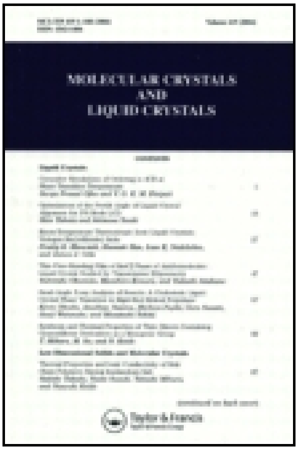

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Cations of Photochromic Spiropyrans as Promising Blocks for Polyfunctional Materials

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Cations of Photochromic Spiropyrans as Promising Blocks for Polyfunctional Materials

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*Molecular and crystalline strucutre has been studied for the single crystals of neutral spiropyran (SP) 1,3,3,6′-tetramethylspiro[indoline-2,2′-[2H]pyran[3,2-b] pyridine (**Ia**) and its salts, 1,3,3,5′,6′-pentamethylspiro[indoline-2,2′-[2H]pyran [3,2-b]pyridinium] iodide (**I**) and 5′-hydroxymethyl-1,3,3,7′,8′-pentamethylspiro [indoline-2,2′-[2H]pyran[3,4-b]-pyridinium iodide (**II**). Compounds are monoclinic, i.e., for **Ia**: $a = 11{,}942(2)$, $b = 11{,}733(2)$, $c = 11{,}493(2)$ Å, $\alpha = 90°$. $\beta = 96{,}96(3)°$, $\gamma = 90°$, $V = 1568{,}5(5)$ Å, $\rho_{calc.} = 1.215\,g/cm^3$, $Z = 4$; I: $a = 24.107(5)$, $b = 10.959(2)$, $c = 15.557(2)$ Å, $\alpha = 90°$, $\beta = 108.74°(3)$, $\gamma = 90°$, $V = 3892.1(13)$, Å^3, $\rho_{calc.} = 1.482\,g/cm^3, Z = 8$, space group P2(1)/c, while for compound **II** $a = 12.789(3)$, $b = 10.807(2)$, $c = 15.612(3)$ Å, $\alpha = 90°$, $\beta = 108.09°(3)$, $\gamma = 90°$, $V = 2050.8(7)$ Å^3, $\rho_{calc} = 1.578\,g/cm^3$, space group P2(1)/n, $Z = 4$. The crystalline structure of salts **I** and **II** differs from that of the neutral SP being formed by the cationic layers separated by I^- ions, thus providing a sufficient volume for spiropyran phototransformations. Photochromism of **I** and **II** single crystals has been first studied. The quantum yield of the open form formation is about 0.1, and of bleaching 0.04. Tenfold reversible photocycling reduces absorption of the colored form by 10% Photochromic properties have been correlated with the single crystals structure.*

Keywords: molecular-based magnets; photochromism; solid phase transformations; spirooxazines; spiropyrans

INTRODUCTION

Recently, photochromic transformations of spiropyrans in the crystalline state have been of great interest from the viewpoints of development of new materials for recording, processing and storing of

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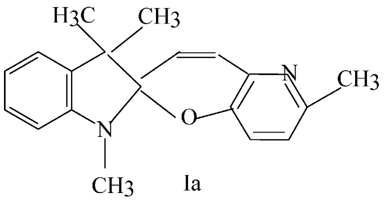
optical information [1,2], as well as synthesis of new polyfunctional materials combining different properties in the same crystalline lattice [3,4]. In such crystals, photoinduced transformations may result in arising of new functions, e.g., "photoswitching" of non-linear optical properties [5]. However, photochromic transformations of spiropyrans (SP) and spirooxazines (SO) due to C_{spiro}-O bond cleavage and the subsequent isomerization of the molecule need free volume, therefore, they are impeded in crystals with dense molecular packing in the lattice. Normally, under steady irradiation, SP and SO microcrystalline powders do not exhibit photocoloring induced by the formation of planar open photomerocyanin structures (PMC), this being typical for solution or the amorphous state. However, by using time resolved and steady state diffuse reflectance spectroscopy [6,7], non-planar open forms were shown to appear in SP and SO crystals under weak femto-second 390-nm laser excitation ($< 1\,\mathrm{mJ\,cm^{-2}}$). A lifetime for such open forms depends on molecular and crystalline structure and lies in the range of ps to ns.

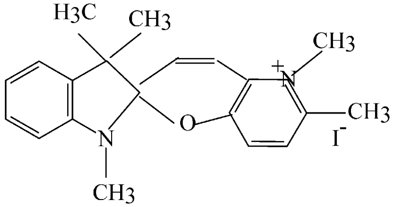
By raising intensity of laser impulse to several $\mathrm{mJ\,cm^{-2}}$, a threshold has been shown to exist in microcrystals of each SP or SO. Then photocoloring was observed, which spectrally coincided with PMC formation in solution and the amorphous state [7,8]. The free volume around SP and SO molecules, which is necessary for isomerization, is supposed to appear at the expense of local deformations of the crystalline lattice in the sites of densely generated excited states and intermediate non-planar open forms [7,8]. Usually, such phototransformations are irreversible.

Recently, SP and SO salts with the pyridine rings $SP^{+}X^{-}$, $SO^{+}X^{-}$ have been synthesized [9,10]. Ultra-fine pressed microcrystalline samples have been examined, and they were shown to undergo colorization under steady UV (365 nm) irradiation giving a wide absorption band between 500 and 650 nm, like in solutions. As it follows from preliminary data, phototransformations in microcrystals do not depend on anion X^{-}. If such unusual behavior is due to the specific features of the crystalline structure, a unique chance appears to introduce functional anions in the crystalline lattice, for example, magnetic ones, and to obtain photochromic magnetic materials.

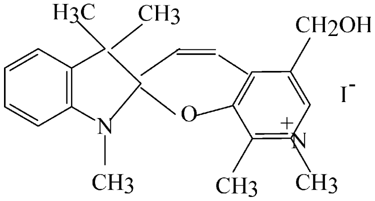
Organic magnets based on bimetallic oxalate salts $A^{x+}[M_1 M_2(ox)^3]^{x-}$ can be promising for development of such materials [11]. In such compounds, anion blocks are magnetically active. For two-dimensional (2D) structures, with a magnetic sub-lattice having layered honeycomb arrangement and cations being located in cavities between the layers, there is possibility to intercalate low-symmetry cations of different sizes (in the range of 8 to 14 Å) into the anionic sub-lattice [11]. In [12], the first successful example of synthesis of a



SP



$[SPCH_3]^+I^-$ (I)



$[SPCH_3]^+I^-$ (II)

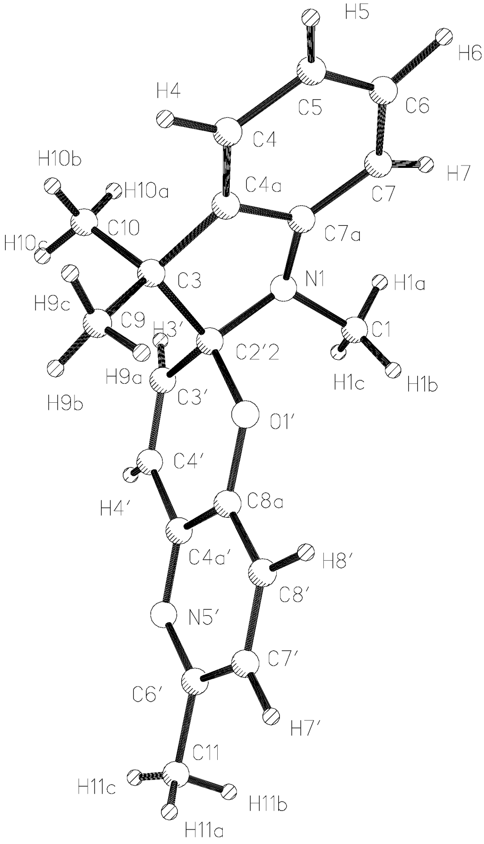
polyfunctional crystalline compound with photochromic SP^+ cation and magnetic anion $[MnCr(ox)^3]^-$ has been reported.

For purposeful crystal chemical engineering of such materials from crystalline blocks of different functionality, systematic investigation of the structural features and properties of such blocks, as well as possibility of their unification in the crystalline lattice is necessary. Main structural features of magnetic bimetallic oxalates have been reported in [11]. The structure of SP^+X^- and SO^+X^- salts, which is responsible for phototransformations in the crystalline state, as well as photochromic properties of such single crystals (that is necessary for determination of direct correlations between the structure and properties) have not been studied so far.

In this work, the neutral SP with the pyridine ring (SP Ia), its iodide containing quaternary nitrogen atom in position 5′ of the pyridine ring, $[SPCH_3]^+I^-$(I), and in position 7′ of the pyridine ring, $[SPCH_3]^+I^-$(II) have been synthesized, their single crystals obtained and their structure and photochromic properties investigated.

RESULTS AND DISCUSSION

The molecular structure of the three compounds is similar to each other and to that of earlier studied SP and SO [13] (Fig. 1).

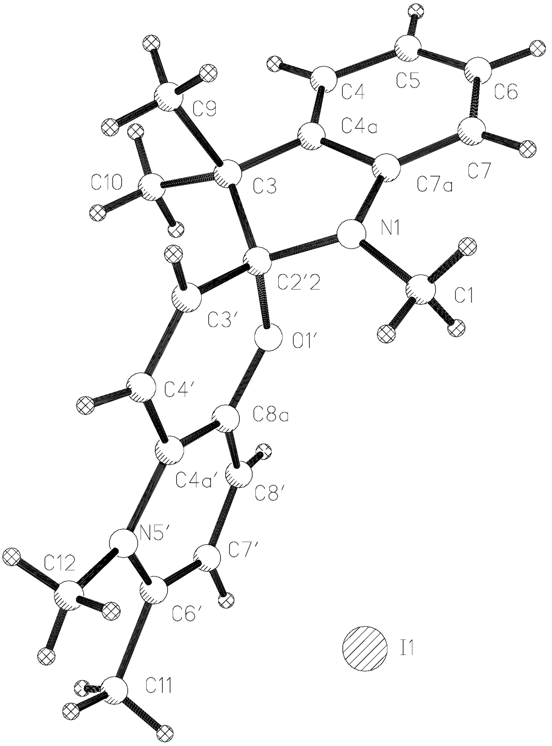


a

FIGURE 1 (a) General view of SP molecule (Ia), (b) General view of one of the independent molecules $[SPCH_3]^+I^-$(I), (c) General view of $[SPCH_3]^+I^-$ molecule (II).

The indoline moiety in all compounds is bent towards the oxygen atom of the pyran ring, thus providing the pyramidal configuration of the nitrogen atom and trans-orientation of the lone electron pair (LEP) of N(1) and the C(22′)-O(1)′ bond.

Such structure of the spiro-center is favorable for the interaction of N(1) LEP with the anti-bonding σ^*-orbital of the polar C(22′)-O(1)′ bond localized at the continuation of this bond at the C(22′) atom side. Such orbital n_{N1}-σ^* C_{spiro}-O interaction results in strengthening and shortening of the C(22′)-N(1) bond and weakening and elongation of the C(22′)-O(1)′ bond, which is ruptured upon photoexcitation of SP



b

FIGURE 1 Continued.

and SO [13]. These interactions become stronger in the excited state, thus facilitating C_{spiro}-O bond cleavage [14].

In the investigated SP, replacement of the benzene ring in the benzopyran moiety with a more EW pyridine ring increases efficiency of n_N-σ^* interaction and results in the elongation of the C_{spiro}-O bond to 1.475(3) Å (Ia) as compared to the benzopyran SP. Quaternarization of the pyridine N atom in salts I and II is accompanied by the further elongation of the C_{spiro}-O bond to 1.55(2) Å* (I), 1.485(9) Å (II), this being comparable with 5′-NO_2 SP [13]. Thus, the molecular structure of SP (Ia) and cations SP (I) and (II) is favorable for efficient C_{spiro}-O bond cleavage upon photoexcitation.

Single crystals Ia, I and II have space group $P2_1/c$ $Z = 4$ (Ia), $P2_1/c$ $Z = 8$ (I) and $P2_1/n$ $Z = 4$ (II) with density 1.215(3), 1.482(3) and

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*accuracy of this bond length is low because of the single crystals poor quality.

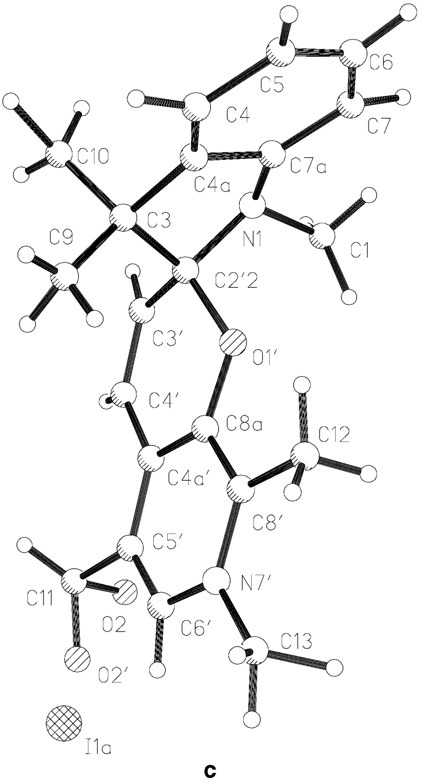


FIGURE 1 Continued.

1.578(3) g/cm^3, respectively (Figs. 2–4). In crystals Ia, I and II, SP molecules are packed in stacks by means of screw axes 2_1. The basic structural difference of these 2_1-stacks is that the neutral SP molecules are packed in stacks by the planes of the pyrido-pyran moieties, while $[SPCH_3]^+$ cations are packed in 2_1-stacks by the planes of the indoline fragments. Hence, in 2_1-stacks of Ia single crystals, the indoline moieties lie outside the stacks on the opposite sides (Scheme 1), and they are approximately parallel to the stacks axis. On the contrary, for cations I and II, the indoline fragments are packed in 2_1-stacks, while the pyrido-pyran ones lie outside the stacks on the opposite sides (Scheme 1). The energy of the intermolecular interaction in 2_1-stacks in Ia, I and II is –7.7, –7.4, –7.8 kkcal/mol, respectively. (Only van der Waals interactions between SP molecules or its cations have been taken into account).

In crystals Ia, I and II, 2_1-stacks are connected with each other by inversion centers ($\bar{1}$) and planes ("c" or "n"). In crystals Ia, the energy

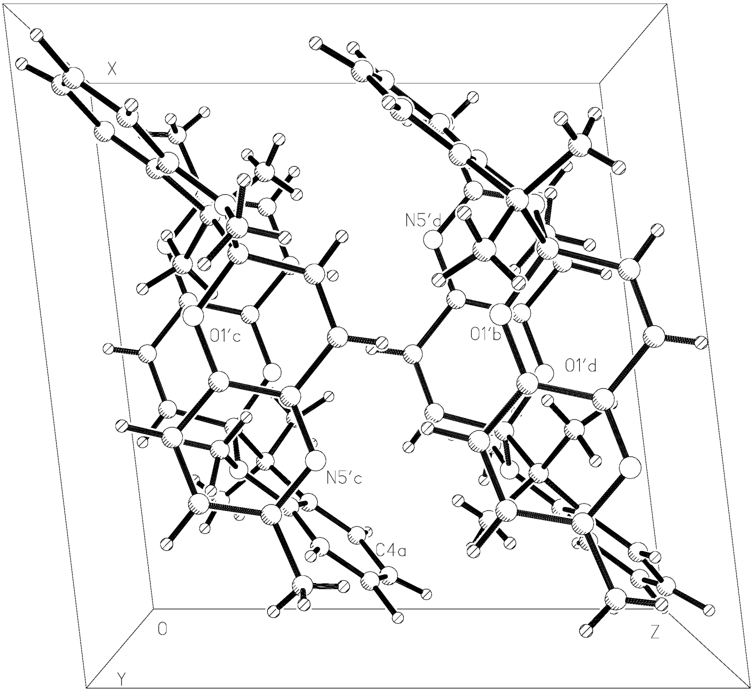


FIGURE 2 Packing of the molecules in crystals of neutral SP (Ia).

of the intermolecular interactions (E_{imi}) of the molecules from 2_1-stacks with the nearest molecules ($\bar{1}$) and ("c") is -4.7 and -8.1 kcal/mol, i.e., the molecule packing in crystals is isotropic. In crystals I independent molecules are packed in 2_1-stacks, which form independent layers by inversion centers ($\bar{1}$) and planes ("c"). Inside the layers, E_{imi} with the nearest molecules ($\bar{1}$) is -6.0 (-5.4) kcal/mol, and with molecules ("c") it is -4.4 (-4.6) kcal/mol. E_{imi} between the layers is less than -2 kcal/mol.

In crystals II 2_1-stacks are packed in layers by plane ("n"). E_{imi} with the nearest molecules in these layers is -5.9 kcal/mol. The layers with I^- ions between them are connected with each other by inversion centers ($\bar{1}$), with E_{imi} -4.2 kcal/mol. Thus, E_{imi} between the layers in crystals I and II, where I^- ions are located, is much lower than it is inside the layers.

Taking into account that C_{spiro}-O bond cleavage and the subsequent isomerization occur in the pyrido-pyran fragment of SP, we can assume that the crystalline structure of single crystals I and II will be favorable for PMC structures formation upon steady UV light irradiation, similar to solutions and the amorphous state.

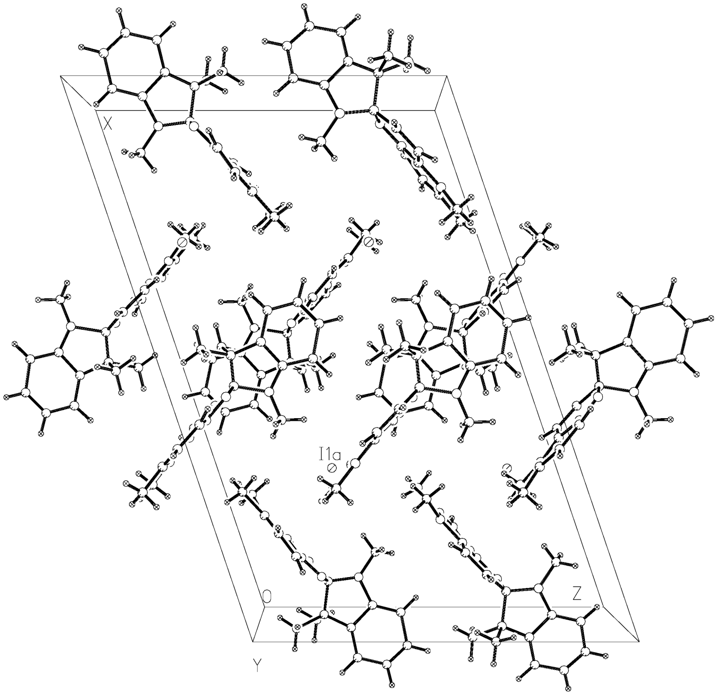


FIGURE 3 Packing of the molecules in crystals of $[SP(CH_3)]^+I^-$ (I).

For single crystals of neutral SP Ia exposed to steady UV light irradiation, we failed to register the increase of optical density in 500–600-nm region. On the contrary, salts I and II have photochromic properties in the crystalline state. Figure 5 shows the absorption spectra of single crystal II before irradiation (curve 1) and after irradiation with 270–370 nm (curve 2). It can be seen that the band (curve 4) appears in the spectrum, which is typical for absorption of SP II open form, which was earlier investigated in solutions and polycrystals [10]. After visible light (500–600 nm) irradiation of this sample, the long-wave absorption band disappears, and the absorption spectrum reverts back to the initial one (curve 3). Such photochromic transitions were observed in the single crystal upon ten-fold reversible irradiation of the sample, with no destruction observed. The absorption of the open form decreased by ~10%. Reversible transitions were accompanied by a small growth of the absorption in the short-wave region (400–450 nm), thus suggesting a partial photodestruction of the substance. This could be due to surface phenomena. The color in the single crystal was kept

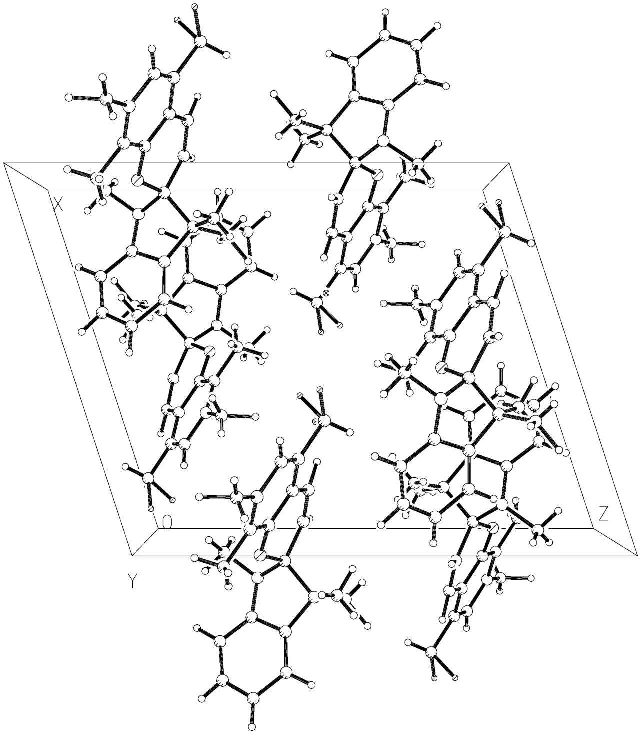
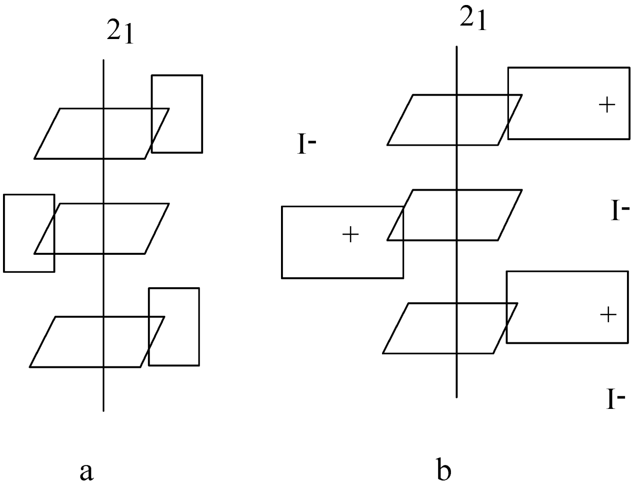


FIGURE 4 Packing of the molecules in crystals of $[SP(CH_3)]^+I^-$ (II).

during a month at room temperature without noticeable changes; the constant of dark bleaching was $k \leq 10^{-8} s^{-1}$.

Similar photochromic transformations have been observed for a single crystal of I too, however, the colored form is less stable under dark conditions, and the constant of bleaching $k = 5 \cdot 10^{-6}\ s^{-1}$, similar to that in crystalline fine-dispersed pressed pellets [10].

Thus, the positively charged pyridine ring in salts I and II is threefold responsible for photochromic transformations of such SP. First, n_N-$\sigma^*_{Cspiro\text{-}O}$ interactions in the spiro-center of the molecules become stronger, and C_{spiro}-O bond cleavage weakens and elongates at the expense of the electron withdrawing effect of this ring; second, the positively charged ring stabilizes the forming PMC; third, electrostatic interactions with anions result in the formation of the crystalline structure, which provides sufficient free volume around the pyrido-pyran moiety and its higher mobility, and hence, possibility of isomerization and PMC formation. Besides, re-distribution of the electron density in the open PMC and arising of the positive charge



SCHEME 1 Packing of the molecules in 2_1-stacks in crystals of neutral SP Ia (Scheme 1a) and SP salts (Scheme 1b).

on the indoline fragment will change the balance of electrostatic interactions in the crystal and provide ion I^- with a higher mobility, thus facilitating the structural re-arrangement in crystals of SP salts.

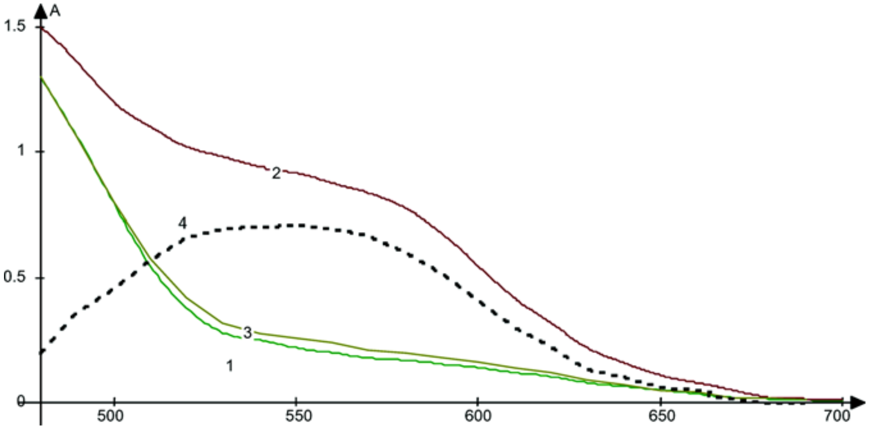


FIGURE 5 1 – absorption spectrum of the single crystal of II before UV irradiation, 2 – after UV irradiation (270–370 nm), 3 – after visible light (500–600 nm) irradiation, 4 – difference absorption spectrum of the irradiated sample (curve 2) and of the initial one (curve 1).

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