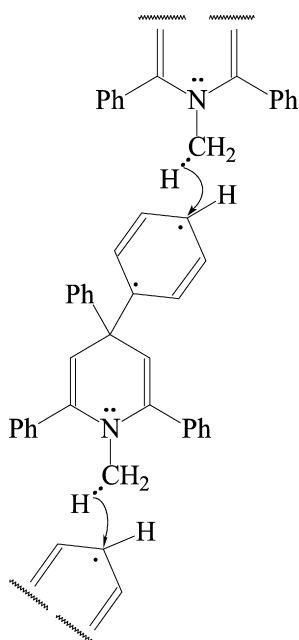


Fig. 12. Intermolecular hydrogen transfer scheme of DHP in the solid state.

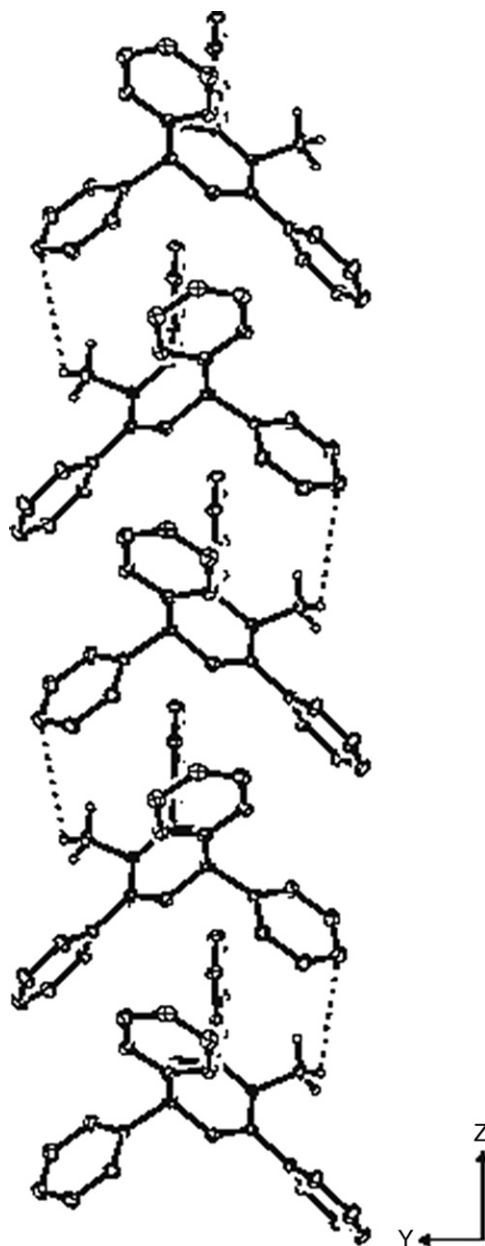


Fig. 13. ORTEPIII drawing (100 view) of the intermolecular  $[-\text{CH}_3 \cdots \text{C}_{\text{Ar}}-\text{CH}_3 \cdots \text{C}_{\text{Ar}}-]$  cascade; all the hydrogen atoms except those in the  $\text{CH}_3$  group are omitted for clarity.

[2], may disrupt the reaction chain of hydrogen atom transfer. As a consequence, photoreaction may be limited to the specific crystal volume only. Comparison of the integral intensities of the experimental bands and oscillator strength obtained from quantum-chemical calculations allows us to estimate that the conversion of DHP to the colored form does not exceed 25% [18]. Identification of the photochromic triplet biradical form in the framework of the intermolecular chain sequence using the X-ray method was unsuccessful. Localization of the H atom for the partly occupied structure, i.e. different in a thin layer close to the surface from that inside of the crystal volume, was impossible because of too low maxima on the Fourier map of density differences. The same difficulty was pointed out in dis-

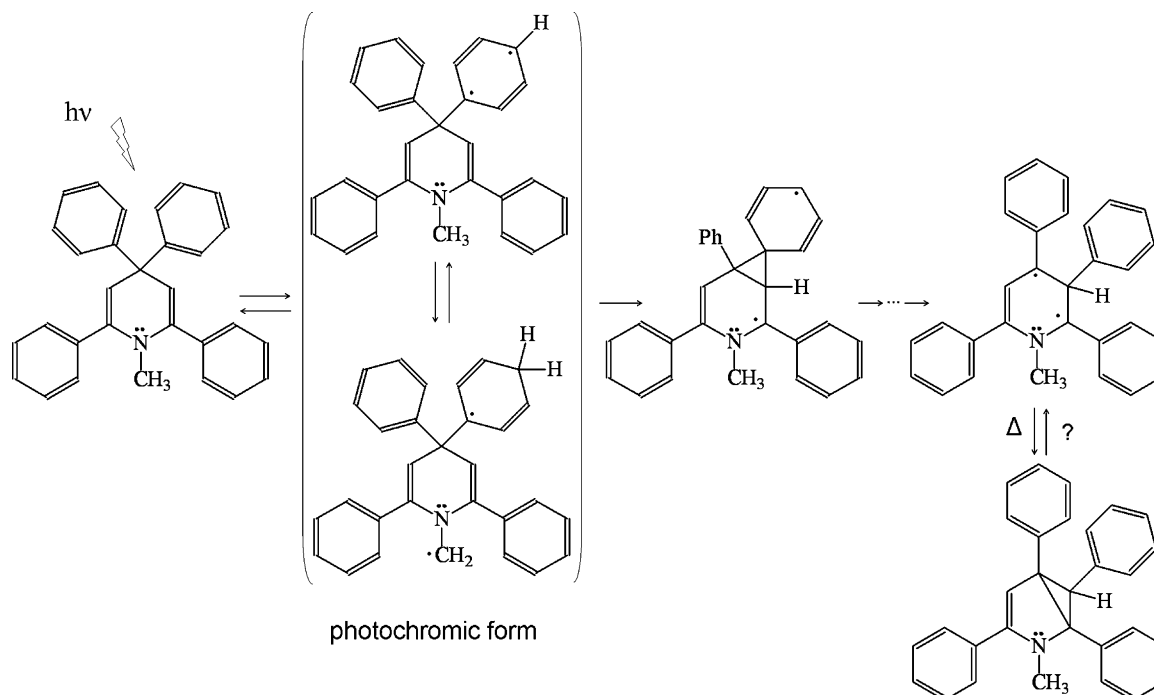


Fig. 14. The proposed reaction pathway of formation of different biradical structures derived from DHP after UV light pulse.

cussion of the photochromic behavior of other compounds, e.g. spiropyranes [26,27].

Fig. 14 shows the proposed sequence of further steps of photochromic behavior of DHP, assuming participation of a triplet biradical. At room temperature, in the dark, the violet crystals returned to the colorless form spontaneously but very slowly. The additional (mostly thermally driven) reaction stream in this figure shows intramolecular phenyl migration. Probably a biradical ‘partner’ for the thermally driven bleaching reaction leads to 2,4-bridge formation, which is proven by the IR spectrum (Fig. 8). In Fig. 14 a reversible reaction within the transformation of the biradicals  $\leftrightarrow$  colorless system is pointed out, as one parallel to the generation of the 2,4-bridged form.

As was stated in [28], the value of activation energy of an intra- and intermolecular photochemical hydrogen-abstraction reaction in liquids, glasses or single crystals is on the whole between 8 kJ/mol and 16 kJ/mol. Our results of non-isothermal kinetics are in agreement with this statement. It seems that the activation energy 10.96 kJ/mol can be related to biradicals and/or to mutual rearrangements in the biradical structure.

In contrast to numerous papers reporting on the photochemical activity, much less attention was paid to their spectroscopic properties, especially those in a rigid matrix. Using low-temperature photoluminescence spectra, the nature of the excited electronic states of DHP was investigated. The luminescence spectra of DHP in *n*-heptane at 77 K are shown in Fig. 15. In addition to the phosphorescence, fluorescence and fluorescence excitation spectra monitored at the 0–1413 vibronic transition, the  $S_n \leftarrow S_0$  absorption spectrum at ambient temperature was determined.

It is interesting to note that the markedly non-planar DHP molecule (cf. Fig. 12) exhibits the structure of  $^1(\pi, \pi^*) \rightarrow S_0$  as

well as of the  $^3(\pi, \pi^*) \rightarrow S_0$  electronic transition in a Shpolskii matrix. The decay curves of phosphorescence are exponential. The phosphorescence lifetime ( $\tau_{ph}$ ) monitored at the 0–0 transition ( $E_T = 67.6$  kcal/mol) was found to be equal to  $4.9 \pm 0.1$  s [29]. The lowest electronic excited singlet and triplet states are of  $\pi, \pi^*$ -type. The singlet–triplet energy gap determined experimentally,  $\Delta E_{ST} = 16.3$  kcal/mol, is rather too low for that of excited states of  $\pi, \pi^*$ -type [30].

Nevertheless, DHP in a Shpolskii matrix did not show photochromic behavior. Probably, the molecular geometry and in consequence the intermolecular interaction of DHP in frozen

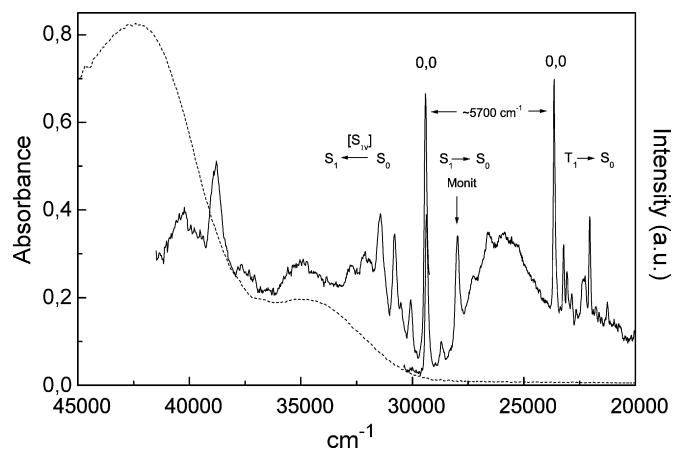


Fig. 15. Low-temperature photoluminescence spectra of DHP in *n*-heptane at 77 K (energy excitation =  $37\,040\text{ cm}^{-1}$ ) and absorption spectrum at 295 K (dotted line). Legend:  $T_1 \rightarrow S_0$ : phosphorescence,  $S_1 \rightarrow S_0$ : fluorescence,  $S_n \xleftarrow{S_1} S_0$  fluorescence excitation spectra monitored at 0–1413 vibronic transition, Monit  $\downarrow$ : monitoring position =  $27\,930\text{ cm}^{-1}$ ; two-sided arrow ( $\leftrightarrow$ ),  $\Delta E(S_1-T_1)$ , in  $\text{cm}^{-1}$ .

solution, is not suitable for creation of the chain structure necessary for the hydrogen transfer process.

Intensive studies of biological systems prove that hydrogen transfer processes are expected to show appreciable quantum mechanical behavior in practical in every example investigated [31–33]. It is interesting to study theoretically how that intermolecular process develops in a photochromic system. Theoretical studies concerning the alternative paths and the structures of transition state and intermediates, their geometry and energy as well as their spectral properties by molecular modeling on the ab initio level are currently being performed and will be a subject of separate paper.

#### 4. Conclusions

It has been demonstrated for the first time that an intermolecular hydrogen transfer process ('hydrogen cascade') induces photochromism in an organic compound in the solid state. Moreover, photomagnetism and photochromism are inseparable. 1-Methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine is the first example of a photochromic material exhibiting this novel feature.

Movement of a hydrogen atom from the CH<sub>3</sub> group to an aromatic carbon atom realizes the intermolecular hydrogen transfer process in the solid state over the distance of 2–3 Å.

Our experimental results allowed us to identify the processes in which non-symmetric biradicals have played a crucial role. The photochromic form as a triplet biradical is relatively stable at room temperature. In the dark, it slowly returns to the state before irradiation.

#### Acknowledgements

The authors thank Prof. S. Nešpůrek (Prague) for supplying a sample of DHP, also Dr. hab. I. Turowska-Tyrk and Dr. K. Janus (both from Institute of Physical and Theoretical Chemistry, Wrocław University of Technology) respectively, for helping in X-ray structure determination and in the analysis of first-order reactions in the isothermal as well as the non-isothermal regime. The EPR measurements were done by courtesy of Prof. M. Komorowska (Institute of Physics, Wrocław University of Technology).

#### References

- [1] G.H. Brown, *Photochromism*, Wiley-Interscience, 1971; H. Dürr, H. Bouas-Laurent (Eds.), *Photochromism: Molecules And Systems*, Elsevier, Amsterdam, 1990; R. Guglielmetti, A. Samat, *Proceedings of the First International Symposium on Organic Photochromism*, *Mol. Cryst. Liq. Cryst.* 246 (1994) (special issue);
- M. Irie (Ed.), *Photochromism – memories and switches*, *Chem. Rev.* 100 (2000) (special issue).
- [2] A. Rajca, *Chem. Rev.* 94 (1994) 871–893.
- [3] A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* 294 (2001) 1503–1507.
- [4] G. Kaupp, *J. Mol. Struct.* 786 (2006) 140–156.
- [5] M.M. Wienk, R.A.J. Janssen, E.W. Mejer, *Synth. Met.* 71 (1995) 1833–1834.
- [6] K. Tanaka, F. Toda, *J. Chem. Soc., Perkin Trans. 1* (2000) 873–874.
- [7] K. Tanaka, Y. Yamamoto, S. Ohba, *Chem. Commun.* (2003) 1866–1867.
- [8] J. Sworakowski, S. Nešpůrek, J. Lipiński, A. Lewanowicz, *J. Photochem. Photobiol. A: Chem.* 129 (1999) 81–87.
- [9] J. Sworakowski, S. Nešpůrek, J. Lipiński, E. Śliwińska, A. Lewanowicz, A. Olszowski, in: *Multiphoton and light driven multielectron processes in organics: new phenomena, materials and applications*, NATO Advanced Research Workshop on Multiphoton and Light Driven Multielectron Processes in Organics: New Phenomena, Materials and Applications (F. Kajzar, M. V. Agranovich Eds.), Kluwer Academic Publ., 2000, NATO Science, Ser. 3, High Technol., vol. 79, pp. 249–260.
- [10] J. Sworakowski, S. Nešpůrek, J. Lipiński, A. Lewanowicz, *Mol. Cryst. Liq. Cryst.* 356 (2001) 163–173.
- [11] J. Shibuya, M. Nabeshima, H. Nagano, K. Maeda, *J. Chem. Soc., Perkin Trans. II* (1988) 1607–1612.
- [12] K. Maeda, M. Nakamura, *J. Photochem.* 17 (1981) 87.
- [13] K. Maeda, M. Nakamura, M. Sakai, *J. Chem. Perkin Trans. 1* (1983) 837–839.
- [14] J. Vojtěchowský, J. Hašek, S. Nešpůrek, M. Adamec, *Coll. Czech. Chem. Commun.* 57 (1992) 1326–1334.
- [15] S. Nešpůrek, W. Schwartz, S. Böhm, J. Kuthan, *J. Photochem. Photobiol. A* 60 (1991) 345.
- [16] S. Nešpůrek, W. Schnabel, *J. Photochem. Photobiol. A* 81 (1994) 37–43.
- [17] A. Lewanowicz, J. Lipiński, S. Nešpůrek, A. Olszowski, E. Śliwińska, J. Sworakowski, *J. Photochem. Photobiol. A* 121 (1999) 125–132.
- [18] A. Lewanowicz, J. Lipiński, A. Olszowski, J. Sworakowski, *Phase Tr.* 76 (2003) 847–855.
- [19] S. Nešpůrek, W. Schnabel, *J. Photochem. Photobiol. A* 60 (1991) 151.
- [20] H. Pirelahi, H. Rahmani, A. Mouradzadegan, A. Fathi, A. Moujoodi, *J. Photochem. Photobiol. A* 101 (1996) 33–37.
- [21] H. Rahmani, H. Pirelahi, *J. Photochem. Photobiol. A* 111 (1997) 15–21.
- [22] Y. Ohashi, *Reactivity in Molecular Crystals*, Kodansha and VCH, 1994 (chapter 5).
- [23] J. Sworakowski, K. Janus, S. Nešpůrek, *Adv. Coll. Int. Sci.* 116 (2005) 97–110; K. Janus, J. Sworakowski, *Struct. Chem.* 15 (2004) 465–472; K. Janus, I.A. Koshets, J. Sworakowski, S. Nešpůrek, *J. Mater. Chem.* 12 (2002) 1657–1663.
- [24] B.M. Showalter, T.C. Benz, L.R. Ryzhkov, Ch.M. Hadad, J.P. Toscano, *J. Phys. Org. Chem.* 13 (2000) 309–312.
- [25] J. Bragin, D. Guthals, *J. Phys. Chem.* 79 (1975) 2139–2144.
- [26] S. Bernard, P. Yu, *Chem. Commun.* (2000) 65–67.
- [27] F. Iwasaki, T. Watanabe, K. Maeda, *Bull. Chem. Soc. Jpn.* 60 (1987) 1255–1259.
- [28] J.P. Colpa, D. Stehlik, *Chem. Phys.* 81 (1983) 163–174; J.P. Colpa, B. Brass, D. Stehlik, *Chem. Phys. Lett.* 107 (1984) 469–474.
- [29] E. Śliwińska, K. Palewska, A. Lewanowicz, J. Lipiński, J. Sworakowski, R. Gancarz, S. Nešpůrek, *Polish J. Chem.* 76 (2002) 235–247.
- [30] N. Turro, *Molecular Photochemistry*, W.A. Benjamin Inc., New York, 1965.
- [31] Y. Cha, C.J. Murray, J.P. Klinman, *Science* 243 (1989) 1325–1330.
- [32] W.J. Bruno, W. Bialek, *Biophys. J.* 63 (1992) 689–699.
- [33] J.P. Klimman, *Pure Appl. Chem.* 75 (2003) 601–608.