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New proton transfer lasing systems — derivatives of 2,2′-bipyridyl. Synthesis and photophysical characteristics*

Ł. Kaczmarek[a], B. Nowak[b], J. Żukowski[c], P. Borowicz[c], J. Sepioł[c] and A. Grabowska[c]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw (Poland)*
[b]*Jagiellonian University, Karasia 3, 30-060 Krakow (Poland)*
[c]*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw (Poland)*

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Abstract

Two new bipyridyl derivatives undergoing the excited state intramolecular proton transfer were synthesized: 5-methyl-[2,2′-bipyridine]-3,3′-diol and 5,5′-dimethyl-[2,2′-bipyridine]-3,3′-diol. Both reveal a strong phototautomeric, largely Stokes-shifted fluorescence and can be used as proton transfer laser dyes. Tuning ranges and lasing efficiences are also reported.

INTRODUCTION

Heteroaromatic molecules containing internal hydrogen bonds are objects of continuous interest as systems undergoing intramolecular proton transfer upon electronic excitation [1]. The phototautomerization reaction is in most cases extremely fast and its excited product can be detected as a source of the strongly Stokes-shifted tautomeric fluorescence. The system may be described as a photochemical proton transfer cycle as the back proton transfer in the ground state takes place, repopulating the primary structure. There are many applications of this type of reactivity. In the present paper we shall focus attention mainly on lasing properties of one particular family of internally H-bonded molecules — derivatives of bipyridyl-diol, shown below.

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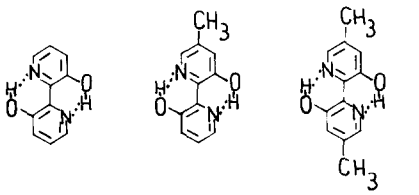


$BP(OH)_2$ $MeBP(OH)_2$ $Me_2BP(OH)_2$

6c **6b** **6a**

The first molecule [2,2′-bipyridyl]-3,3′-diol ($BP(OH)_2$) has already been introduced in the literature by our series of papers reporting synthesis [2], photophysics [3], lasing properties [4] and photostabilizing ability — the protection of polymers against photodegradation [5]. The particularly important photophysical features of $BP(OH)_2$ are (i) a strong tautomeric fluorescence revealing the Stokes shift $\approx 9000\ cm^{-1}$ and (ii) an intramolecular excited state double proton transfer. The main aim of this study was to extend previous work to new compounds closely related to $BP(OH)_2$ but substituted in the aromatic ring by one or two methyl groups.

The first substituted molecule, 5-methyl-[2,2′-bipyridyl]-3,3′-diol ($MeBP(OH)_2$) represents a very delicate symmetry destruction of the parent system ($BP(OH)_2$). The second, 5,5′-dimethyl-[2,2′-bipyridyl]-3,3′-diol ($Me_2BP(OH)_2$) is a reference compound that provides the possibility of observing the influence of methyl substitution on the photophysical behaviour, without lowering the symmetry of $BP(OH)_2$. Both new compounds offer the chance of better solubility in polyethylene or polypropylene. We report on the synthesis of $MeBP(OH)_2$ and $Me_2BP(OH)_2$, and on the comparative photophysical study of the three molecules from the same family.

EXPERIMENTAL

Apparatus

Absorption, fluorescence and fluorescence excitation spectra were measured with the Specord M40 spectrophotometer and Jasny spectrofluorimeter described elsewhere [6].

Fluorescence lifetimes were measured with the set-up described earlier [7] equipped with the laser MSG 350-S. The lifetimes were monoexponential within the experimental accuracy. Fluorescence quantum yields were determined with the application of the following standards: quinine sulphate, 3-aminophthalimide, both in 0.1 N H_2SO_4 [8], and $BP(OH)_2$ in 3-methylpentane [9]. Lasing power of the three investigated bipyridyl-diols, $BP(OH)_2$, $MeBP(OH)_2$ and $Me_2BP(OH)_2$, was determined with the application of the set-up composed of

a N_2 laser IGL 300/2 (ZWG, East Germany) and a simple resonator containing the cell with the investigated solution, the diffraction grating (1200 lines mm^{-1}), a glass prism for beam expansion and the quartz plate serving as an outcoupler. For the energy determination a PEM 521 (ZWG) pyroelectric laser energy meter was used. The lasing yield, η_L, is defined by the formula

$$\eta_L = \frac{\epsilon_{out}}{\epsilon_{in}} 100\%$$

where ϵ_{in} is the energy of the pumping pulse of the N_2 laser and ϵ_{out} is the output energy of the dye. Melting points (m.p.) were determined with the Kofler type apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian EM-360 spectrometer and are expressed in p.p.m. (TMS as an internal standard).

IR spectra were measured with a Unicam SP-200 spectrophotometer in KBr pellets. Mass spectra (-70 eV) were obtained with an LKB-9000 A apparatus. The purity and identity of compounds were checked by TLC on the Merck DC-Alufolien Kieselgel 60 F_{254}. Column chromatography was performed on the Merck Kieselgel 60, 230–400 mesh, and high pressure liquid chromatography on the instrument produced by the Institute of Physical Chemistry of the Polish Academy of Sciences, equipped with the UV detector, $\lambda = 254$ nm.

Solvents

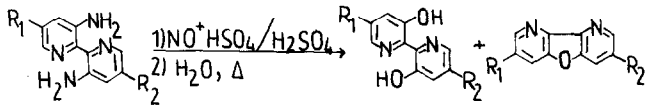
3-Methylpentane (3MP) was purified by column chromatography on silica gel and Al_2O_3. Cyclohexane was used for UV spectroscopy while ethyl alcohol and 0.1 N H_2SO_4 were used for fluorescence spectroscopy, all without purification. All solvents were checked for absorption and fluorescence before use. Both synthesized compounds, $MeBP(OH)_2$ and $Me_2BP(OH)_2$, were purified up to spectroscopic purity by additional recrystallization from hexane and by sublimation.

Quantum Chemical calculations were performed by the INDO/S method with the original parametrization of Ridley and Zerner [10].

RESULTS

Synthesis of $MeBP(OH)_2$ and $Me_2BP(OH)_2$

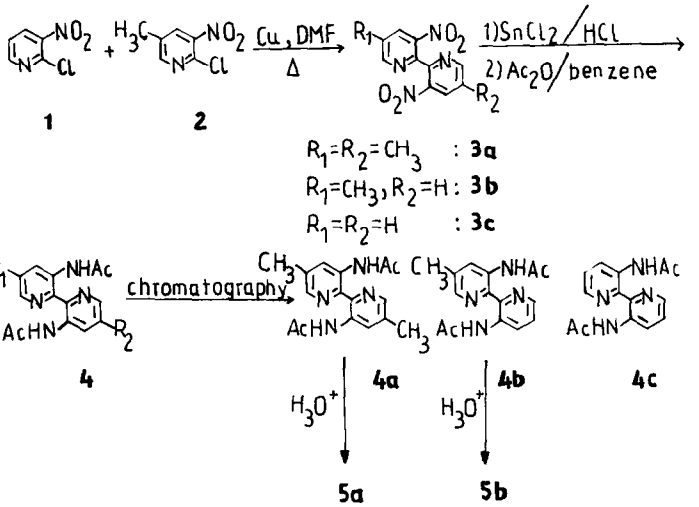
$MeBP(OH)_2$ (5-methyl-[2,2′-bipyridine]-3,3′-diol, (**6b**)) and $Me_2BP(OH)_2$ (5,5′-dimethyl-[2,2′-bipyridine]-3,3′-diol, (**6a**)) were obtained by diazotization of corresponding bipyridinediamines, **5a**, **5b** and **5c**, with nitrosylsulfuric acid [11].



$R_1=R_2=CH_3$:	**5a**	**6a**(14%)	**7a**
$R_1=CH_3, R_2=H$:	**5b**	**6b**(21%)	**7b**
$R_1=R_2=H$:	**5c**	**6c**	**7c**

Diols **6a–c** can be readily separated from furo[3,2-b:4,5-b′]dipyridines (**7a–c**) due to the solubility of **6** in NaOH solution.

Since the mixture of **6a–c** was not separable by any chromatographic method, the desired unsymmetrical compound **6b** was already separated from the other two symmetrical derivatives, **6a** and **6c**, as dinitrobipyridine (**3b**) by HPLC or as the acetamide derivative (**4b**) by normal column chromatography. Both procedures are described in detail below. The starting bipyridinediamines **5a** and **5b** were synthesized as shown in Scheme 2.



The mixture of dinitrobipyridines **3** obtained by the Ullman reaction of 2-chloro-3-nitropyridine (**1**) with 2-chloro-5-methyl-3-nitropyridine (**2**) [13], was subsequently reduced with $SnCl_2$ in HCl and acetylated with acetanhydride in benzene. The mixture of acetamido derivatives **4** was chromatographed on a silica gel column with $CHCl_3$–hexane 1:1 to separate compounds **4a**, **4b** and **4c**. Compounds **4a** and **4b** were then hydrolysed with dilute HCl to afford the desired amines **5a** and **5b**.

The amine **5a** was also obtained in a good yield when the Ullman reaction was carried out using methylpyridine **2**, and the bipyridine derivative (**3a**)

formed was reduced with $SnCl_2$ in HCl. When this work was nearly complete, Naumann and Langhals described an alternative synthesis of $Me_2BP(OH)_2$ (**6a**) by reductive organometallic coupling of 2-bromo-6-methyl-3-pyridinol [12].

*General procedure for synthesis of dinitrobipyridines (**3**)*

2-Chloro-3-nitropyridine (**1**) (4.0 g, 25 mmol) and 2-chloro-5-methyl-3-nitropyridine (**2**) [13] (4.3 g, 25 mmol), or only compound **2** (8.6 g, 50 mmol), were dissolved in dry dimethylformamide (50 ml) and powdered copper (10 g) was added. The mixture was stirred at 100–105°C for 4 h and then filtered. The filter cake was washed with boiling dimethylformamide (2×20 ml) and the collected filtrates were diluted with water (200 ml) and 25% ammonia (50 ml). The precipitate was filtered off and washed with water to give the mixture of dinitrobipyridines **3** (4.8 g) or 5,5′-dimethyl-3,3′-dinitro-2,2′-bipyridine (**3a**) (4.3 g, 63%) (yellow crystals, m.p. 198–200°C, from dimethylformamide–water). ^1H NMR (60 MHz, CF_3COOH): 9.0 (s, 4H), 2.8 (s, 6H); IR (cm^{-1}): 1555, 1525, 1350; MS (m/e): 274 (12%), 228 (100%). Analysis for $C_{12}H_{10}N_4O_4$ (274.26) — calc., C 52.55, H 3.68, N 20.43%; found, C 52.68, H 3.66, N 20.53%.

5-Methyl-3,3′-dinitro-2,2′-bipyridine (**3b**) was isolated from the mixture by HPLC with the application of the following procedure. Two columns working together were filled with Lichroprep Si 60: the grain diameter was 15–25 μm. As an eluant the mixture hexane–chloroform–isopropanol (100:50:1 volume ratio) was used. A typical chromatogram is shown in Fig. 1.

After separation, compound **3b** was crystallized from a dimethylformamide–water mixture, giving creamy crystals, m.p. 173–175°C. ^1H NMR (60 MHz, CF_3COOH): 9.2–9.0 (m, 4H), 8.3 (m, 1H), 2.8 (s, 6H); IR (cm^{-1}): 1570, 1535,

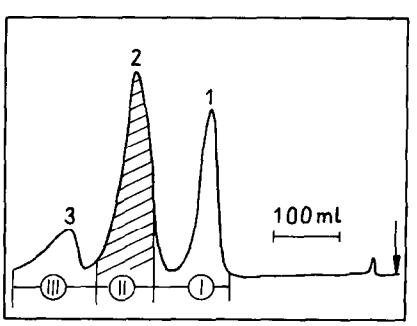


Fig. 1. A typical HPLC chromatogram of the mixture of dinitro-derivatives of 2,2′-bipyridine: Peak 1, compound **3a**; peak 2, **3b**; peak 3, **3c**. See text for experimental details.

1365; MS (m/e): 260 (7%), 239 (3%), 214 (100%). Analysis for $C_{11}H_8N_4O_4$ (260.21) — calc., C 50.77, H 3.10, N 21.53%; found, C 50.80, H 3.07, N 21.42%. 3,3′-Dinitro-2,2′-bipyridine (**3c**) is described in the literature [14].

Synthesis of acetamidobipyridines ***4***

The mixture of dinitrobipyridines **3** (4.8 g) was added portionwise to the solution of $SnCl_2$ (35 g) in HCl (50 ml) and the mixture was heated on a steam bath for 30 min. After cooling the mixture was made alkaline with 20% NaOH and extracted with chloroform. The extract was dried over $MgSO_4$, evaporated and the residue was dissolved in benzene (100 ml). Acetanhydride (5 ml) was added to the solution and the whole was refluxed for 1 h and then the solvent was evaporated. The residue was dissolved in chloroform and passed through a short silica gel column. After evaporation of the solvent the crystalline, colorless residue (3.5 g) was chromatographed on a silica gel column (400 g) with chloroform–hexane 1:1 to give compounds **4a** (1.0 g), **4b** (1.7 g) and **4c** (0.8 g).

3,3′-Bis(acetamido)-5,5′-dimethyl-2,2′-bipyridine (**4a**); colorless crystals, m.p. 243–245°C (from benzene). ^{1}H NMR (60 MHz, $CDCl_3$): 13.3 (b.s., 2H), 8.1 (s, 2H), 2.4 (s, 6H), 2.2 (s, 6H); IR (cm^{-1}): 2900, 1690, 1575, 1565, 1520-1510, 1430; MS (m/e): 298 (88%), 283 (80%), 241 (100%). Analysis for $C_{16}H_{18}N_4O_2$ (298.35) — Calc., C 64.41, H 6.08, N 18.80%; found, C 64.41, H 6.02, N 18.75%.

3,3′-Bis(acetamido)-5-methyl-2,2′-bipyridine (**4b**); colorless crystals m.p. 211–213°C (from benzene). ^{1}H NMR (60 MHz, $CDCl_3$): 13.3 (b.s., 2H), 9.1 (d–d, 1H, J 8 Hz, 1 Hz), 8.95 (d, 1H, J 1 Hz), 8.3 (d–d, 1H, J 5Hz, 1 Hz), 8.1 (d, 1H, J 1 Hz), 7.3 (d–d, 1 H, J 8 Hz, 5Hz), 2.4 (s, 3 H), 2.2 (s, 6 H); IR (cm^{-1}): 2950, 1695, 1570, 1530–1515, 1445, 1385, 1370, 1315, 1240; MS (m/e): 284 (36%), 269 (24%), 227 (59%), 57 (100%). Analysis for $C_{15}H_{16}N_4O_2$ (284.32) — calc., C 63.37, H 5.67, N 19.71%: found, C 63.61, H 5.70, N 19.69%.

3,3′-Bis(acetamido)-2,2′-bipyridine (**4c**) is described in the literature [14].

Synthesis of bipyridinediamines ***5***

*5,5′-Dimethyl-[2,2′-bipyridine]-3,3′-diamine (**5a**)*

*Reduction of **3a**.* Dinitrobipyridine (**3a**) (5.5 g, 0.02 mol) was added portionwise to the solution of $SnCl_2$ (0.35 g) in HCl (50 ml), the mixture was heated on the steam bath for 30 min and refrigerated overnight. The precipitate was filtered off and stirred in 20% NaOH (100 ml) at room temperature for 30 min. Compound **5a** was collected, washed with 5% ammonia and recrystallized. Yield 3.3 g (77%).

*Hydrolysis of **4a**.* Compound **4a** (1.49 g, 5 mmol) was refluxed in 10% HCl (20

ml) and the mixture was chilled, made alkaline with ammonia and extracted with chloroform. The extract was dried ($MgSO_4$), the solvent evaporated and the residue recrystallized to give **5a**. Yield 0.85 g (79%).

Creamy crystals, m.p. 176–177°C (from benzene). ^1H NMR (60 MHz, $CDCl_3$): 7.8 (s, 2H), 6.8 (s, 2H), 5.9 (b.s., 4H), 2.2 (s, 6H); IR (cm^{-1}): 3390, 3280, 1610, 1585, 1190, 860, 735; MS (m/e): 214 (74%), 198 (100%). Analysis for $C_{12}H_{14}N_4$ (214.27) — calc., C 67.27, H 6.59, N 26.15%; found, C 67.29, H 6.53, N 25.91%.

*5-Methyl-[2,2′-bipyridine]-3,3′-diamine (**5b**)*

Synthesized by reduction of **3b** (yield 70%) and hydrolysis of **4b** (yield 85%) with synthesis and work up as for **5a**.

5b; creamy crystals, m.p. 104–105°C (from benzene–hexane). ^1H NMR (60 MHz, $CDCl_3$): 8.0 (m, 1H), 7.8 (s, 1H), 7.0 (m, 2H), 6.8 (s, 1H), 6.2 (b.s, 4H), 2.3 (s, 3H); IR (cm^{-1}): 3420, 3250, 1600, 1585–1575, 1445, 1145; MS (m/e): 200 (80%), 184 (100%). Analysis for $C_{11}H_{12}N_4$ (200.25) — calc., C 65.98, H 6.04, N 27.98%; found, C 65.95, H 5.99, N 27.85%.

*General procedure for diazotization of bipyridinediamines **5***

Bipyridinediamine **5a** or **5b** (10 mmol) was dissolved in 80% formic acid (10 ml) and dropped into stirred nitrosylsulfuric acid (obtained by dissolving 1.0 g $NaNO_2$ in 10 ml of H_2SO_4 $d = 1.82$) at 0–5°C. The mixture was stirred for 30 min at this temperature, then water (5 ml) was added and it was heated at 50–60°C until gas evolution stopped and then for a further 10 min at 90–95°C. The mixture was cooled, diluted with water (100 ml), made alkaline with 20% NaOH and extracted with ether. The extract was washed with 5% NaOH and with water, then dried and evaporated to give the corresponding furodipyridine **7**. The alkaline water layer (after extraction) was adjusted to pH 6.5 (HCl, $NaHCO_3$) and extracted again with ether. The extract was dried and the solvent evaporated to give bipyridinediol **6**.

5,5′-Dimethyl-[2,2′-bipyridine]-3,3′-diol (**6a**); yellow crystals, m.p. 231–233°C (from hexane), yield 14%. ^1H NMR (60 MHz, $CDCl_3$): 14.6 (b.s, 2H), 7.9 (s, 2H), 7.2 (s, 2H), 2.4 (s, 6H); IR (cm^{-1}): 2700–2500, 1405, 1340, 1245, 1170, 860; MS (m/e): 216 (90%), 199 (100%), 187 (15%). Analysis for $C_{12}H_{12}N_2O_2$ (216.25) — calc., C 66.65, H 5.59, N 12.95%; found, C 66.46, H 5.75, N 12.94%.

5-Methyl-[2,2′-bipyridine]-3,3′-diol (**6b**); yellow crystals, m.p. 150–151°C (from hexane, then sublimation), yield 21%. ^1H NMR (60 MHz, $CDCl_3$): 14.5 (s, 1H), 14.4 (s, 1H), 8.0 (d–d, 1H, J 5Hz, 2Hz), 7.8 (s, 1H), 7.4–7.0 (m, 3H), 2.3 (s, 3H); IR (cm^{-1}): 2700–2500, 1495, 1350, 1320, 1245, 805; MS (m/e): 202 (100%), 185 (99%), 173 (13%). Analysis for $C_{11}H_{10}N_2O_2$ (202.22) — calc., C 65.33, H 4.98, N 13.85%; found, C 65.38, H 4.70, N 13.7%.

3,7-Dimethylfuro[3,2-b:4,5-b']dipyridine (**7a**); colourless crystals, m.p. 169–170°C (from benzene–hexane), yield 75%. ^{1}H NMR (60 MHz, $CDCl_3$): 8.6 (s, 2H), 7.6 (s, 2H), 2.5 (s, 6H): IR (cm^{-1}): 3020, 1400, 1165, 1140: MS (m/e): 198 (100%), 183 (4%). Analysis for $C_{12}H_{10}N_2O$ (198.23) — calc., C 72.71, H 5.09, N 14.13%; found, C 72.60, H 5.09, N 14.12%.

3-Methylfuro[3,2-b:4,5-b']dipyridine (**7b**); colorless crystals, m.p. 129–131°C (from hexane), yield 72%. ^{1}H NMR (60 MHz, $CDCl_3$): 8.7 (d–d, 1H, J 5 Hz, 2Hz), 8.6 (s, 1H), 7.8 (d–d, 1H, J 9Hz, 2Hz), 7.6 (s, 1H), 7.3 (d–d, 1H, J 9Hz, 5Hz), 2.5 (s, 3H); IR (cm^{-1}): 3020, 1420, 1405, 1390, 1215, 1150, 880, 800, 740; MS (m/e): 184 (93%), 183 (100%), 158 (34%), 157 (34%), 156 (34%), 155 (42%), 123 (42%). Analysis for $C_{11}H_8N_2O$ (184.20) calc., C 71.73, H 4.38, N 15.21%; found, C 71.63, H 4.20, N 15.26%.

Photophysics of $MeBP(OH)_2$ and $Me_2BP(OH)_2$ as compared with $BP(OH)_2$

The room temperature absorption, fluorescence and its excitation spectra of $MeBP(OH)_2$ and $Me_2BP(OH)_2$ are reproduced in Figs. 2a and 2b. They show remarkable features strongly resembling the parent molecule, $BP(OH)_2$. Firstly, a strongly Stokes-shifted fluorescence is seen demonstrating that an excited state reaction takes place. The magnitude of this shift ≈ 10000 cm^{-1} is common, e.g. for a proton transfer process occurring in the singlet state. Secondly, no trace of the primary, normal Stokes-shifted fluorescence is detected even at temperatures as low as 10 K. Such behaviour is generally considered as proof that the excited state process is "barrierless", much faster than the radiative depopulation of the excited primary structure. The third observation, also in full analogy with the parent molecule and rather exceptional in this category of excited state reactions, is the high quantum yield of this largely Stokes-shifted fluorescence (Table 1).

Systems undergoing an efficient excited state proton transfer reaction are

TABLE 1

Quantum yields (η) and lifetimes (τ) of the ketotautomeric fluorescence of the three investigated bipyridyl-diols. Solvent, 3 MP

Compound	τ (ns)	η Air saturated	η Air-free solution
$BP(OH)_2$	3.2±0.2	0.32±0.03 [9]	-
$MeBP(OH)_2$	2.6±0.3	0.32±0.03	0.37±0.03
$Me_2BP(OH)_2$	2.5±0.3	0.27±0.03	0.30±0.03

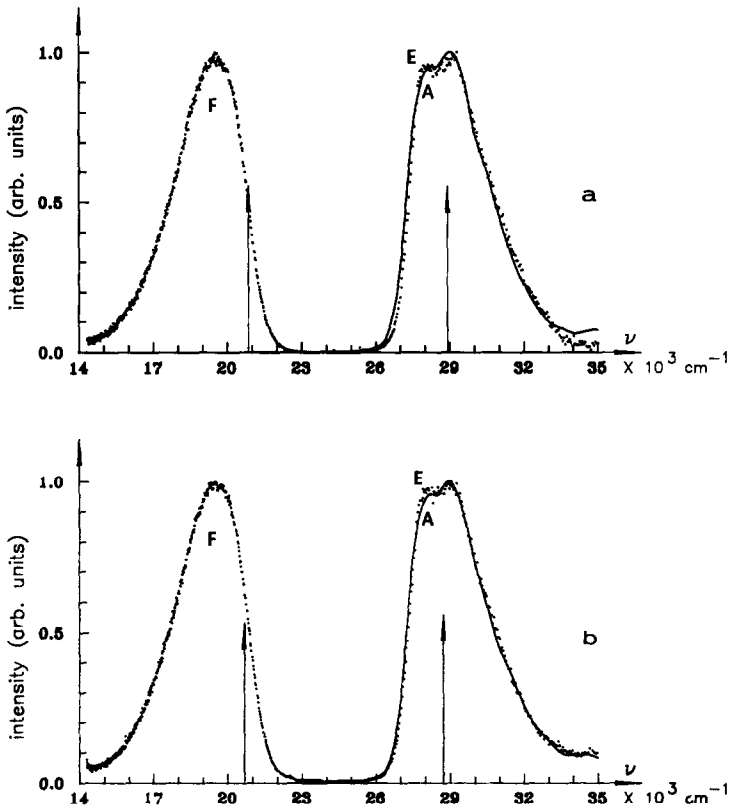


Fig. 2. Absorption (A), fluorescence (F) and fluorescence excitation (E) spectra of: a, $MeBP(OH)_2$; b, $Me_2BP(OH)_2$; room temperature; solvent, 3MP.

predicted to be good candidates for lasing action [15]. Indeed, several have already been reported and recommended as fairly strong lasing photostable systems [16]. One of these is $BP(OH)_2$ described in our earlier paper [4]. Below we report on the comparative study of lasing properties of three investigated molecules.

In both new bipyridyl derivatives the lasing ability was stated. In Fig. 3 the output energy of three investigated molecules and the corresponding tuning ranges were compared with the typical lasing dye, coumarin 153. The concentration of $BP(OH)_2$ could reach 3×10^{-3} M, so in this case the lasing efficiency was exactly equal to that of coumarin 153. The other two bipyridyl-diols are slightly less soluble in 3MP but can still be recommended as good stable lasing dyes. The typical concentration of the studied compound was 1×10^{-3} M.

None of the three molecules investigated can however be recommended as a

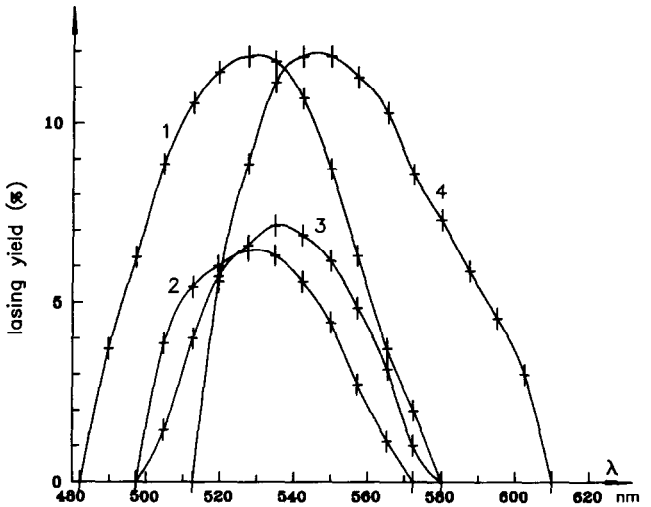
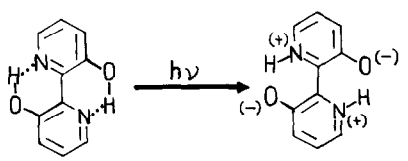


Fig. 3. Lasing yield and tuning range of: 1, $BP(OH)_2$; 2, $MeBP(OH)_2$; 3, $Me_2BP(OH)_2$ in cyclohexane; 4, coumarin 153 in ethyl alcohol.

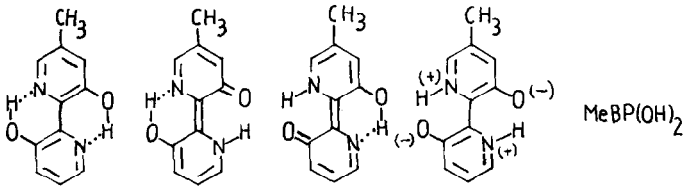
lasing dye in alcoholic solvents, since the efficiency drops to very low values, probably because of competing hydrogen bond formation with the solvent.

DISCUSSION

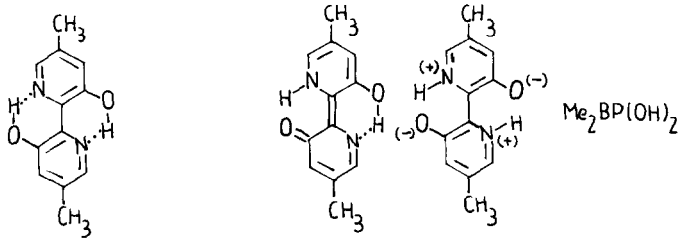
In this work we introduce two new compounds to the existing one already reported previously. They constitute the group of three molecules showing a strong largely Stokes-shifted fluorescence that, by analogy with the parent molecule, is assigned as an emission from the diketotautomeric structure — an electronically excited product of the cooperative intramolecular double proton transfer.



This rather exceptional phenomenon was stated for $BP(OH)_2$ and proved by comparison with several model compounds and excited state dipole moment determination [3]. In this paper we attempted to distinguish between a single and double proton transfer in the excited singlet state of three molecules under consideration. This was done with the application of INDO/S quantum chemical calculation of transition energies and oscillator strengths of the lowest $S_0 \rightarrow S_1$ transitions of the following structures:



A B C D



The monoketo and diketo-tautomeric forms were simulated only by the increased distance between O and H atoms. The results are shown in Table 2.

The above results of quantum chemical calculations reproduce well the excitation energies of the dihydroxy-forms stable in the ground state as well as the high oscillator strengths of the lowest energy transitions. Although the calculation cannot offer the unambiguous argument in favour of the symmetric double proton transfer in the S_1 state of both molecules, the deeper stabilization (lower transition energies) in the diketo-tautomers is easily seen. The arrows in Fig. 2a and 2b represent the calculated data.

Finally, the photostabilizing ability of $BP(OH)_2$ in respect to polyethylene

TABLE 2

Energies and oscillator strengths of the lowest $S_0 \rightarrow S_1$ transitions of $MeBP(OH)_2$ and $Me_2BP(OH)_2$ calculated by the INDO/S method

Structure	Transition energy (cm^{-1})	Oscillator strength
$MeBP(OH)_2$		
A	28890	0.55
B	21400	0.46
C	21230	0.44
D	20840	0.55
$Me_2BP(OH)_2$		
A	28730	0.56
C	21320	0.46
D	20680	0.53

and polypropylene films reported in our patent [5] is expected to be improved by methylation in the aromatic ring, since the solubility of the methyl-derivatives in non-polar polymer should increase. The structure of the excited ketotautomeric forms of the reported family of compounds and their detailed photophysics will be the subject of a forthcoming paper.

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