

## The Luminescence of Cluster Derivatives of Boron Hydrides, and Some Applied Aspects

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### Abstract

Luminescence properties of a series of cluster borane derivatives, carboranes of the types  $B_{10}H_{12}[Py(X)]_2$ ,  $C_2B_9H_{11}Py(X)$  and  $C_2B_9H_{10}BrPy(X)$  and the salts of hydroborate anions  $[B_{10}H_{13}Py(X)]^-$ ,  $B_{10}H_{10}^{2-}$  and  $B_{12}H_{12}^{2-}$  with the cations of quaternary pyridinium bases have been investigated. This row includes 42 compounds of 12 types. The derivatives of decaborane(14)  $6,9-B_{10}H_{12}Py_2$  and  $6,9-B_{10}H_{12}[Py(X)]_2$  where Py and Py(X) are pyridine and its derivatives are proposed as the basis of luminescent materials to register and visualize the synchrotron radiation within the energy range 10–40 eV. The results and outlooks of the studies of the luminescence properties of borane derivatives are discussed.

### INTRODUCTION

Chemistry of boron hydrides has developed into a vast area of chemical science which is reflected in a large number of original papers, communications presented at conferences, reviews and monographs (for example, see [1–5]). This area of inorganic chemistry was founded in 1912 and developed in the following years by the investigations of A. Stock and co-workers who synthesized and identified the first representatives of this class of compounds and some derivatives [6–8]. The modern chemistry of boranes started its development in late 40ies when the perspective of their use as the components of high-energy fuels appeared. Industrial methods of the synthesis of technologically important boranes were developed [9]. This circumstance was depicted in the chemistry of boron hydrides by determining its intensive development rates and high scientific level of investigations. Because of this, the 60ies and following decades were marked by the discovery of new classes of compounds including higher boranes, carboranes, metal- and element-containing boranes, metal complexes with borane

ligands, etc. At the same time, functional properties and qualities of the materials based on boranes were revealed. Mechanical engineering, inorganic and organic synthesis, electronics, metallurgy, catalysis, analytical chemistry, processes involving the deposition of layers and coatings, paper industry, medicine comprise the areas in which borane derivatives are used or proved to be useful.

A characteristic feature of the molecules and ions of higher boron hydrides and their derivatives is the spatial cluster deltahedral structures of several types exhibiting three-dimensional aromaticity or even superaromaticity [10, 11]. Three-dimensional aromatic character is connected with a high degree of electron density delocalization over the atoms of borane clusters which can lead to the appearance of valuable optical, magnetic, electrophysical and other functional properties. Therefore, the compounds of these types are considered at present as the basis of new molecular materials for the technology of the 21th century (see, for example, pp. 41 and 106 in [12]). It should be noted that, in spite of the fact that borane chemistry has developed into a vast and diverse area of in-

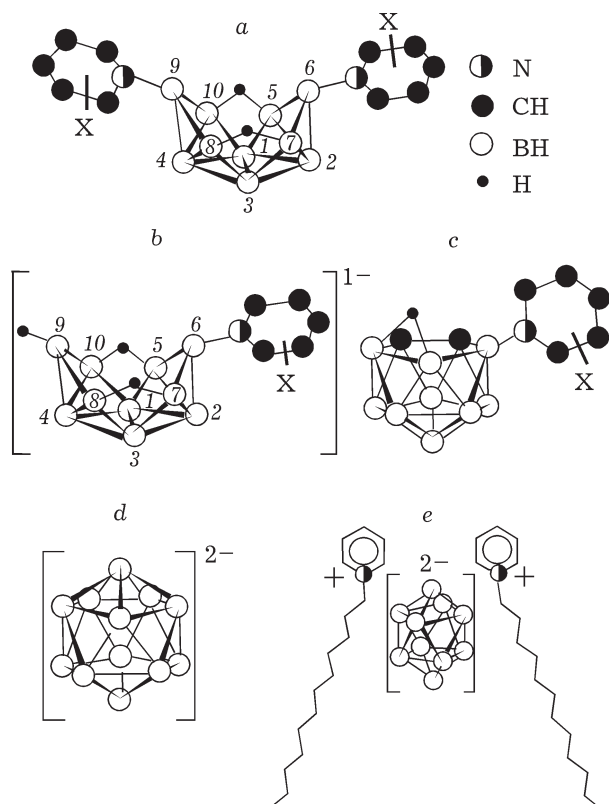


Fig. 1. Schemes of the molecules and ions of borate derivatives exhibiting luminescent properties (examples): *a* – adducts  $6,9\text{-B}_{10}\text{H}_{12}[\text{Py}(\text{X})]_2$ ; *b* – *nido*-anion  $[\text{B}_{10}\text{H}_{13}[\text{Py}(\text{X})]]^-$ ; *c* –  $\text{C}_2\text{B}_9\text{H}_{11}\text{Py}(\text{X})$ ; *d* – *closo*-anion  $[\text{B}_{12}\text{H}_{12}]^{2-}$ ; *e* – salt-like complex  $[\text{PyC}_{12}\text{H}_{23}]_2^+[\text{B}_{10}\text{H}_{10}]^{2-}$  [18].

organic chemistry, publications concerning luminescent properties of the compounds of these classes are very rare, fragmentary and unsystematic. It is quite evident that the observation and investigation of the luminescence of the substances related to principally new classes is of certain scientific and applied importance. Technological importance of luminescence is generally recognized (radiation control, laser technologies, luminescent cloth, coatings, dyes, *etc.*). Inorganic and organic substances that are able to emit light under irradiation are applied as the substantial basis for technological luminophors. Many original papers and monographs concerning the nature and application of luminophors have been published (for example, see [13–15]). A characteristic feature of organic luminophors is that in most cases their molecules and molecular aggregates include structural fragments of planar aromatic rings, heterocycles and condensed systems of benzoid

character, as well as unsaturated bonds [13, 15]. Examples can be anthracene, stilbene (diphenyl ethylene), tolan (diphenyl acetylene), and sodium salicylate [15]. In principle, cluster borane three-dimensional aromatic systems can be considered as possible luminophors.

In our investigations into the synthesis of decaborane(14) derivatives, *i. e.* its adducts with the Lewis bases (L) of the type  $\text{B}_{10}\text{H}_{12}\text{L}_2$  where  $\text{L} = \text{Py}(\text{X})$  – pyridine or its alkyl-substituted derivatives, we discovered that some of these compounds exhibit intensive photoluminescence under UV irradiation [5, p. 107; 16]. Later the luminescence of other types of borane compounds was discovered, in particular, *ortho*-carborane(12) derivatives  $\text{C}_2\text{B}_9\text{H}_{11}\text{Py}(\text{X})$ ,  $\text{C}_2\text{B}_9\text{H}_{10}\text{BrPy}(\text{X})$  and salt-like complexes of hydroborate anions  $[\text{B}_{10}\text{H}_{13}\text{Py}(\text{X})]^-$ ,  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{B}_{12}\text{H}_{12}^{2-}$  with the cations of quaternary pyridinium bases  $[\text{Py}(\text{Y})]^+$  where  $\text{Y} = \text{H}$ ,  $\text{C}_2\text{H}_5$  (Et),  $\text{C}_{12}\text{H}_{25}$  (general formula  $[\text{PyY}]_2^+[\text{B}_n\text{H}_n]^{2-}$ ) [17, 18]. Figure 1 shows some schemes of the structure of the molecules and ions of borane derivatives that exhibited photoluminescence. The presence of two types of aromatic systems is characteristic of the luminophors under consideration. The first type includes organic planar structures  $\text{Py}(\text{X})$  and their analogs; the second type includes three-dimensional aromatic systems based on borane clusters  $[\text{B}_{10}\text{H}_{12}]$ ,  $[\text{C}_2\text{B}_9\text{H}_{11}]$ ,  $\text{B}_n\text{H}_n^{2-}$  anions and their derivatives. A similarity with the organic luminophors based on aromatic cyclic structures exists. The present study has resulted in the primary information concerning the main characteristics of the listed borane derivatives. Basing on this information we determined the luminophors suitable for use as working substances to measure and visualize the synchrotron radiation (SR) which is described in [19, 20].

The progress of elementary particle acceleration technique has lead to the application of the accompanying SR to research and technological purposes. A broad energy spectrum of the quanta is characteristic of SR that is electromagnetic by its nature. So, the task arises to measure and visualize SR region related to the vacuum UV. This problem can be solved with the help of luminophors sensible to photon energies of 5–10 eV. These luminophors should meet the following demands: a) high quantum yield of

luminescence ( $\eta$ ) with respect to SR in order to provide sufficient intensity of emission to be recorded ( $I$ ); b) their luminescence spectrum should agree with the sensitivity ranges of measuring detectors, *i. e.* with the spectral sensitivity of alkaline-metal photomultipliers and photore-sists, as well as with the spectral sensitivity of human eye, c) it is desirable that  $\eta$  should only slightly depend on photon energy ( $E$ ) within the required spectral region which would allow to simplify the measuring schemes; d) the shortest possible rapid decay ( $\delta$ ). Sodium salicylate (a salt of *o*-oxybenzoic acid) is used as the main luminophor in the investigations involving SR. Its anion structure includes a benzoid aromatic fragment. This luminophor exhibits rather high  $\eta$  within the excitation energy range 6–40 eV. However, its luminescence spectrum with the maximum  $I$  at  $\lambda_f = 450$  nm (blue luminescence) has a low conformity coefficient (0.4–0.6) with respect to the spectral sensitivity of technical photomultipliers and photoresists [21, 22]. Its maximum  $I$  also poorly corresponds to the maximum of spectral sensitivity of human eye (550–570 nm, conformity coefficient 0.1). Therefore, it is urgent to search for new luminophors for the investigations involving SR [16, 17, 19, 20]. The most favourable results have been obtained for the compounds of the type  $B_{10}H_{12}[Py(X)]_2$ , namely, for  $B_{10}H_{12}(C_5H_5N)_2$  and  $B_{10}H_{12}[3,4-(CH_3)_2C_5H_3N]_2$  (6,9-bis(pyridine)-*nido*-decaborane(12) and 6,9-bis-(3,4-dimethylpyridine)-*nido*-decaborane(12), respectively). This fact can be the first example of the importance of the new type of luminophors for applied areas.

## EXPERIMENTAL

The compounds necessary for the optical investigations ( $B_{10}H_{12}[Py(X)]_2$  where  $Py(X) = Py$ , 3-MePy, 3,4-Me<sub>2</sub>Py, 3-BrPy, *etc.*, Me = CH<sub>3</sub>) were synthesized according to the known chemical principle [1, p. 137; 23, 24] by substituting Me<sub>2</sub>S in decaborane(14) derivative  $B_{10}H_{12}(Me_2S)_2$  by stronger pyridine bases  $Py(X)$  in hot toluene. Salt-like complexes of hydroborate anions  $B_{10}H_{10}^{2-}$ ,  $B_{12}H_{12}^{2-}$ ,  $B_{10}H_{13}Py^-$ , and  $B_{10}Cl_{10}^{2-}$  with the

cations of the type  $[Py(Y)]^+$ , namely, with  $PyH^+$ ,  $PyEt^+$ ,  $PyC_{12}H_{25}$  and  $Et_3NH^+$  were obtained by the deposition in aqueous medium under the action of soluble halide salts of the cations  $[Py(Y)]^+$  on the solutions of the mentioned anion salts with the cations  $K^+$  or  $Cs^+$ . Amorphous precipitates of the target compounds were re-crystallized from the mixture MeCN – H<sub>2</sub>O and dried in vacuum till constant mass similarly to [18]. The derivatives of *ortho*-carborane(12) of the type  $C_2B_9H_{11}Py(X)$  and  $C_2B_9H_{10}BrPy(X)$  where  $Py(X)$  corresponds to Py, 4-MePy, 3-MePy, 3-BrPy, and 3,4-Me<sub>2</sub>Py were synthesized and identified according to [17, 25, 26]. The compounds were characterized by means of IR, NMR-<sup>11</sup>B spectroscopy and chemical analysis. The structures of the compounds  $B_{10}H_{12}Py_2$ ,  $[PyC_{12}H_{25}]_2^+B_{10}H_{10}^{2-}$  and  $C_2B_9H_{11}(4-CH_3C_5H_4N)$  were studied by means of X-ray diffraction patterns [17, 18, 27, 28].

Luminescence spectra were recorded with a DFS-24 spectrometer equipped with a tight cryostat with quartz windows. Luminescence was excited by the 313 and 365 nm bands of UV radiation from the PRK-4 mercury lamp. Some luminescence spectra were at the same time recorded with a set-up composed of two DMR-4 monochromators, under the excitation with a DKSSh-500 xenon lamp. A sample under investigation was placed into the holder in the cryostat to perform measurements within the range 77–300 K under a pressure of  $\sim 10^{-6}$  Torr. The set-up and measurement regime are described in [16].

The compounds  $B_{10}H_{12}Py_2$  and  $B_{10}H_{12}(3,4-Me_2Py)_2$  were chosen for a more detailed measurement of luminescent characteristics in order to use them as the materials to register SR. The experiment was performed at the SR Centre of the Institute of Nuclear Physics, SB RAS, using the experimental equipment available. Luminescence excitation spectra of the samples  $B_{10}H_{12}[Py(X)]_2$  and the reference substance were recorded. SR was passed through a system of diaphragms onto the diffraction grating (Au;  $R = 2$  m; 600 strips per a millimetre) of the monochromator according to the Wordsworth's scheme, with the vertical dispersion plane, and further on, to the outlet slit onto the sample. Luminescence emitted by

TABLE 1  
Luminescence characteristics of borane derivatives

No.	L or LR	$\lambda_f$ , nm	$W_{1/2}$ , nm	$I$ (298 K)	$k$
<b>B<sub>10</sub>H<sub>12</sub>·L<sub>2</sub></b>					
1	Py (I)	525	81	0.15	3.1
2	2-MePy	515	71	0.12	3.2
3	3-MePy	532	78	0.32	2.7
4	3-BrPy	579	75	0.02	4.5
5	3-CNPy	603	89	0.003	7.7
6	4-MePy	515	76	0.98	3.0
7	4-(PhCH <sub>2</sub> )Py	545	86	0.22	2.6
8	4-(PhC <sub>2</sub> H <sub>2</sub> )Py	653	84	0.002	4.1
9	2,6-Me <sub>2</sub> Py	526	78	0.005	10.9
10	3,4-Me <sub>2</sub> Py	535	79	0.86	—
11	3,5-Br <sub>2</sub> Py	595	79	0.006	3.7
12	Me <sub>2</sub> S	498	106	0.001	1.0
13	MeCN	501	128	0.0005	4.4
<b>C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>·L</b>					
14	Py	465	77	0.74	—
15	3-MePy	486	85	0.25	—
16	3-BrPy	493	85	0.03	2.4
17	4-MePy (I)	484	85	0.45	—
18	4-MePy (II)	490	87	0.14	—
19	4-(PhCH <sub>2</sub> )Py	472	83	0.14	—
20	4-(PhC <sub>2</sub> H <sub>2</sub> )Py	525	86	0.03	—
21	3,4-Me <sub>2</sub> Py	461	79	1.00	0.8
<b>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Br·L</b>					
22	Py	476	87	0.06	~1
23	3-MePy	466	82	0.35	~1
24	3-BrPy	495	100	0.07	1.3
25	4-MePy	477	87	0.25	1.3
26	4-(PhCH <sub>2</sub> )Py	475	89	0.15	~1
<b>C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>I·L</b>					
27	Py	476	84	0.11	—
<b>B<sub>9</sub>H<sub>13</sub>·L</b>					
28	Py	464	83	0.06	—
<b>B<sub>9</sub>SH<sub>11</sub>·L</b>					
29	Py	490	88	0.06	—
<b>[LR]<sup>+</sup>[B<sub>10</sub>H<sub>13</sub>·Py]<sup>-</sup></b>					
30	Me <sub>4</sub> N	536	100	0.0086	8.6
31	Et <sub>3</sub> NH	535	79	0.43	2.8
<b>[LR]<sub>2</sub><sup>+</sup>[B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup></b>					
32	PyH	518	110	0.0005	13
33	PyMe	527	96	0.0006	230
34	PyEt	535	93	0.001	330
35	PyC <sub>12</sub> H <sub>25</sub>	536	78	0.01	52
36	4-(PhCH <sub>2</sub> )PyH	525	95	0.002	21
37	2,6-Me <sub>2</sub> PyH	527	78	0.005	16
38	2,2'-bipyH	548	99	0.0006	6

TABLE 1 (continued)

	$[\text{LR}]_2^+[\text{B}_{12}\text{H}_{12}]^{2-}$				
39	PyC <sub>12</sub> H <sub>25</sub>	467	87	0.009	10
	$[\text{LR}]_2^+[\text{B}_{10}\text{Cl}_{10}]^{2-}$				
40	PyC <sub>12</sub> H <sub>25</sub>	486	100	0.003	74
	$[\text{LR}]_2^+[\text{B}_{10}\text{Br}_{10}]^{2-}$				
41	PyC <sub>12</sub> H <sub>25</sub>	520	84	0.01	47
	$[\text{LR}]_2^+[\text{C}_2\text{B}_9\text{H}_{12}]^-$				
42	2,2'-bipyMe	540	107	0.0005	3.4

Notes. L is a Lewis-type base, R is H or an organic radical,  $\lambda_f$  is the wavelength of the fluorescence maximum,  $W_{1/2}$  is the width of band at semi-height,  $I$  (298 K) is relative intensity at 298 K,  $k$  is the change of intensity during cooling, determined as  $I(78\text{ K})/I(298\text{ K})$ , Py is C<sub>2</sub>H<sub>5</sub>N, Me is CH<sub>3</sub>, Et is C<sub>2</sub>H<sub>5</sub>, Ph is C<sub>6</sub>H<sub>5</sub>, bipy is 2,2'-bipyridyl; compounds No. 1 and 17 in the solid phase exist in crystal modifications I and II [16], a line means that measurements were not performed.

the samples was separated with a glass optical filter 3C-8 and recorded with a FEU-71 multiplier operated in the counting regime. Normalization per equal number of photons was done using sodium salicylate. Spectral data were collected and processed automatically in the KAMAK system. The quantum yield  $\eta$  of luminescence was measured with respect to the reference ZnS. The kinetic data on luminescence decay were used to determine  $\delta$ . The excitation of samples was performed through a UFS-1 glass optical filter, luminescence was separated with a MDR-23 monochromator and recorded with a dissector. The curves of the spectral sensitivity of human eye, photocathodes of the photomultipliers and photoresists were taken from [21, 22].

## RESULTS AND DISCUSSION

Table 1 shows luminescence characteristics of the investigated borane derivatives (42 compounds as a total) belonging to 12 types. Thus we confirmed the fact that the luminescence is characteristic of a large number of the compounds from this class since it is possible to obtain very long rows of borane derivatives with different L and LR;  $\lambda_f$  is within the range 461–653 nm (see compounds No. 21 and 8, respectively). Compound No. 5 with  $\lambda_f = 603$  nm should also be noted.

Luminescence properties of the adducts of borane clusters with heterocyclic L is strongly affected by their mutual orientation and the character of antibonding  $\pi^*$  orbitals of L. In the general case, the increase of the basic character of L is accompanied by a shift towards shorter wavelengths and the increase of the fluorescence intensity [16, 17, 26]. An increase in the acceptor ability of borane cluster, especially when passing from  $[\text{B}_{10}\text{H}_{12}]$  to  $[\text{C}_2\text{B}_9\text{H}_{11}]$ , is accompanied by a short-wavelength shift of  $\lambda_f$ , but the fluorescence intensity is changed not systematically [17, 26]. This allows us to suppose that the features of crystal packing (see compounds No. 17 and 18), as well as steric strains caused by the substituents X in positions 2(6) of the Py(X) cycles, the formation of intramolecular cycles due to a weak hydrogen bond H...H and geometrical distortions of the boron carcass under the action of the halogen atom (in  $[\text{C}_2\text{B}_9\text{H}_{10}\text{Hal}]$ , where Hal = Br, I) have a strong impact on the fluorescence of the compounds of this type [16, 17, 26]. A broadening of the p-system of L by the addition of functional groups with unsaturated bonds (C $\equiv$ N, CH=CHPh, compounds No. 5, 8, 20), similar to the case of quinoline in  $\text{B}_{10}\text{H}_{12} \cdot \text{Quin}_2$  [16], causes a substantial long-wavelength shift of  $\lambda_f$  with a sharp decrease of  $\eta$ .

Attention should be paid to one more property of the luminescent borane derivatives. Some

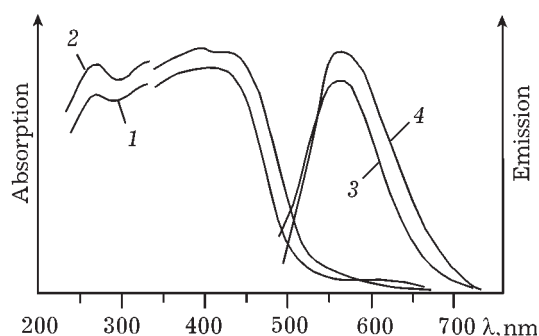


Fig. 2. Diffusion reflection spectra (1 and 2) and fluorescence spectra (3 and 4) of the two crystal modifications of  $B_{10}H_{12}Py_2$ ; 1 and 3 – intrinsic modification I (see Table 1, No. 1), 2 and 4 – extrinsic modification II [16].

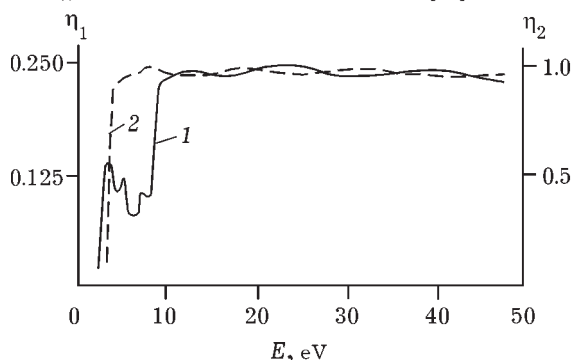


Fig. 3. Energy dependences  $\eta$  of the  $B_{10}H_{12}Py_2$  luminophor (1) and sodium salicylate (2).

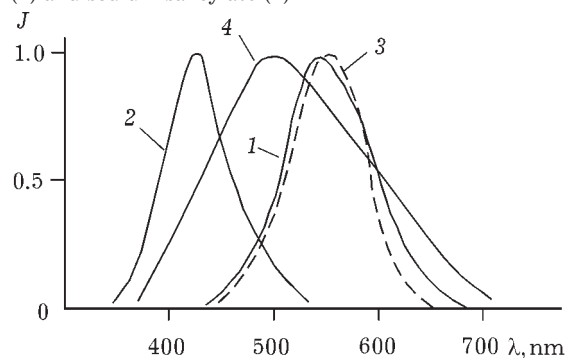


Fig. 4. The diagrams of spectral conformity of the  $B_{10}H_{12}Py_2$  (1) and sodium salicylate (2) photoluminescence with light sensitivity curves for human eye (3) and C-8 photocathode (4) [21, 22].

salts of the anion  $B_{10}H_{10}^{2-}$  exhibit an unusually large change of luminescence intensity ( $k$ ) when temperature is changed from 78 to 298 K (see Table 1, compounds No. 33–35 for which  $k$  is within the range 52–330).

The appearance of colouring (and fluorescence) in the salts of the type  $[Py(Y)]_2^+[B_{10}H_{10}]^{2-}$  is believed to be connected with the features of their crystal structure (see, for example, [18]) characterized by short contacts between different atoms of counter-ions, in particular  $H^{\delta+} \dots H^{\delta-}$  contacts. The decrease in temperature should lead to an additional shortening of these contacts which is likely to be exhibited by a sharp increase of fluorescence intensity in the salts under consideration at 78 K.

Figure 2 shows the diffusion reflection spectra (curves 1 and 2) and fluorescence spectra (curves 3 and 4) of the two crystal modifications of  $B_{10}H_{12}Py_2$ . Both modifications are characterized by  $\lambda_f = 560$  nm. The behaviour of these spectral curves is also characteristic of some other compounds of the row under investigation. Figure 3 represents the comparison between energy dependences  $\eta = f(E)$  for the  $B_{10}H_{12}Py_2$  luminophor ( $\eta_1$ ) and sodium salicylate which is the reference compound ( $\eta_2$ ) within the energy range 0–40 eV. Curve 2 has a plateau within the range 6–40 eV at  $\eta_2 = 0.96$ –1.0. Curve 1 has a plateau at  $\eta_1 \sim 0.25$ . So, the new luminophor is also characterized by a plateau at the  $\eta = f(E)$  plot. The correspondence between the photoluminescence spectra of  $B_{10}H_{10}Py_2$  reference sodium salicylate and radiation receiver sensitivity curve, as well as the sensitivity curve for human eye, is shown schematically in Fig. 4. Relative positions of curves char-

TABLE 2

The characteristics of the studied luminophors in comparison with sodium salicylate

Luminophor	Excitation region*, eV	$\lambda_f$ , nm	$\delta$ , ns	$\eta^{**}$	$K^{***}$		
					Photocathodes S-20, C-8	Photoresistors FSD, SF-2	Human eye
6,9- $B_{10}H_{12}(C_5H_5N)_2$	10–40	560	6; 30	0.25	0.7–0.8	0.8–0.9	1.0
6,9- $B_{10}H_{12}[3,4-(CH_3)_2C_5H_3N]_2$	10–40	560	< 40	0.63	0.7–0.8	0.8–0.9	1.0
Na[2-(HO)- $C_6H_4$ -COO]	6–40	450	–	0.95	0.5–0.6	0.4–0.5	0.1

\* $\eta = \text{const.}$

\*\*With respect to the reference ZnS (295 K).

\*\*\*Conformity coefficient of the photoluminescence spectrum with the radiation receiver sensitivity to light.

racterize better correspondence for the spectrum of the new luminophor  $B_{10}H_{12}Py$  (curve 1) with curves 3 and 4 than for the sodium salicylate spectrum (curve 2). A quantitative characteristic of this property is the conformity coefficient. The characteristics of the luminophors studied in detail are shown in Table 2. These data suggest that the luminophor  $6,9-B_{10}H_{12}[3,4-(CH_3)_2C_5H_3N]_2$  exceeds sodium salicylate in all the conformity coefficients and in  $I_f$  but exhibits somewhat lower  $\eta$  and only insignificantly less SR excitation range with  $\eta = \text{const}$ . The compound  $B_{10}H_{12}Py_2$  also exceeds sodium salicylate by some characteristics but gives lower  $\eta$ . These results allowed us to recommend  $B_{10}H_{12}[Py(X)]_2$  as the basis for luminescent materials intended for the visualization and measurements of SR [19, 20].

## CONCLUSIONS

1. On the basis of the studies into the primary photoluminescence properties of a series of cluster derivatives of decaborane (14), *o*-carborane (12) and some salts of the anions  $B_nH_n^{2-}$ , etc. (42 compounds of 12 types), it is demonstrated that the luminescence is inherent for boron hydrides. A clear perspective of their use as new luminophor materials is evident.

2. It is demonstrated that the use of  $B_{10}H_{12}[Py(X)]_2$  compounds as materials for SR is promising since they possess some advantages in comparison with the reference luminophor usually used for this purpose.

3. The luminescence of borane derivatives has been studied only poorly till present though the chemistry of these compounds has developed into a separate vast scientific area. It is evident that the first published data on the simplest luminescent properties do not limit either scientific or applied importance of these compounds as new luminophors. It is necessary to develop investigations in this direction for the purpose of discovering valuable functional properties of these substances as the basis for novel materials.

## REFERENCES

- 1 E. L. Muettterties, *The Boron Hydride Chemistry*, Academic Press, New York, 1975.
- 2 R. N. Grimes, *Carboranes*, Academic Press, New York – London, 1970.
- 3 R. N. Grimes (Ed.), *Metal Interaction with Boron Clusters*, Plenum Press, New York, 1982.
- 4 R. W. Parry and G. Kodama (Eds.), *Boron Chemistry-4, Lectures Presented at the 4th Intern. Meeting on Boron Chemistry*, Utha, USA, 1979, Pergamon Press, Oxford – New York, 1980.
- 5 European Conf. on Boron Chemistry'97 (Euroboron I): Program and Abstracts, Catalunya, Spain, 1997.
- 6 A. Stock, and C. Nassenz, *Berichte*, 45 (1912) 3529.
- 7 A. Stock, and E. Kuss, *Ibid.*, 47 (1914) 3115.
- 8 A. Stock, *Hydrides of Boron and Silicon*, Coornell University Press, Ithaca, New York, 1933.
- 9 R. L. Hughes, I. C. Smith and E. D. Lawless, in R. T. Holzmam (Ed.), *Production of Boranes and Related Research*, Academic Press, New York – London, 1967.
- 10 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 36 (1962) 3489.
- 11 R. B. King, *Izv. AN SSSR. Ser. khim.*, 8 (1993) 1353.
- 12 R. N. Grimes, *Appl. Organometallic Chem.*, 10 (1996) 209.
- 13 B. M. Krasovitsky and B. M. Bolotin, *Organicheskiye lyuminofory*, Khimiya, Moscow, 1984.
- 14 Yu. A. Egorov, *Stsintillyatsionnyy metod spektrometrii gamma-izlucheniya i bystrykh neutronov*, Gosatomizdat, Moscow, 1963.
- 15 R. N. Nurmukhametov, *Pogloshcheniye i lyuminestsentsiya aromatcheskikh soyedineniy*, Khimiya, Moscow, 1971.
- 16 E. A. Il'inchik, V. V. Volkov and S. T. Dunayev, *Zhurn. struktur. khimii*, 37 (1996) 59.
- 17 O. V. Volkov, E. A. Il'inchik, V. V. Volkov et al., *Zhurn. neorgan. khimii*, 38 (1993) 418.
- 18 A. V. Virovets, N. N. Vakulenko, V. V. Volkov and N. V. Podberezhskaya, *Zhurn. struktur. khimii*, 35 (1994) 72.
- 19 A. c. 1351078 USSR, 1987.
- 20 A. c. 1550925 USSR, 1989.
- 21 Yu. A. Tsirlin, A. R. Daich, A. M. Radyvayuk, *Stsintillyatsionnye bloki detektirovaniya*, Atomizdat, Moscow, 1976.
- 22 V. Yu. Lavrinenko, *Spravochnik po poluprovodnikovym priboram*, Tekhnika, Kiev, 1984.
- 23 R. J. Pace, J. Williams and R. L. Williams, *J. Chem. Soc. (London)*, (1961) 2196.
- 24 V. V. Volkov, K. G. Myakishev, O. G. Potapova et al., *Izv. SO AN SSSR. Ser. khim. nauk*, 3 (1988) 20.
- 25 O. V. Volkov, E. A. Il'inchik, V. V. Volkov et al., *Koordinats. khimiya*, 23 (1997) 824.
- 26 O. V. Volkov, E. A. Il'inchik, V. V. Volkov et al., *Zhurn. neorgan. khimii*, 43 (1998) 210.
- 27 T. M. Polyanskaya and V. V. Volkov, *Zhurn. struktur. khimii*, 30 (1989) 116.
- 28 T. M. Polyanskaya, V. V. Volkov, V. I. Andrianov, and E. A. Il'inchik, *Izv. AN SSSR. Ser. khim.*, (1989) 1905.