Strongly modified [2,2′-bipyridyl]-3,3′-diol (BP(OH)$_2$): a system undergoing excited state intramolecular proton transfer as a photostabilizer of polymers and as a solar energy collector

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Abstract

Six new compounds, derivatives of [2,2′-bipyridyl]-3,3′-diol (BP(OH)$_2$) are recommended as useful modifications of the parent structure. One group, three molecules with conjugate aromatic substituents (6-methyl-6′-styryl-BP(OH)$_2$, 6-(4-methoxystyryl)-6′-methyl-BP(OH)$_2$, 6-methyl-6′-(4-phenylstyryl)-BP(OH)$_2$), are potential solar energy concentrators — they have absorption spectra red shifted with respect to BP(OH)$_2$. To the second group belong the derivatives with the aliphatic side chains, better "accepted" by polyethylene than the parent molecule. These compounds are designed to improve their function as photostabilizers of polymers. All six new compounds were synthesized and their photophysical characteristics were studied. Absorption spectra, phototautomeric fluorescences and their excitation spectra, as well as quantum yields and lifetimes are reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bipyridyl-diol derivatives; Solar concentrators; Photostabilizers

1. Introduction

Photophysics of [2,2′-bipyridyl]-3,3′-diol (BP(OH)$_2$) (see Fig. 1) is a matter of numerous papers published within the last 15 years. It involves the ultrafast intramolecular proton transfer (PT) kinetics, the single vs. double PT mechanism of phototautomerisation, which are studied theoretically [1,2] and experimentally with application of electro-optical and femtosecond techniques [3–7].

In the course of photophysical studies [8], it was also observed that BP(OH)$_2$ and its simple derivatives in the inert solvents may serve as efficient dye lasers [9]. Moreover, since they reveal a very large Stokes shift due to the excited state intramolecular proton transfer (ESIPT) reactions, resulting in the phototautomeric fluorescence of a relatively high quantum yield (about 30%), they are recommended as potential solar energy concentrators [10,11]. Finally, BP(OH)$_2$, like some other systems undergoing ESIPT, is a very efficient agent protecting polyethylene against photo-degradation [12–14]. The last observation is considered prospective for protection of polyethylene films used widely in farming.

The two above presented potential applications point to a need of structural modifications of BP(OH)$_2$ that could make the model system more applicable and efficient. We have already shown that BP(OH)$_2$ framework may be modified in a predictable way [15].

First, solar energy concentrators should have the absorption spectra shifted to the red with respect to BP(OH)$_2$, to be better adjusted to the solar spectrum reaching the earth surface. Secondly, the BP(OH)$_2$ functional structure should become better soluble in polyethylene.

Our present work is then addressed to the demand for increasing lipophilicity as well as evocation of batochromic effect in BP(OH)$_2$ molecule. In order to accomplish these goals, we decided to synthesize derivatives of BP(OH)$_2$ substituted with long aliphatic chains, which should dramatically increase its lipophilicity, and also to introduce a styryl substituent in order to obtain the batochromic effect.
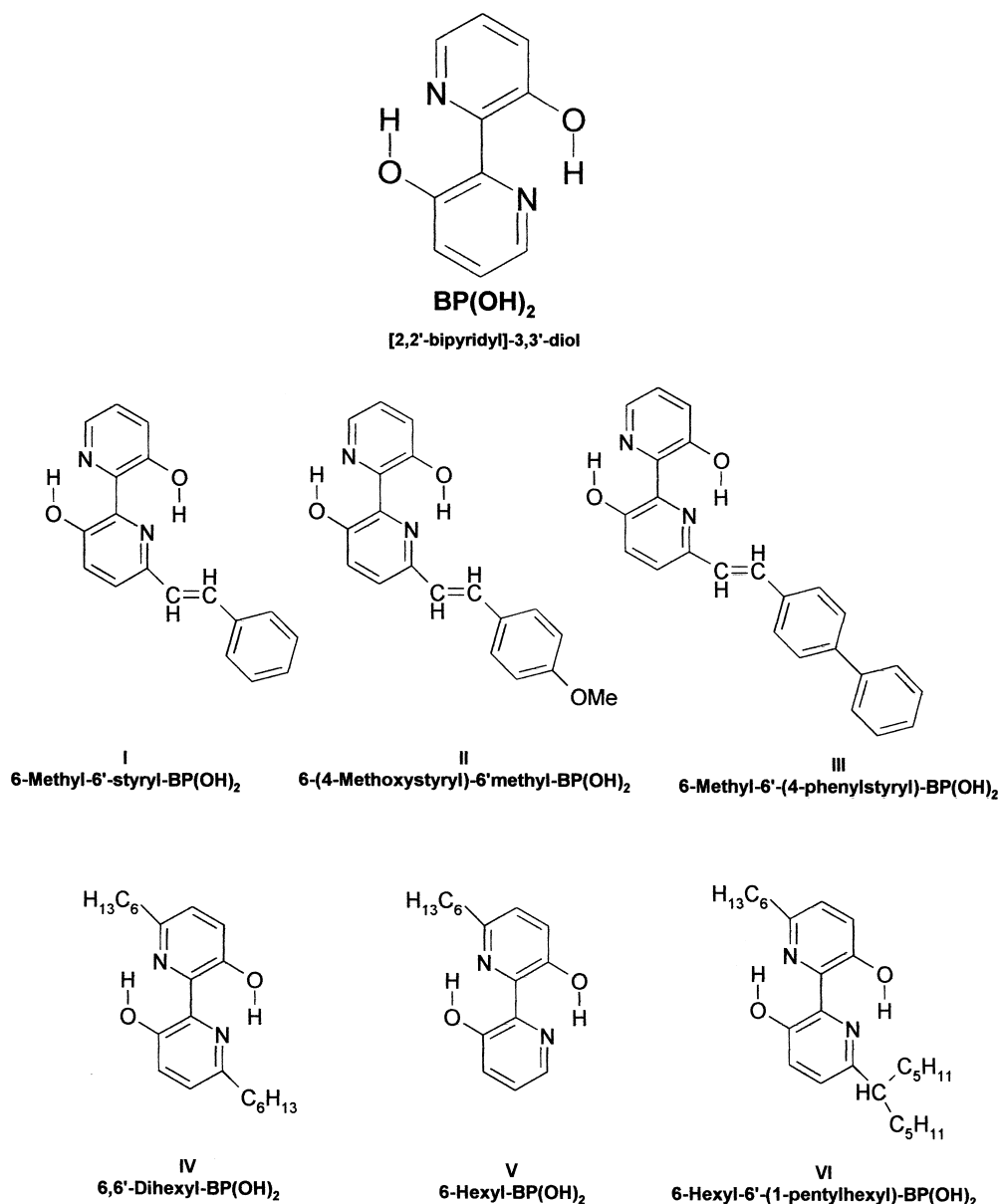
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Fig. 1. Formulae of investigated compounds together with the parent molecule.

2. Experimental

2.1. Apparatus

Absorption spectra were measured with Shimadzu UV/VIS/NIR 3400 spectrophotometer. Emission spectra were recorded with two types of Jasny spectrofluorimeter [16,17] and with the FS900 spectrofluorimeter (Edinburgh Analytical Instruments). The latter was also used for the determination of fluorescence lifetimes.

2.2. Chemicals

3-Methylpentane (3MP) was chromatographically purified with the column filled with silica gel and aluminum oxide. Hexane (for fluorescence spectroscopy, Merck), $CHCl_3$ (Aldrich, spectrophotometric grade) and polyethylene: commercially available samples were used without purification.

Doping of polymer samples was done by keeping the polymer film in 0.003–0.04 M solutions of the studied compounds in $CHCl_3$. After the saturation was achieved, the film was rinsed with methanol in order to remove aromatic molecules under study from the surface. Then the absorption of the doped sample was measured against pure polyethylene. The same procedure was applied to the same dry sample in the course of its aging in air (see Fig. 3). The concentration of the probe was determined under the assumption that the molar absorption coefficients (ε) were the same as in hexane.

All compounds studied in this work are thermally stable. They do not decompose up to 573 K. This could be important for doping the polymers.
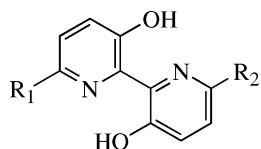
3. Results

Fig. 1 presents six new compounds that are derived from the parent structure, also shown in the same chart. I–III are the compounds with substituents of type B. IV–VI present three derivatives of BP(OH)$_2$ substituted with long aliphatic chains (type A) (vide infra).
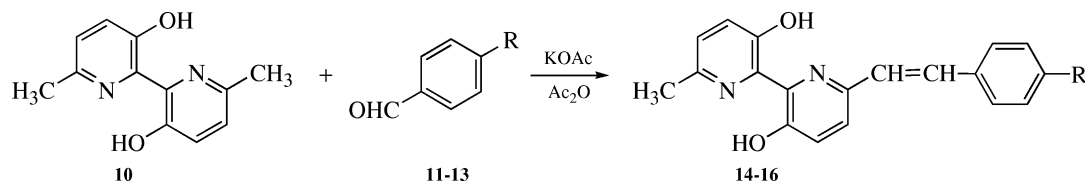
3.1. Synthesis

Two kinds of substituents, A and B, were introduced to the molecular framework of BP(OH)$_2$.


A: $R_1, R_2 = -C_nH_{2n+1}$,
B: $R_1 = -CH=CH-Ph$.

Both groups of derivatives were obtained from common starting material, i.e. 3,3′-dimethoxy-6,6′-dimethyl-2,2′-bipyridyl (**1**) or 3,3′-dimethoxy-6-methyl-2,2′-bipyridyl (**2**) [18].

In the reaction of **1** with an excess of 1-bromopentane (**3**) in the presence of sodium amide in boiling toluene a mixture of alkyl derivatives **4** and **5** was obtained. Both compounds are easily isolable by chromatography:
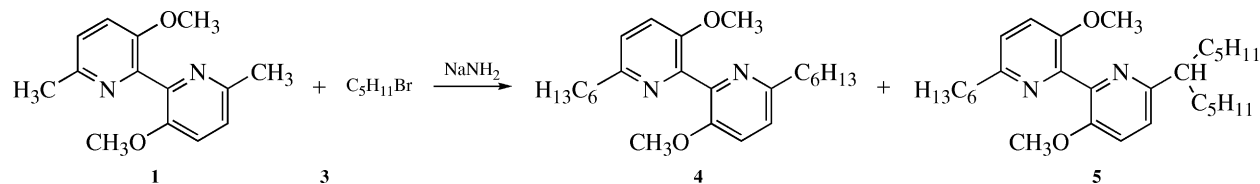
However, when the monomethyl analog of **1**, i.e. **2**, was used, only one compound **6** was isolated:
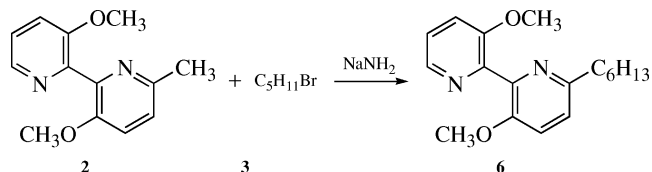
Compounds **4**–**6** were transformed into target bipyridine diols **7**–**9** by heating with HCl:
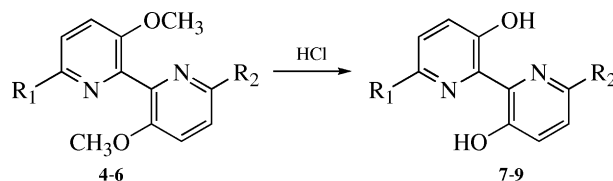
Desired styryl derivatives of BP(OH)$_2$ **14**–**16** were obtained when 6,6′-dimethyl-[2,2′-bipyridyl]-3,3′-diol (**10**) [18] was heated with the corresponding benzaldehyde **11**–**13** (R=H, OCH$_3$, Ph) in the presence of potassium acetate in acetic anhydride [19]:

It is interesting that in this reaction only mono-styryl substituted derivatives were formed, independent of the quantity of aldehyde used.

3.1.1. Details, NMR and elemental analyses

Melting points (m.p.) (in open capillary tubes) are uncorrected. ^{1}H NMR spectra in CDCl$_3$ were recorded with a Varian Gemini 200 (200 MHz) spectrometer. Chemical shifts are expressed in ppm using TMS as an internal standard. The IR spectra were taken using a Beckman 4240 spectrometer. The MS spectra were obtained with LKB-9000A apparatus (−70 eV).

Elemental microanalyses were performed by the Analytical Laboratory of the Institute of Organic Chemistry of the Polish Academy of Sciences. Column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh) and preparative TLC using Merck PSC Fertigplatten Kieselgel 60. The purity and identity of compounds was checked by TLC using Merck DC Alufolien Kieselgel 60 F254. Commercially available solvents and chemicals (Aldrich) were used without extensive purification.

*Alkylation of 3,3′-dimethoxy-6,6′-dimethyl-2,2′-bipyridyl (**1**) [9] or 3,3′-dimethoxy-6-methyl-2,2′-bipyridyl (**2**) [18]:* bipyridyl **1** (0.49 g, 2 mmol) or **2** (0.46 g, 2 mmol) was dissolved in toluene (20 ml), then 1-bromopentane (0.75 g, 5 mmol) and sodium amide (50%, 2 g, 20 mmol) were added and the mixture was refluxed for 8 h. After cooling water (20 ml) was added, an organic layer separated and a

water layer extracted with toluene (10 ml). The combined organic layers were dried over magnesium sulfate and chromatographed on a silica gel column using hexane–acetone 20:1 as an eluent.

6,6′-Dihexyl-3,3′-dimethoxy-2,2′-bipyridyl (*4*): yield 250 mg (33%), yellow oil; ^{1}H NMR: 7.18 (qAB, 4H, $J =$ 8.5 Hz), 3.74 (s, 6H), 2.79 (t, 4H, $J = 7.5$ Hz), 1.70 (quint., 4H, $J = 7.5$ Hz), 1.41–1.23 (m, 12H), 0.90–0.84 (m, 6H). MS (*m/e*, rel. int.): 384 (M$^{+\bullet}$, 33), 327 (29), 314 (100). IR (film, cm^{-1}): 2927, 2956, 1464, 1431, 1275. Analysis for $C_{24}H_{36}N_2O_2$ (384.56) — calculated: 74.96% C, 9.44% H, 7.28% N; found: 74.99% C, 9.46% H, 7.13% N.

6-Hexyl-3,3′-dimethoxy-6′-(1-pentylhexyl)-2,2′-bipyridyl (*5*): yield 295 mg (59%), yellow oil; ^{1}H NMR: 7.22 (dd, 2H, $J = 8.5$–0.5 Hz), 7.13 (ABq, 2H, $J = 8.5$ Hz), 3.74 (s, 3H), 3.71 (s, 3H), 2.82–2.69 (m, 3H), 1.77–1.57 (m, 6H), 1.41–1.20 (m, 18H), 0.91–0.80 (m, 9H). MS (*m/e*, rel. int.): 454 (M$^{+\bullet}$, 19), 384 (80), 327 (100). IR (film, cm^{-1}): 2955, 2927, 2856, 1462, 1430, 1277. Analysis for $C_{29}H_{46}N_2O_2$ (454.69) — calculated: 76.60% C, 10.20% H, 6.16% N; found: 75.89% C, 10.26% H, 6.20% N.

6-Hexyl-3,3′-dimethoxy-2,2′-bipyridyl (*6*): yield 212 mg (35%), yellow oil; ^{1}H NMR: 8.33 (t, 1H, $J = 2$ Hz), 7.29 (d, 2H, $J = 2.5$ Hz), 7.20 (ABq, 2H, $J = 8$ Hz), 3.78 (s, 3H), 3.75 (s, 3H), 2.80 (t, 2H, $J = 8$ Hz), 1.71 (quint, 2H, $J = 8$ Hz), 1.41–1.26 (m, 6H), 0.91–0.84 (m, 3H). MS (*m/e*, rel. int.): 300 (M$^{+\bullet}$, 10); 230 (100). IR (film, cm^{-1}): 2929, 1461, 1429, 1280. Analysis for $C_{18}H_{24}N_2O_2$ (300.40) — calculated: 71.97% C, 8.05% H, 9.32% N; found: 71.53% C, 7.82% H, 9.03% N.

Transformation of 3,3′-dimethoxy-2,2′-bipyridyl derivatives *4*–*6* *into [2,2′-bipyridyl]-3,3′-diol derivatives* *7*–*9*. General procedure: the corresponding dimethoxybipyridyl *4*–*6* (0.5 mmol) and 36% HCl (10 ml) were heated in a sealed tube at 120°C for 12 h. After cooling, the solution was diluted with water (50 ml), neutralized with NaHCO$_3$ and extracted with ether (3 × 50 ml). The extract was dried over magnesium sulfate and evaporated in vacuo to afford the pure product.

6,6′-Dihexyl-[2,2′-bipyridyl]-3,3′-diol (*7*): yield 60 mg (34%), yellow crystals, m.p. 69–70°C; ^{1}H NMR: 14.90 (s, 2H), 7.35 (d, 2H, $J = 8.5$ Hz), 7.11 (d, 2H, $J = 8.5$ Hz), 2.77 (t, 4H, $J = 7.5$ Hz), 1.80 (quint., 4H, $J = 7.5$ Hz), 1.42–1.22 (m, 12H), 0.90–0.84 (m, 6H). MS (*m/e*, rel. int.): 356 (M$^{+\bullet}$, 85), 313 (35), 299 (100), 285 (65). IR (KBr, cm^{-1}): 2916, 2853, 2660–2536, 1494, 1465, 1392, 1304, 1251, 882, 831. Analysis for $C_{22}H_{32}N_2O_2$ (356.50) — calculated: 74.12% C, 9.05% H, 7.86% N; found: 74.30% C, 9.27% H, 8.05% N.

6-Hexyl-6′-(1-pentylhexyl)-[2,2′-bipyridyl]-3,3′-diol (*8*): yield 115 mg (54%), yellow oil; ^{1}H NMR: 14.98 (s, 1H), 14.88 (s, 1H), 7.33 (d, 1H, $J = 8.5$ Hz), 7.325 (d, 1H, $J = 8.5$ Hz), 7.11 (d, 1H, $J = 8.5$ Hz), 7.07 (d, 1H, $J = 8.5$ Hz), 2.77 (t, 2H, $J = 7.5$ Hz), 2.67 (quint., 1H, $J = 7.5$ Hz), 1.78–1.57 (m, 6H), 1.34–1.13 (m, 18H), 0.92–0.79 (m, 9H). MS (*m/e*, rel. int.): 426 (M$^{+\bullet}$, 100), 369 (54), 355 (93). IR

(film, cm^{-1}): 2956, 2927, 2857, 1489, 1300. Analysis for $C_{27}H_{42}N_2O_2$ (426.65) — calculated: 76.01% C, 9.92% H, 6.56% N; found: 75.92% C, 10.10% H, 6.61% N.

6-Hexyl-[2,2′-bipyridyl]-3,3′-diol (*9*): yield 77 mg (57%), yellow crystals, m.p. 53–55°C; ^{1}H NMR: 15.19 (s, 1H), 14.41 (s, 1H), 8.04 (dd, 1H, $J = 4.5$–1.5 Hz), 7.40 (dd, 1H, $J = 8.5$–1.5 Hz), 7.35 (d, 1H, $J = 8.5$ Hz), 7.27 (dd, 1H, $J = 8.5$–4.5 Hz), 7.13 (d, 1H, $J = 8.5$ Hz), 2.78 (t, 2H, $J = 7.5$ Hz), 1.74 (q, 2H, $J = 7.5$ Hz), 1.43–1.22 (m, 6H), 0.91–0.84 (m, 3H). MS (*m/e*, rel. int.): 272 (M$^{+\bullet}$, 62), 229 (34), 215 (80), 202 (100). IR (KBr, cm^{-1}): 2554, 1494, 1292, 1238, 887, 824. Analysis for $C_{16}H_{20}N_2O_2$ (272.35) — calculated: 70.66% C, 7.35% H, 10.29% N; found: 70.88% C, 7.44% H, 10.47% N.

Synthesis of 6-styryl-[2,2′-bipyridyl]-3,3′-diol derivatives *14*–*16*. General procedure [19]: the mixture of 6,6′-dimethyl-[2,2′-bipyridyl]-3,3′-diol (*10*) [18] (216 mg, 1 mmol), corresponding benzaldehyde *11*, *12* or *13* (4 mmol), potassium acetate (132 mg, 2 mmol), acetanhydride (612 mg, 6 mmol) and a trace of iodine were refluxed under argon atmosphere for 48 h. After cooling, the mixture was diluted with 50% aqueous ethanol (20 ml), NaOH (1 g) was added and the solution was refluxed for additional 2 h. Ethanol was distilled off, water (50 ml) was added and the mixture was neutralized with HCl (pH 7). Then the mixture was extracted with chloroform (3 × 25 ml), the extract was dried over MgSO$_4$, evaporated and chromatographed.

6-Methyl-6′-styryl-[2,2′-bipyridyl]-3,3′-diol (*14*): purified by threefold chromatography on silica gel preparative plates, using hexane–acetone 20:1, yellow crystals, m.p. 138–140°C (from hexane), yield 110 mg (36%); ^{1}H NMR: 15.17 (s, 1H), 14.82 (s, 1H), 7.57 (dt, 2H, $J = 8$–1 Hz), 7.43–7.29 (m, 7H), 7.21 (d, 1H, $J = 16.5$ Hz), 7.10 (d, 1H, $J = 16.5$ Hz), 2.54 (s, 3H). MS (*m/e*, rel. int.): 304 (M$^{+\bullet}$, 100). IR (KBr, cm^{-1}): 3447, 1492, 1383, 1298, 822. Analysis for $C_{19}H_{16}N_2O_2$ (304.35) — calculated: 74.98% C, 5.30% H, 9.21% N; found: 74.22% C, 4.83% H, 9.10% N.

6-(4-Methoxystyryl)-6′-methyl-[2,2′-bipyridyl]-3,3′-diol (*15*): chromatographed on a silica gel column with hexane–acetone 10:1, dark yellow crystals, m.p. 164–166°C (from hexane), yield 150 mg (45%); ^{1}H NMR: 15.10 (s, 1H), 14.92 (s, 1H), 7.51 (dt, 2H, $J = 8.5$–2 Hz), 7.38 (s, 2H), 7.26 (s, 2H), 7.30 (d, 1H, $J = 16$ Hz), 6.97 (d, 1H, $J = 16$ Hz), 6.92 (dt, 2H, $J = 8.5$–2 Hz), 3.85 (s, 3H), 2.54 (s, 3H). MS (*m/e*, rel. int.): 334 (M$^{+\bullet}$, 100). IR (KBr, cm^{-1}): 2800–2300, 1513, 1492, 1303, 1255, 826. Analysis for $C_{20}H_{18}N_2O_3$ (334.37) — calculated: 71.84% C, 5.42% H, 8.38% N; found: 71.68% C, 5.24% H, 8.37% N.

6-Methyl-6′-(4-phenylstyryl)-[2,2′-bipyridyl]-3,3′-diol (*16*): chromatographed on a silica gel column with hexane–acetone 10:1, then on silica gel preparative plates using hexane–acetone 5:1 and crystallized from hexane, but still contains a considerable amount of another unidentified compound. Yield 70 mg (18%), m.p. 174–176°C; ^{1}H NMR: 15.19 (s, 1H), 14.85 (s, 1H), 7.67–7.60 (m, 7H),
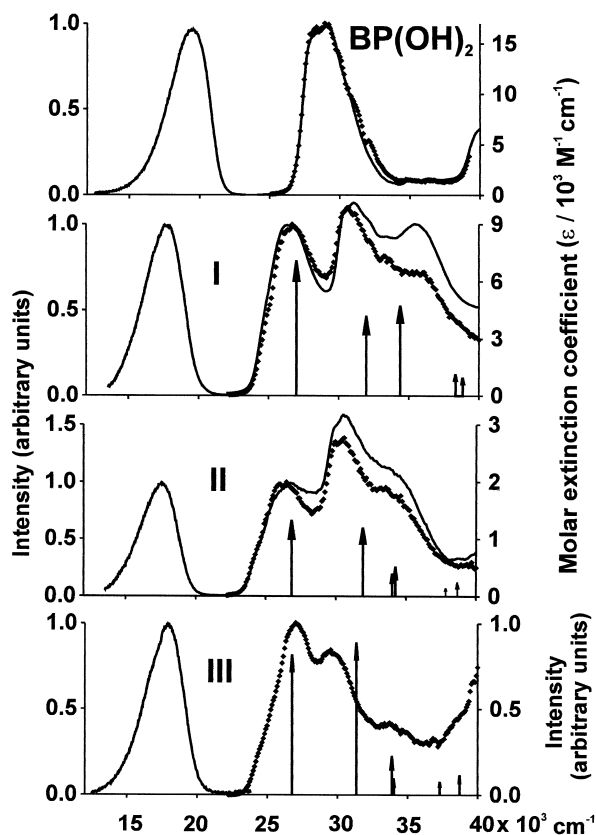
Fig. 2. Absorption, fluorescence (full curves) and its excitation spectra (dotted curves) of compounds I–III together with the analogous spectra of parent molecule — BP(OH)$_2$. Solvent: hexane, $T = 293$ K. Arrows mark transition energies as calculated with INDO/S method.

7.53–7.36 (m, 5H), 7.23 (d, 1H, $J = 16$ Hz), 7.14 (td, 2H, $J = 8$–1.5 Hz), 2.56 (s, 3H). MS (*m/e*, rel. int.): 380 (M$^{+\bullet}$, 100).

3.2. Spectra and photophysics

Fig. 2 shows absorption and fluorescence spectra of compounds I–III compared with those of BP(OH)$_2$. The maxima of fluorescence bands are normalized to the corresponding lowest energy absorption bands.

The compounds I–III emit strongly Stokes shifted fluorescence that, by analogy to BP(OH)$_2$, should be attributed to the emission of their phototautomers. The lowest energy absorption bands are, as expected, red shifted as compared to the mother compound. This shift is partly reflected in the fluorescence spectra. Fluorescence excitation spectra of compounds I and II are in good agreement with the absorption bands, as also seen in Fig. 2. Compound III was available in a minute amount, so that instead of absorption, the phototautomeric fluorescence excitation spectrum could only be measured. Fig. 2 shows also the transition energies as calculated with the INDO/S method [20,21]; they are marked with arrows, well reproducing the experimental absorption maxima.

The compounds IV–VI photophysically are almost copies of BP(OH)$_2$. The quantitative characteristics of the photophysical data of all six derivatives studied in the present work are collected in Tables 1 and 2.

The absorption maxima of compounds I–III representing more extended aromatic systems than BP(OH)$_2$ are shifted to the red by ca. 2000–3000 cm^{-1}. Thus, they are better adjusted to the solar energy spectrum than the parent system (see Fig. 4). The red shifts of the phototautomeric fluorescence bands are much smaller than the shifts of absorption spectra, as can be read out from the last column of Table 1; they change from ca. 1300 cm^{-1} (compound I) to ca. 1800 cm^{-1} (compound II), what is of course reflected in the somewhat smaller Stokes shift (see column 4 of Table 1). Stokes' shifts are still very large and characteristic of the systems undergoing the excited state reactions. Molecules IV–VI differ much less from the parent structure than the compounds I–III.

Table 2 presents the fluorescence quantum yields and corresponding lifetimes. Again it can be observed that the structures IV–VI, molecules with the aliphatic side chains, essentially resemble BP(OH)$_2$, the room temperature fluorescence quantum yields even exceeding (compound IV) the value of the parent molecule. In contrast, the compounds of the first group (I–III) reveal a considerable decrease of the fluorescence quantum yield with respect to BP(OH)$_2$. However, compound I, the most promising one, has the low temperature fluorescence quantum yield as high as about 50%.

Table 1
Spectral characteristics of the studied compounds. Absorption and fluorescence spectra were measured in 3MP

Structure	Absorption $\tilde{v}_{max}$ (cm^{-1})	ε_{max}[a] (M^{-1} cm^{-1})	Emission $\tilde{v}_{max}$ (cm^{-1})	Stokes shift $\Delta\tilde{v}$ (cm^{-1})	Shift of the absorption maximum vs. BP(OH)$_2$ $\Delta\tilde{v}$ (cm^{-1})	Shift of the fluorescence maximum vs. BP(OH)$_2$ $\Delta\tilde{v}$ (cm^{-1})
BP(OH)$_2$	29 120	17100	19 420	9700	–	–
I	26 180	8950	18 100	8080	−2940	−1320
II	26 620	1980	17 590	9030	−2500	−1830
III	27 020[b]	–	17 980	9040[b]	−2100[b]	−1440
IV	28 240	16630	19 160	9080	−880	−260
V	28 570	16860	19 080	9450	−550	−340
VI	28 200	16470	19 130	9070	−920	−290

[a] The value of molar extinction coefficient in the maximum of the first band.
[b] The values were obtained from fluorescence excitation spectrum.

Table 2
Fluorescence quantum yield and lifetimes of the studied compounds in 3MP. The quantum yields were determined with the quinine sulfate as a fluorescence standard [22]. Corresponding values at 88 K are given in parentheses

Structure	Excitation $\tilde{\nu}_{exc}$ (cm^{-1})	Quantum yield at room temperature	Fluorescence lifetime at room temperature (ns)
BP(OH)$_2$ [23]	–	0.30 ± 0.03 (0.70)	3.2 ± 0.1
I	28 490	0.13 ± 0.02 (0.48)	1.5 ± 0.2
II	28 490	0.09 ± 0.01	1.8 ± 0.2
III[a]	28 490	0.07 ± 0.01 (0.18)	–
IV	28 570	0.35 ± 0.04 (0.52)	3.9 ± 0.4
V	28 570	0.21 ± 0.03 (0.66)	2.9 ± 0.3
VI	28 570	0.40 ± 0.04 (0.59)	3.9 ± 0.5

[a] Lifetime could not be measured, since only minute amount of compound III was available. See text.

The second potential application, the photostabilization of polymers, will be illustrated below: as an example, Fig. 3 presents the absorption spectrum of V introduced into the polyethylene film as described in the experimental part. It shows that the derivative of BP(OH)$_2$ with two aliphatic chains as substituents can be dissolved in polyethylene film 11 μm thick, giving the absorbance as high as 0.75; this corresponds to the concentration of compound V about 0.037 M. The spectrum measured against pure polyethylene as reference does not differ from the absorption measured in the
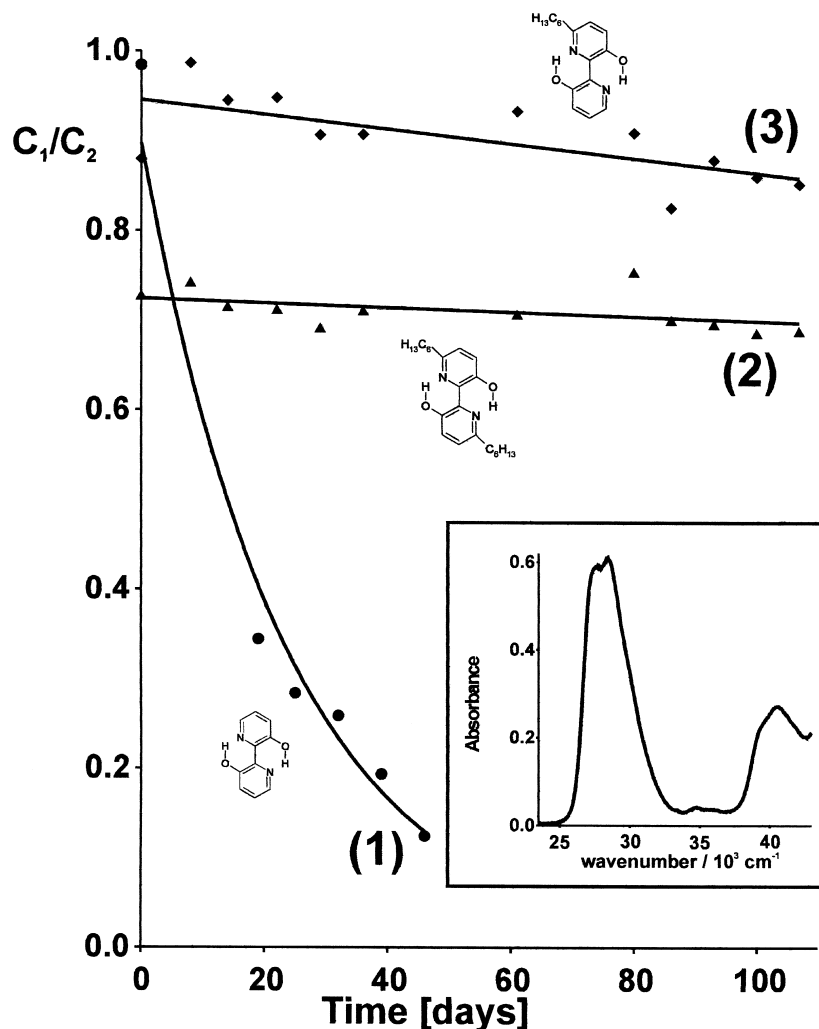

Fig. 3. C_1/C_2: the ratio of concentration of the compound in the polymer (C_1) to that in the CHCl$_3$ solution (C_2) as a function of the age of the dry sample. The concentration in polyethylene was determined from the absorbance at the maximum of the first band. The lines represent the best fits. Inset: absorption spectrum of the compound V in polyethylene.
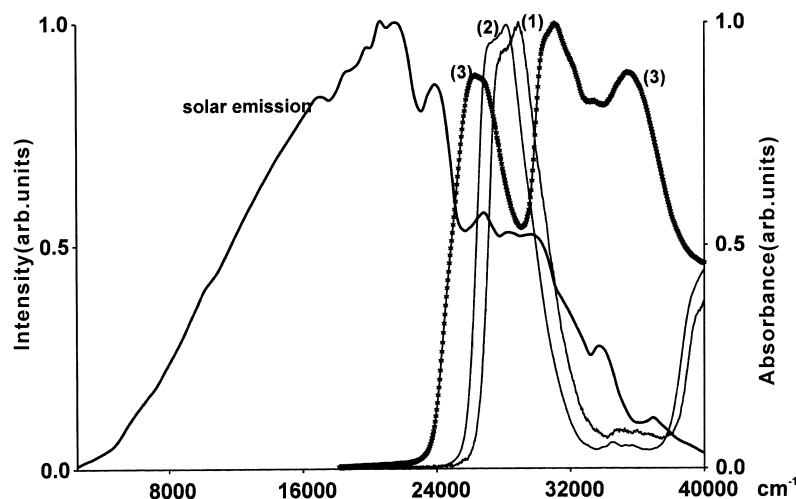
Fig. 4. The solar emission spectrum measured on the earth [24] and the absorption spectra in alkanes as solvents, $T = 293$ K: (1), $BP(OH)_2$; (2), compound IV; (3), compound I.

liquid inert solvents like *n*-hexane or 3MP (see inset of Fig. 3).

Fig. 3 compares the molecules studied with the parent one in the polyethylene film: three different behaviors are easily distinguished; $BP(OH)_2$ introduced into polyethylene "leaves" it with time, as seen from the decrease of the absorbance (Fig. 3, curve 1). This effect was already qualitatively stated [12]. In contrast, molecules of the second group are comparatively easily dissolved in polyethylene and do not escape from the medium (Fig. 3, curves 2 and 3).

This demonstrates the desired effect: the introduction of an aliphatic "anchor" to the aromatic system does not change its photophysical character, increasing considerably the tolerance of polyethylene to such a guest that may, according to the expectations, fulfill the function of a photostabilizer much better than $BP(OH)_2$.

4. Conclusions

It was demonstrated that the molecule undergoing the ESIPT process, the widely studied [2,2′-bipyridyl]-3,3′-diol $(BP(OH)_2)$, may be structurally modified by the suitably introduced substituents adapting the parent structure to different applications.

The six new compounds indeed represent the two groups differing by the character of the substituent. The first group, three molecules with aromatic substituents, have the absorption and phototautomeric fluorescence spectra red shifted with respect to parent molecule. They are then better "adapted" to the solar spectrum and could be used as solar concentrators, almost free of negative effects caused by reabsorption. This is shown in Fig. 4.

The second group, molecules with long aliphatic side chains, proved to be potentially useful as photostabilizers

of polymers, since they preserve all spectral features of $BP(OH)_2$, but are much better soluble in polyethylene. It was also shown that two members of this group (structures V and VI) are even stronger emitters than the parent one. To conclude, the desired modification of the proton transferring system $BP(OH)_2$ is achieved; the synthesis of six new compounds is reported and possible applications discussed.

A part of the results of the present work prospective for practical applications were submitted as the Polish Patent Application P-341124.

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