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IR Spectra of Azinobenzimidazoles and Compounds Containing an Azacyanine Chromophore

A. N. Frolov

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 198013 Russia

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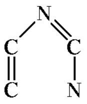
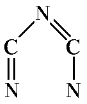
Abstract—Stretching vibration bands of the endocyclic C=C and C=N bonds in the IR spectra of pyrido[1,2-*a*]benzimidazoles, pyrimido[1,2-*a*]benzimidazoles, and boron and neutral Pd(II) chelates on the basis of 2,2′-dipyridylamine and benz[*c*,*d*]indolylamine are located at 1640 ± 10, 1610 ± 10, and 1470 ± 10 cm^{-1}. In addition, pyrido[1,2-*a*]benzimidazole derivatives, borone chelates like diphenylboryl[pyridin-2(1*H*)-ylidene]aminopyridinium, and palladium chelates like bis(2-[pyridin-2(1*H*)-ylidene]aminopyridine)palladium are characterized by strong C=C absorption at 1505 ± 10 cm^{-1}; the corresponding band of boron and palladium chelates and dimethylpyrimido[1,2-*a*]benzimidazole derivatives is observed at 1540 ± 10 cm^{-1}.

Azinobenzimidazoles constitute a class of nitrogen-containing heterocycles which are relatively difficult to obtain, and their properties have been studied poorly. These compounds are fluorophores and potential pharmacophores. Taking into account that only a few data are available on spectroscopic properties of azinobenzimidazoles, the present article describes the IR spectra of some representatives, namely pyrido[1,2-*a*]benzimidazoles **Ia**–**Ig** and dimethylpyrimido[1,2-*a*]benzimidazoles **IIa**–**IIg**. The IR bands were assigned on the basis of the data in [1].

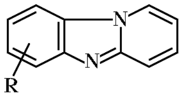
For the sake of comparison, consider the electron absorption spectra of compounds **Ia** and **IIa** and cyclic azacyanine **IIIc**. Figure 1 shows that azino-



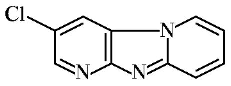
A



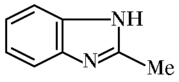
B



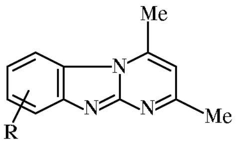
Ia–If



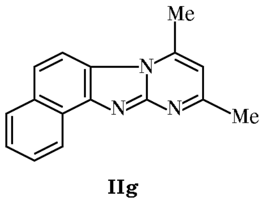
Ig



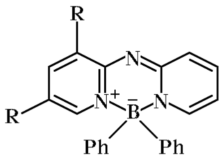
Ih



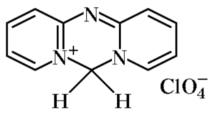
IIa–IIf



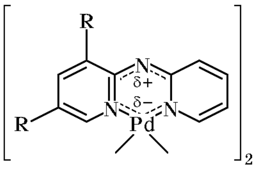
IIg



IIIa, IIIb



IIIc



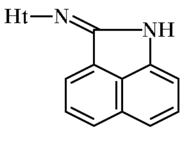
IVa, IVb

Ph_2BL

Va, Vb

PdL_2

VIa–VIc



VIIa–VIIc

I, R = H (**a**), 7-Cl (**b**), 9-Me (**c**), 8-F (**d**), 6,7,8,9-F_4 (**e**), 8-SO_2Me (**f**); **II**, R = H (**a**), 7-Cl (**b**), 8-Cl (**c**), 7,8-Cl_2 (**d**), 6,7,8,9-F_4 (**e**), 8-SO_2Me (**f**); **III**, **IV**, R = H (**a**), Cl (**b**); **V**, **VI**, L = **VIIa** (**a**), **VIIb** (**b**), **VIIc** (**c**); **VII**, Ht = 2-pyridyl (**a**), benz[*c*,*d*]indol-2-yl (**b**), 2-benzothiazolyl (**c**).

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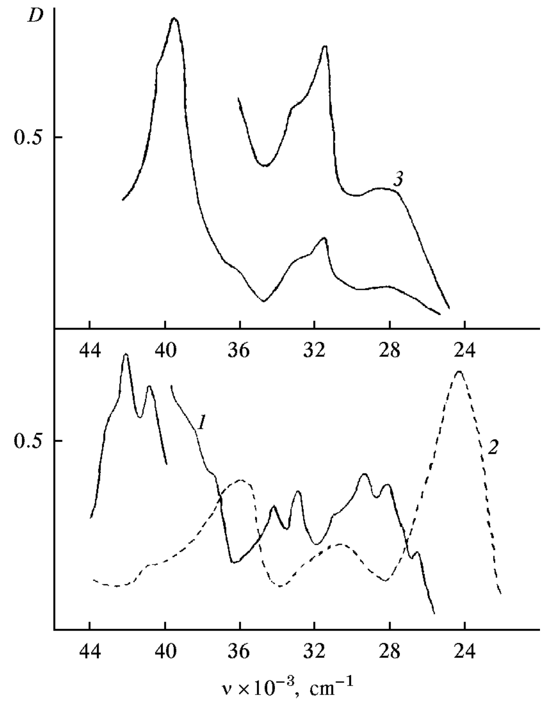

Fig. 1. Electron absorption spectra of (*1*) pyrido[1,2-*a*]benzimidazole (**Ia**), (*2*) *N*,*N*′-methylene-2-[pyridin-2(1*H*)-ylidene]aminopyridinium perchlorate (**IIIc**), and (*3*) 1,3-dimethylpyrimido[1,2-*a*]benzimidazole (**IIa**).

azoles **Ia** and **IIa** are characterized by two absorption bands in the region 25 000–36 000 cm^{-1}. The band corresponding to transition to the lowest singlet state (25 000–31 000 cm^{-1}) can be identified taking into account mirror symmetry of the absorption and emission spectra. In the frequency range from 36 000 to 43 000 cm^{-1} compounds **Ia** and **IIa** give rise to two transitions which appear as a shoulder at 35 000–36 000 cm^{-1} and a maximum at 40 000–42 000 cm^{-1}.

The first two absorption bands of azacyanine **IIIc** are located in the region 22 000–34 000 cm^{-1}; also, a high-frequency absorption maximum at 36 000 cm^{-1} and a shoulder at 40 000 cm^{-1} are observed.

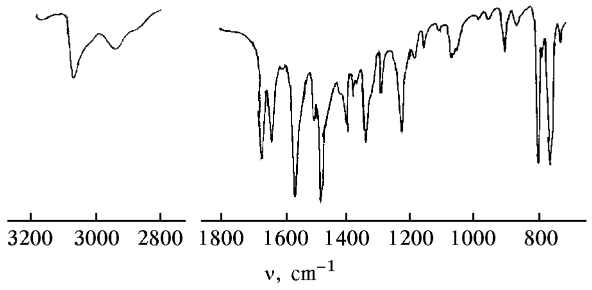

Fig. 2. IR spectrum of 1,3-dimethylpyrimido[1,2-*a*]benzimidazole (**IIa**).

It is seen that the electron absorption spectra of **Ia**, **IIa**, and **IIIc** are fairly similar. The differences include the lack of vibrational structure, molar absorption coefficients, and red shift of the spectrum of **IIIc**. Presumably, these data reflect a greater contribution of the charge-transfer state, as compared to locally excited states, for azacyanines like **IIIc**. Isoelectronic character of chromophores **A** and **B** in molecules **I**–**III** may be responsible for the analogy in their electron spectra (cf. [2]).

Taking the above into account, apart from the IR spectra of compounds **I** and **II**, spectral parameters of cyclic carbon- and boron-containing azacyanines **IIIa**–**IIIc**, **Va**, and **Vb** and of Pd(II) chelates **IVa**, **IVb**, and **VIa**–**VIc** were also examined. It was presumed in [3] that the ligand in neutral Pd(II) chelates with diheterylamines exists in the azacyanine form.

IR region 3100–2600 cm^{-1}. The absorption arising from C–H stretching vibrations of compounds **Ia**–**Ig** and **IIa**–**IIg** is observed in the frequency range from 2900 to 3080 cm^{-1}. The corresponding bands of Pd(II) chelates **IVa**, **IVb**, and **VIa**–**VIc** are located in the region 2850–3070 cm^{-1}, and of cyanines **III** and **V**, at 2800–3100 cm^{-1}. These are relatively weak and broadened bands which slightly change in going from one compound of the series to another.

IR region 1700–1400 cm^{-1}. Pyrido[1,2-*a*]benzimidazole derivatives Ia–Ig. Table 1 lists the IR absorption maxima in the region 1650–1400 cm^{-1}, grouped by frequency. Pyridobenzimidazole **Ia** gives six relatively strong bands of variable intensity in that region. The absorption at 1640–1650 cm^{-1} is typical of all compounds **I** and benzimidazole derivatives [4, 5] and was assigned to vibrations of the C=N bond. In addition, the IR spectra of pyridobenzimidazoles **I** contain an absorption maximum at 1600–1610 cm^{-1}. Presumably (as reported for pyridine derivatives [6]), this band has a composite nature, i.e., it originates from C=N and C=C stretching vibrations. Strong absorption bands in the spectra of **I** were observed at 1490–1510 and 1470–1490 cm^{-1}, and variable-intensity absorption was present at 1440–1450 and 1410–1420 cm^{-1}. By analogy with derivatives of benzimidazole [4, 5], azines, and benzene [1, 6, 7], the above bands were attributed to combinations of pairs of nondegenerate normal vibrations of the C=C bond in **Ia**–**Ig**, having different symmetries.

For comparison, Table 1 contains the IR data for 2-methylbenzimidazole (**Ih**), taken from [4]. The spectra of **Ia** and **Ih** are similar, but the latter lacks absorption at 1600–1610 cm^{-1}. The band at 1510 cm^{-1} in the spectrum of **Ia** is strong, while the corresponding band of **Ih** has a low intensity. These findings are

Table 1. IR spectra of compounds **I–VI** in the frequency range from 1700 to 1400 cm^{-1}

Comp. no.	Frequency ν, cm^{-1}							
Ia	1650 m	1610 m	1590 w		1510 s	1470 s	1455 w	
Ib	1650 m	1610 m	1590 w		1505 v.s	1490 m	1440 m	
Ic	1650 s	1605 s		1550 w	1510 v.s		1450 m	1410 m
Id	1650 m	1600 m		1520 w	1495 v.s	1480 m	1450 m	
Ie	1640 m			1550 s	1490 v.s		1450 m	
If	1650 m	1600 s	1580 w		1500 v.s	1470 m	1440 w	1420 w
Ig	1655 m	1610 m			1500 s	1470 m	1440 w	1410 m
Ih[a]	1652 w		1592 m	1560 m	1512 w	1492 m	1457 s	1422 s
IIa	1650 s	1620 m	1580 w	1540 s		1470 w		1400 w
IIb	1640 m	1615 m	1580 w	1530 v.s		1470 m		1400 m
IIc	1650 m	1620 w	1580 w	1540 s		1460 s		
IId	1650 s	1615 s	1580 w	1535 v.s		1470 m	1440 m	1400 m
IIe	1640 s			1560 v.s				
IIf	1640 m	1610 s		1540 s		1470 pl		
IIg	1630 s		1570 w	1540 s	1510 s	1460 s		1400 s
IIIa	1650 pl	1620 s	1560 m			1450 v.s 1460 v.s	1430 s	1400 m
IIIb	1640 m	1610 s	1560 s	1540 s	1490 s	1450 v.s		1410 s
IIIc	1650 sh	1620 s	1580 s		1520 s 1510 s			1400 m
IVa	1640 w	1610 m		1550 m	1490 m		1440 v.s	1390 m
IVb		1620 m	1590	1550	1510 1490 v.s	1450 v.s		1400 s
Va	1630 w	1610 w	1580 s	1540 s		1470 v.s	1450 s	1400 m
Vb	1640 w	1600 m			1500 v.s 1490 v.s	1480 s	1440 s	1390 w
VIa	1640 w	1620 w		1560 m	1510 s	1460 s	1430 s	1380 m
VIb	1640 w				1500 sh	1460 v.s		1380 m
VIc	1640 w	1600 w			1500 s	1460 s	1430 v.s	1380 s

[a] Data of [4].

consistent with the more extended π system in **Ia**, as compared to **Ih**, and with the assignment of bands at 1600–1610 and 1510 cm^{-1} to C=C stretching vibrations in **Ia**.

The IR spectrum of tetrafluoro derivative **Ie** contains a relatively strong band at 1550 cm^{-1} rather than at 1600 cm^{-1}. The low-frequency shift may be explained in terms of stronger electron-acceptor properties of the tetrafluorobenzene fragment in **Ie**, as compared to nonfluorinated analog **Ia**.

Apart from the above discussed bands, compounds **I** are characterized by IR absorption at 1350–1370 and 1330–1340 cm^{-1}, i.e., in the boundary region between stretching C=C vibrations and in-plane bending C−H vibrations. The origin of these bands is not clear.

Also, pyridobenzimidazoles **I** show in the IR spectra absorption bands belonging to vibrations of substituents: stretching vibrations of C−Cl bonds (**Ib** and **Ig**), asymmetric and symmetric stretching vibrations of S=O group (**If**), C−F stretching vibrations (**Id** and **Ie**), and asymmetric and symmetric bending vibrations of methyl group (**Ic**). The corresponding frequencies are collected in Table 2. It should be noted that the methyl group absorption at 1470 cm^{-1} is usually overlapped by C=C stretching vibration band (Tables 1, 2). Therefore, the origin of the peak with its maximum at 1470 cm^{-1} is not always unambiguous.

Pyrimido[1,2-*a*]benzimidazole derivatives IIa–IIg. Dimethylpyrimidobenzimidazole **IIa** shows

Table 2. IR absorption frequences of functional groups in compounds **I**–**III**, ν, cm^{-1}

Comp. no.	Cl	F	Me (CH_2)	SO_2Me	ClO_4^-
Ib	800 s				
Ic			1470 m 1370 s		
Id		1180 s 1160 s			
Ie		1020 v.s 1060 v.s			
If				1300 v.s 1150 v.s	
Ig	780 m				
IIa			1450 s 1380 m		
IIb	790 v.s		1430 v.s 1390 m		
IIc	800 s		1440 s 1380 m		
IId	780 m		1450 v.s 1380 m		
IIe		1080 v.s 1100 s	1470 m 1390 s		
IIf			1450 s 1390 s	1300 v.s 1150 v.s	
IIg			1470 s 1390 s		
IIIc			1460 s 1350 v.s 1320 v.s		1130 v.s 1100 v.s

five relatively strong absorption bands in the region 1650–1300 cm^{-1}. Two of these may arise from asymmetric and symmetric C–H bending vibrations in the methyl groups (Table 2). Methyl group absorption [δ(C–H)] is typical of all compounds **IIa**–**IIg**. It should be noted that ν(C=C) of **IIe** coincides with δ(C–H) of the methyl group (as in the case of compound **Ic**; Tables 1, 2).

Like isoelectronic azinoazoles **I**, compounds **IIa**–**IIg** are characterized by strong absorption bands in the region of C=N stretching vibrations of the heteroring (1630–1650 cm^{-1}). Taking into account the data given in [6] for azines, the absorption in the region 1620–1400 cm^{-1} was assigned to C=C stretching vibrations of the heteroring in **II** (for particular maxima, see Table 1). In the region 1400–1300 cm^{-1} the δ(C–H) band (methyl group) of compounds **II** is more intense (Table 2). The other bands have low intensity and are irregular; therefore, it is difficult to assign them unambiguously. Functional groups in compounds **II** give rise to absorption in the expected frequency ranges (Table 2).

Azacyanines IIIa–IIIc and Va–Vc. The C=N stretching vibrations bands in the IR spectra of compounds **IIIa**–**IIIc** and **Va**–**Vc** (1630–1650 cm^{-1}) have a relatively low intensity. Symmetric boron chelates containing an azacyanine chromophore (compounds **IIIa** and **Vb**) and azacyanine **IIIc** are characterized by similar C=C vibration frequencies in the range from 1600 to 1400 cm^{-1}; especially strong absorption is observed at 1450–1500 cm^{-1} (**IIIa** and **Vb**) and 1510–1520 cm^{-1} (**IIIc**). Unsymmetrical cyanines **IIIb** and **Va** give rise to an additional C=C absorption band at 1540 cm^{-1} due to reduced molecular symmetry.

Comparison of the spectral parameters of compounds **Ia**–**Ig** and **IIa**–**IIg** with those of **IIIa**–**IIIc**, **Va**, and **Vb** reveals a qualitative tendency to reduction of the relative intensity of the C=N absorption band (1630–1650 cm^{-1}) and to increase in intensity of the C=C absorption bands (1560–1580, 1460–1490, and 1430–1450 cm^{-1}). Because of the lack of quantitative data, this fact will not be discussed in more detail. Insofar as the intensity of absorption bands is related to charge distribution in the molecule [1], the observed tendency may be regarded as an evidence in favor of higher polarity of azacyanines **III**, as compared to azinobenzimidazoles **I** and **II**. This conclusion is qualitatively consistent with the differences observed in their electron absorption spectra.

Palladium(II) chelates IVa, IVb, and VIa–VIc. Palladium complexes **IVa**, **IVb**, and **VIa**–**VIc** are characterized by the presence of a relatively weak absorption in the region 1600–1700 cm^{-1}, corresponding to stretching vibrations of the C=N (1650–1630 cm^{-1}) and C=C bonds (1620–1600 cm^{-1}). The spectral range 1600–1400 cm^{-1} contains a series of bands of variable intensities due to C=C stretching vibrations and stronger bands at 1490, 1500, and 1450 cm^{-1} for chelates **IVa** and **IVb** based on dipyridylamine or at 1460 and 1420 cm^{-1} for chelates **VIa**–**VIc** derived from benz[*c*,*d*]indolylamine. This pattern is explained by charge transfer from the ligand to the metal, which is typical of Pd(II) complexes [3]. Hence the explanation given above for analogous feature of boron chelates **III** and **V** is also applicable to palladium(II) chelates **IV** and **VI**.

Table 1 shows that all compounds **I**–**VI** exhibit IR absorption bands at 1630–1650 cm^{-1} (C=N) and 1600–1620 and 1460–1490 cm^{-1} (C=C stretching vibrations, one of the couple of nondegenerate normal

Table 3. IR spectra of compounds **I**–**VI** in the frequency range from 1300 to 700 cm^{-1}

Comp. no.	Frequency ν, cm^{-1}						
Ia–**If**	1300–1320[a]	1210–1290	1130–1150	1010–1090	900–970	805–890	710–790
Ih [4]	–	1210–1278	–	1010–1048	900–968	838–852	735, 770
IIa–**IIg**	1300–1315[b]	1210–1280	1130–1190	1020–1090	900–970[c]	820–880	710–780
IIIa–**IIIc**	1300[d]	1210–1280	1100–1180	1040–1060[e]	880–900	850	700–790
IVa, **IVb**	–	1250–1270	1120–1160	1020	960[f]	810–890	740–790
Va, **Vb**	1300–1310	1220–1270	1100–1190	1010–1080	940–950	830–880	710–790
VIa–**VIc**	1300–1310	1200–1290	1100–1180	1020–1080	910–940	830–870	730–780

[a] Compounds **Ia**, **Ib**, and **Ie**.

[b] Compounds **IIa**, **IId**, and **IIg**.

[c] Compounds **IIa**, **IIb**, **IId**, and **IIg**.

[d] Compound **IIIc**.

[e] Compounds **IIIa** and **IIIb**.

[f] Compound **IVa**.

vibrations). The latter band also tends to change its intensity in the series **I**–**VI** due to charge transfer. An analogous conclusion follows from comparison of the 1440-cm^{-1} band intensities. Unlike the other bands, some compounds lack absorption at 1440 cm^{-1}.

A specific feature of azinobenzimidazoles **I** is the presence in their IR spectra of a strong C=C stretching band at 1505 ± 10 sm^{-1}. No such band is observed in the spectra of pyrimido[1,2-*a*]benzimidazoles **II**. By contrast, compounds **II** give rise to a strong band at 1540 ± 10 cm^{-1}, which is either very weak or absent in the IR spectra of **I**. Exceptions are fluorinated compound **Ie** and angular azinobenzimidazole **IIg** which absorb at both frequencies. Both absorption bands are also typical of boron and Pd(II) chelates (Table 1). Thus, the above frequencies can be used as analytical for azinobenzimidazoles **I** and **II** having a simple structure.

IR region 1300–700 cm^{-1}. The absorption maxima located below 1300 cm^{-1} are given in Table 3. The band at 1300–1310 cm^{-1} is not regular, it has variable intensity, and its nature is not clear. All compounds are characterized by IR absorption maxima at 1200–1290 and 1100–1180 cm^{-1}, whose intensity changes in going from one compound to another. According to the data of [1, 4–7], this absorption was assigned to in-plane bending vibrations of C–H bonds. Among other bands, those observed at 1010–1090, 900–970, and 810–890 cm^{-1} should be noted. These bands have variable intensity (compounds **I** and **II**) and are generally weak (**III**–**V**). The region is typical of γ(C–H) bending vibrations of various symmetries [1] and of breathing vibrations of heterorings, e.g., of pyridine ring [1]. Therefore, the above bands were assigned to heterorings in the compounds under study.

All compounds **I**–**VI** strongly absorb in the region 790–700 cm^{-1}. This spectral range is typical of out-of-plane bending vibrations of ring C–H bonds [1]. The absorption maxima are located within a relatively narrow frequency range, and their number and intensity depend on the structure of particular compound. For example, compound **Ia** is characterized by three strong bands at 770, 760, and 720 cm^{-1}; compound

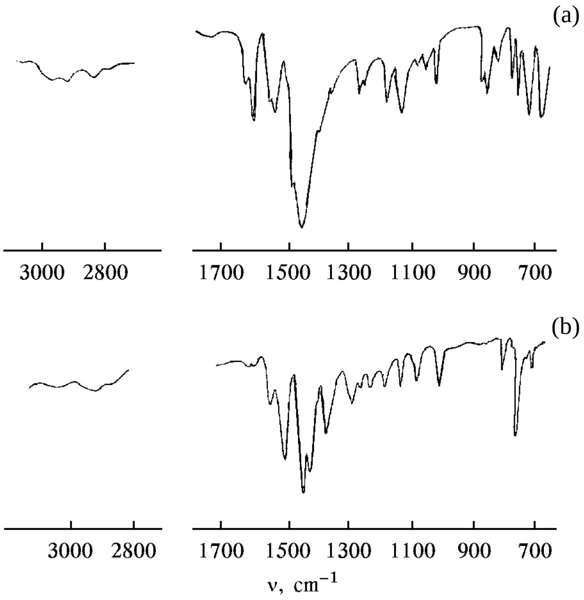

Fig. 3. IR spectra of (a) *N*,*N*′-diphenylboryl-2-[pyridin-2(1*H*)-ylidene]aminopyridinium (**IIIa**) and (b) bis[2-(benz[*c*,*d*]indol-2(1*H*)-ylideneamino)pyridine]palladium(II) (**VIa**).

IIa shows two intense maxima at 780 and 770 cm^{-1} with concomitant weak peaks at 760 and 710 cm^{-1}. Insofar as the available data are limited, no detailed correlation of the absorption in that region with the structure was performed.

Comparison of the IR spectra of compounds **IIa** and **IIe** shows that introduction of fluorine atoms into the benzene ring leads to disappearance of bands at 960 and 930 cm^{-1}, while the absorption at 860 and 820 cm^{-1} is retained. Unlike **IIa**, the 800–700-cm^{-1} region of the IR spectrum of **IIe** contains a strong band at 770 cm^{-1} with a weak concomitant band at 710 cm^{-1}, whereas no maximum at 740 cm^{-1} is observed. Therefore, the absorption at 960, 930, and 740 cm^{-1}, which is absent in the spectrum of tetrafluoro derivative **IIe**, can be assigned to C–H bending vibrations of the benzene ring in **IIa**.

EXPERIMENTAL

The UV spectra were recorded in 2-propanol using Specord M-40 and SF-20 spectrophotometers. The IR spectra were measured on a UR-10 spectrometer in KBr (1.5–3 mg/750 mg KBr). The IR spectra of **Ia** and **IIIa**, recorded in perfluorinated oil (for comparison), did not differ appreciably from the spectra obtained in KBr. Figures 2 and 3 show typical IR spectra of **IIa**, **IIIa**, and **VIa**. Compounds **Ia**, **Ib**, **Id** [8], **Ic** [9], **Ie** [10], **If** [11], **IIa**–**IIc** [12], **IId** [10], **IIe** [9], **IIf** [11], **III**, **Va**, **Vb** [13], **IVa**, **IVb**, and **VIa**–**VIc** [3] were synthesized by known methods.

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