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Synthesis of isomeric (*E*)-[4-(dimethylamino)phenyl]-vinylquinoxalines – precursors for a new class of nonlinear optical chromophores

Sirina M. Sharipova[1], Alina A. Gilmutdinova[1], Dmitry B. Krivolapov[1], Zilya R. Khisametdinova[2], Olga N. Kataeva[1], Alexey A. Kalinin[1]*

[1] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, 8 Akademika Arbuzova St., Kazan 420088, Russia; e-mail: kalinin@iopc.ru*

[2] *A. M. Butlerov Institute of Chemistry, Kazan Federal University, 18 Kremlevskaya St., Kazan 420008, Russia; e-mail: zika0527@mail.ru*

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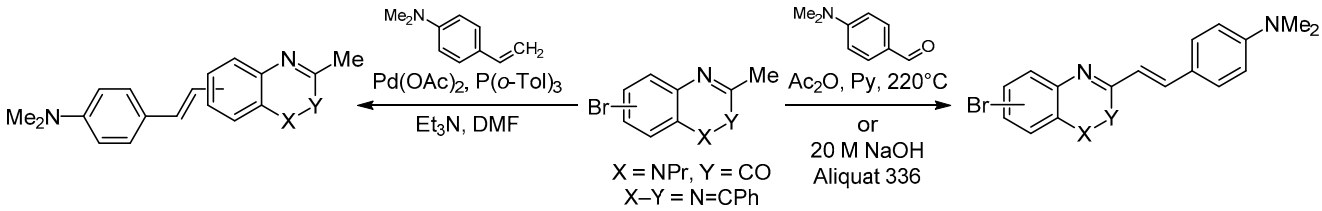


Methods are presented for the preparation of isomeric (*E*)-3-, (*E*)-6-, (*E*)-7-[4-(dimethylamino)phenylethenyl]quinoxalin-2-ones and 2-phenylquinoxalines – compounds of "donor–π-bridge" type, which serve as precursors for new nonlinear optical chromophores with potentially high first hyperpolarizability values. The introduction of dimethylanilinoethenyl moiety at position 3 of the quinoxaline system was achieved in good yields by fusion of 3-methyl derivatives with 4-(dimethylamino)benzaldehyde at 220°C in the presence of catalytic amounts of acetic anhydride and pyridine during the synthesis of 3-(dimethylaminophenylethenyl)quinoxalin-2-ones or as a result of condensation of these reactants by the action of 20 M sodium hydroxide solution in the presence of Aliquat 336 during the synthesis of 3-(dimethylaminophenylethenyl)-2-phenylquinoxalines. The introduction of dimethylanilinoethenyl moiety at positions 6 and 7 was achieved by Heck reaction of *p*-dimethylaminovinylbenzene with 6- or 7-bromoquinoxalines in the presence of palladium acetate. The structures of isomeric 6-bromo- and 7-bromo-3-methyl derivatives of quinoxalines were confirmed by X-ray diffraction analysis.

Keywords: (*E*)-[4-(dimethylamino)phenyl]ethenylquinoxalines, first hyperpolarizability, nonlinear optical chromophores, X-ray diffraction analysis.

Synthesis of new chromophores with high values of first hyperpolarizability, the molecular characteristic of nonlinear optical (NLO) chromophores, provides the foundation for the creation of NLO materials, which find use in the design of devices for information storage and fast processing.[1] Wide application of heterocyclic compounds for the synthesis of NLO chromophores started in the last decade of the 20th century. Heterocyclic moieties can be included in one, two, or all three components of such chromophores – the donor and acceptor and the π-bridge. The main attention of researchers has been focused on chromophores with one[2] or several[3] thiophene rings within the π-bridge. One of the new directions in this field is the synthesis and characterization of NLO effects in chromophores with fused heterocyclic moieties, such as thienothiophene,[4] carbazole,[5] and phenothiazine,[5] in the structure of π-bridge as well as in the donor[6] and acceptor.[7]

Recently we predicted theoretically[8] that the replacement of thiophene in the FTC chromophore[9] (one of the best NLO chromophores, Fig. 1) with a quinoxaline moiety (compounds **1** and **2**, Fig. 2) should result in increased first hyperpolarizability values.

The quinoxaline ring system is a part of compounds with valuable biological properties;[10] its derivatives[11–14] serve as initial compounds for the preparation of other heterocycles that may contain quinoxaline[12] or other moieties,[13] as well

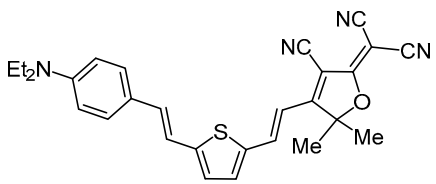


Figure 1. The structure of FTC chromophore.

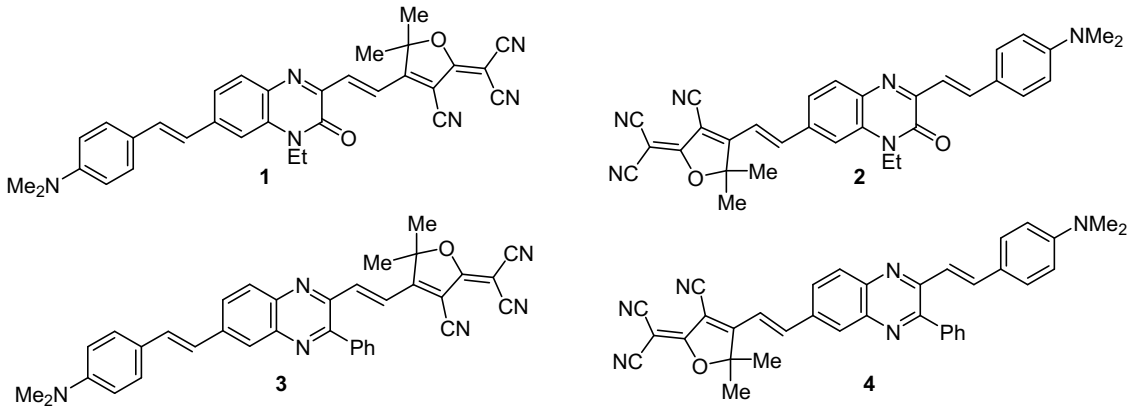


Figure 2. Chromophores **1**–**4** with divinylquinoxaline π-bridge.

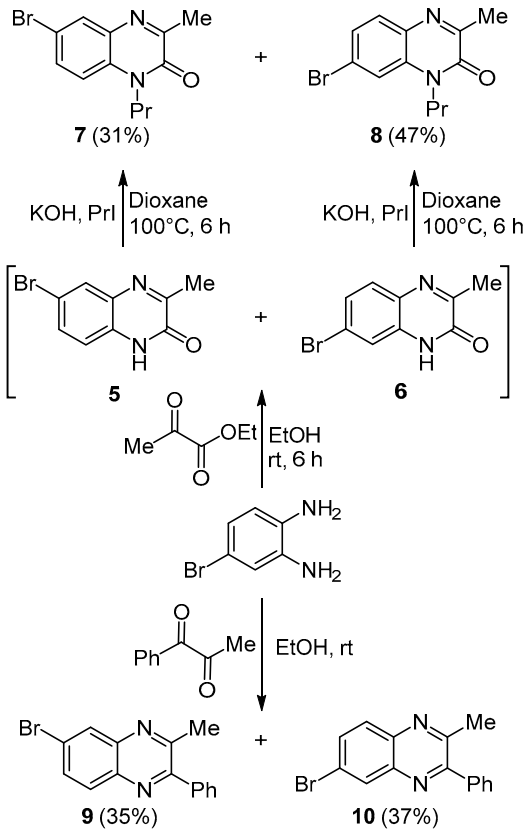
as for the synthesis of macrocycles,[14] but have not yet been applied in the synthesis of effective NLO chromophores.

In the current work, we present a method for the preparation of isomeric (*E*)-[4-(dimethylamino)phenyl]-ethenylquinoxalines, which can be used for the synthesis of new, effective NLO chromophores with quinoxalinone (compounds **1** and **2**) or 2-phenylquinoxaline (compounds **3** and **4**) moieties in the π-bridges (Fig. 2). Despite the structural similarity of all compounds **1**–**4**, compounds **3** and **4** differ from compounds **1** and **2** by the presence of a bulky phenyl substituent, which can function as an isolating group, decreasing the aggregation of chromophores in the material[15] and thus enabling higher NLO activity of such material.

A highly successful strategy for the synthesis of NLO chromophores is the construction of π-conjugated system within the precursor of the electron-donating fragment by linking it with the precursor of π-bridge, followed by modification and introduction of the acceptor as the last step. The introduction of electron-donating dimethylaniline moiety in the structure of quinoxaline derivatives, depending on the regioposition of its addition, was based on either the Heck raction – addition through vinyl group to the carbon atom at position 6 or 7 of quinoxaline system, or Knoevenagel condensation – addition to the carbon atom at position 3. In order to emply these approaches, derivatives of 6- and 7-bromo-3-methylquinoxalines were obtained. Condensation of ethyl pyruvate with 4-bromo-1,2-benzenediamine allowed to synthesize 6- and 7-bromo-3-methylquinoxalin-2-ones **5** and **6**, which were further subjected to alkylation with propyl iodide in the presence of KOH in order to increase the solubility of the new precursors for π-bridge – *N*-propyl derivatives **7** and **8** (Scheme 1). The condensation of 4-bromo-1,2-benzenediamine with 1-phenylpropane-1,2-dione provided access to phenylquinoxalines **9**, **10**. Compounds **7**–**10** were readily soluble in organic solvents. Isomers **7** and **8**, in contrast to isomers **9** and **10**, had practically the same R_f values, complicating their separation by column chromatography. Nevertheless, the use of a longer column eventually allowed to chromatographically isolate isomer **7**. The isomeric mixture that was enriched with compound **8** was separated by several recrystallization steps using hexane.

^{1}H NMR spectra provided some clues for the assignment of isomeric products formed as a result of these reactions. The examples of various quinoxalinone derivatives[12,14b] have shown that their spectra contain characteristic downfield signals of the H-5 proton belonging to the quinoxalinone moiety, and therefore, due to the presence of a substituent at the aromatic ring, these isomers can be identified by their spin-spin coupling constants. Thus, the isomer showing ^{1}H NMR spectrum with the most downfield signal being a doublet with J = 8.9 Hz at 7.65 ppm was identified as compound **8**, while the isomer with a doublet at 7.83 ppm with J = 2.1 Hz as the most downfield ^{1}H NMR signal was identified as compound **7**. The

Scheme 1



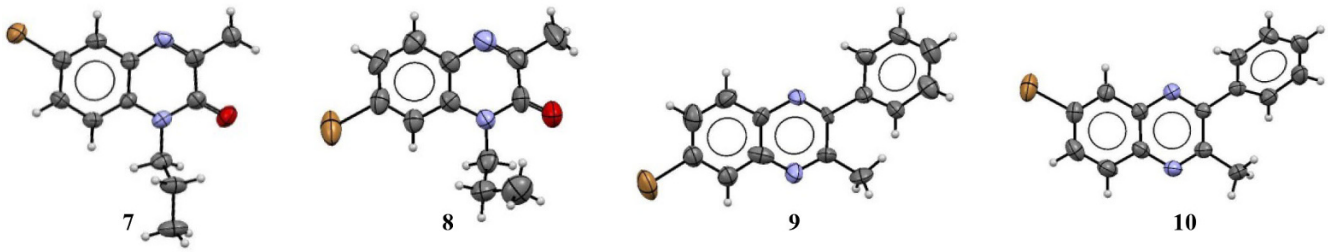


Figure 3. The molecular structures of bromoquinoxalines **7**–**10** with atoms represented by thermal vibration ellipsoids of 50% probability.

following assumption can be made for the other isomeric pair of compounds **9** and **10**: the isomer with ^{1}H NMR signal of the *ortho* protons of phenyl group at a lower field and the signal of methyl group at a higher field corresponds to compound **10**. Then the isomer showing the signal of *ortho* protons of phenyl group at higher field, and the signal of methyl group at lower field coresponds to isomer **9**.

The structures of compounds **7**–**10** were established by X-ray diffraction analysis (Fig. 3). The asymmetric part of the unit cell in the crystal of compound **8** contained three independent molecules that differed by the conformation of propyl substituents. Analogously, the crystal of compound **9** contained two independent molecules that differed by the orientation of the phenyl group. Our assumptions about the structure of these compounds, based on ^{1}H NMR spectral data, were in complete agreement with the X-ray diffraction analysis results for these crystals. Isomers **5** and **6**, **9** and **10** were formed in approximately equal ratios (according to the ^{1}H NMR data), with a small excess (3–5%) of compounds **6** and **9**.

The methyl group in π-electron-deficient heterocycles, which is linked to the carbon atom of the endocyclic imine group, had enhanced reactivity and readily underwent Knoevenagel condensation with aldehydes. The synthesis of 3-styrylquinoxalin-2(1*H*)-ones was achieved with such methods as fusion of the starting reagents or reaction in acetic anhydride. The first method with the reaction temperature reaching 180°C provided yields above 90% in the case of benzaldehyde and its halo and nitro derivatives,[16a] while in the case of 4-(dimethylamino)-benzaldehyde the reaction at 200°C allowed to achieve 85% yield.[16b] At the same time, fusion in the presence of piperidine allowed to decrease the temperature to 165°C, leading to the target product in 70% yield.[16c] The use of acetic anhydride as solvent provided 46% yield of the target product in the case of benzaldehyde and merely 12% yield in the case of 4-(dimethylamino)phenylbenz-aldehyde.[16d] The use of acetic anhydride with catalytic amounts of pyridine has been described for the synthesis of *trans*-arylquinoxalinonylethylenes, but the starting aldehydes in that case were 2-nitrobenzaldehyde and 5-chloro-2-nitro-benzaldehyde, instead of 4-(dimethylamino)benzaldehyde.[16e]

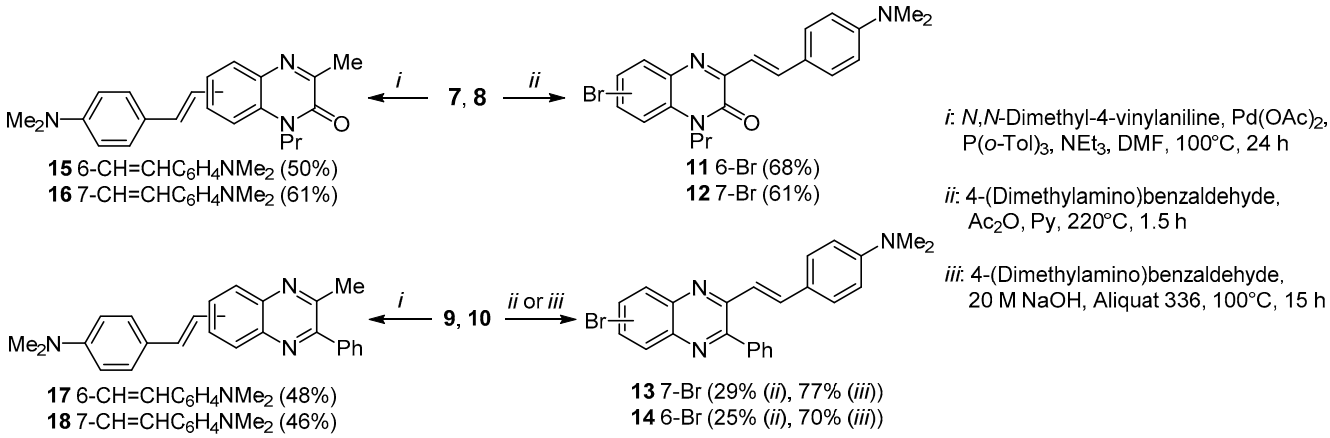
According to literature data, the replacement of benzaldehyde or nitrobenzaldehyde with the less reactive 4-(dimethylamino)benzaldehyde resulted in a lower yield of the target product. The probably diminished reactivity of methyl group in 6- and 7-bromo-3-methyl-1-propyl-quinoxalin-2-ones, caused by the presence of two electron-donating substituents, can lead to a further decrease in the yield of their reactions with 4-(dimethylamino)-benzaldehyde. Indeed, 4-(dimethylamino)benzaldehyde doesn't react with compound **8** at 200 and 165°C in the presence of piperidine, while the reaction according to the published method[16e] – heating of the starting compounds in acetic anhydride in the presence of pyridine, provided the target product **12** in 15% yield. In order to increase yields of compounds **11** and **12**, we performed the reaction of compounds **7** and **8** with 4-(dimethylamino)benzaldehyde under the following conditions: fusion at 225°C in open test tube in the presence of catalytic amounts of acetic anhydride and pyridine (Scheme 2). These experimental conditions allowed to increase the yields of compounds **11** and **12** up to 60–70%.

This experimental procedure was found to be ineffective for the synthesis of quinoxalines **13** and **14**. The formation of these compounds occurred with considerably lower yields, and further increase of temperature resulted in resinification of the reaction mixture. In a recent article,[17] a procedure was proposed for the condensation of methylazines with aldehydes upon heating in aqueous 20 M NaOH solution in the presence of Aliquat 336. This procedure was found to be effective also for the conden-sation of phenylquinoxalines **9**, **10** with 4-(dimethylamino) benzaldehyde, leading to the formation of compounds **13** and **14** in 77 and 70% yields, respectively (Scheme 2). It should be noted that the method described above was, in turn, less effective for the preparation of quinoxalinones **11** and **12** due to resinification and partial hydrolysis.

The introduction of 4-(dimethylamino)phenylethenyl moiety at position 6 or 7 of the quinoxaline ring system was achieved by using the Heck reaction between compounds **7**–**10** and 4-(dimethylamino)vinylbenzene, obtained by Wittig reaction from 4-(dimethylamino)phenyl-benzaldehyde and methyltriphenylphosphonium bromide.[18] The Heck reaction proceeded in DMF in the presence of $Pd(OAc)_2$, tri(*o*-tolyl)phosphine, and NEt_3 (Scheme 2).

(Dimethylamino)phenylethenylquinoxalines **11**–**18** were isolated as *trans*-isomers, as evidenced by the presence of two ^{1}H NMR doublet signals of the ethene protons with a spin-spin coupling constant of ~16 Hz. When changing from 3-dimethylaminophenylvinyl derivatives **11**–**14** to 6- and 7-dimethylaminophenylvinyl derivatives **15**–**18**, a hypsochromic shift of the UV absorption maximum was observed (see Experimental); the powder color was in the range from red (compounds **11**–**14**) to orange (compounds **16**–**18**) and yellow (compound **15**).

Scheme 2



Thus, we have proposed methods for the synthesis of various (*E*)-[4-(dimethylamino)phenyl]ethenylquinoxalines – precursors for new nonlinear optical chromophores, which showed high first hyperpolarizability values.

Experimental

IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra of compounds **9**, **15**–**17** were acquired on a Bruker Avance 600 instrument (600 and 150 MHz, respectively). ^{1}H and ^{13}C NMR spectra of the other compounds were acquired on a Bruker Avance 400 instrument (400 and 100 MHz, respectively). Chemical shifts were experimentally determined relative to the respective signals of deuterated solvents and are reported on δ scale. The solvents were: acetone-d_6 (2.05 and 29.8 ppm, respectively, compounds **15**, **16**) and $CDCl_3$ (7.26 and 77.0 ppm, respectively, the rest of the compounds). UV spectra were recorded on a PerkinElmer Lambda-35 UV/Vis spectrometer in CH_2Cl_2 solution. Mass spectra (MALDI TOF) were recorded on a Bruker Daltonics Ultraflex III mass spectrometer by using *p*-nitroaniline as matrix. Elemental analysis was performed on a Euro EA 3000 CHNS–analyzer, while halogens were determined according to the Schöniger method. Melting points were determined on a Boetius hot stage. The reaction progress and the purity of the obtained compounds were controlled by TLC on Sorbfil UV-254 plates with visualization under UV light.

Preparation of 6-bromo-3-methylquinoxalin-2(1*H*)-one (5) and 7-bromo-3-methylquinoxalin-2(1*H*)-one (6). A solution of ethyl pyruvate (3.1 g, 27 mmol) in EtOH (5 ml) was added to a solution of 4-bromo-1,2-diaminobenzene (5.0 g, 27 mmol) in EtOH (30 ml). The reaction mixture was stirred for 6 h (precipitate formed after 5 min) and left overnight. The crystals that formed were filtered off and washed with EtOH. The isolated product (5.20 g) was a mixture of isomers. The filtrate was evaporated, and the residue was washed with EtOH, resulting in 0.53 g of isomeric mixture. The precipitates were combined, the obtained mixture of isomers was used without separation in the next reaction.

Preparation of 6-bromo-3-methyl-1-propylquinoxalin-2(1*H*)-one (7) and 7-bromo-3-methyl-1-propylquinoxalin-2(1*H*)-one (8). A mixture of compounds **5** and **6** (5.4 g, 23 mmol) and solid potassium hydroxide (2.5 g, 45 mmol) were added to dioxane (30 ml). The reaction mixture was stirred for 5 min at 100°C, cooled, treated with a solution of PrI (4.6 g, 27 mmol) in dioxane (5 ml), stirred for 6 h at 100°C, cooled, poured into water, and extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous $MgSO_4$, and CH_2Cl_2 was removed at reduced pressure. The residue was separated by column chromatography (eluting with a gradient from petroleum ether to a 3:1 mixture of petroleum ether – EtOAc) and purified by recrystallization from petroleum ether. The chromatographic separation first yielded a mixture of compounds **7** and **8**, enriched in isomer **8**, which was separated by several recrystallization steps. Isomer **7** was isolated at the end of the chromatographic separation.

Isomer **7**. Yield 2.1 g (31%), white powder, mp 102–104°C. R_f 0.43 (petroleum ether – EtOAc, 4:1). IR spectrum, ν, cm^{-1}: 3280, 3232, 3083, 2961, 2931, 2874, 1643, 1592, 1558, 1478, 1464, 1420, 1381, 1337, 1313, 1281, 1244, 1190, 1149, 1120, 1021, 897, 878, 815. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (3H, t, *J* = 7.4, CH_3); 1.67–1.75 (2H, m, CH_2); 2.51 (3H, s, CH_3); 4.10 (2H, t, *J* = 7.8, NCH_2); 7.08 (1H, d, *J* = 8.9, H-8); 7.49 (1H, dd, *J* = 2.1, *J* = 8.9, H-7); 7.83 (1H, d, *J* = 2.1, H-5). ^{13}C NMR spectrum, δ, ppm: 11.8; 20.6; 21.5; 43.8; 115.0; 115.6; 115.7; 132.0; 132.1; 133.7; 154.4; 159.8. Found, %: C 51.13; H 4.53; N 9.99; Br 28.79. $C_{12}H_{13}BrN_2O$. Calculated, %: C 51.26; H 4.66; N 9.96; Br 28.42.

Isomer **8**. Yield 3.0 g (47%), white powder, mp 96–98°C. R_f 0.43 (petroleum ether – EtOAc, 4:1). IR spectrum, ν, cm^{-1}: 3295, 3245, 3110, 3024, 2967, 2936, 2876, 1653, 1596, 1557, 1481, 1469, 1453, 1437, 1391, 1371, 1349, 1335, 1304, 1286, 1226, 1192, 1119, 1086, 1062, 1016, 986, 947. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 (3H, t, *J* = 7.4, CH_3); 1.72–1.82 (2H, m, CH_2); 2.57 (3H, s, CH_3); 4.15 (2H, t, *J* = 7.8, NCH_2); 7.39–7.44 (2H, m, H-6,8); 7.65 (1H, d, *J* = 8.9, H-5). ^{13}C NMR spectrum, δ, ppm: 11.3; 20.5; 21.5; 43.9; 116.6; 123.4; 126.6; 130.9; 131.7; 133.6; 154.5; 158.8. Found, %: C 51.17; H 4.58; N 9.89; Br 28.61. $C_{12}H_{13}BrN_2O$. Calculated, %: C 51.26; H 4.66; N 9.96; Br 28.42.

Preparation of 6-bromo-3-methyl-2-phenylquinoxaline (9) and 6-bromo-2-methyl-3-phenylquinoxaline

(10). A solution of 1-phenylpropane-1,2-dione (7.9 g, 53 mmol) was added to a solution of 4-bromo-1,2-benzenediamine (10.0 g, 54 mmol) in EtOH (10 ml), the mixture was stirred for 6 h (precipitate formed after 5 min) and left overnight. The crystals that formed were filtered off and washed with EtOH. The product (14.1 g) was a mixture of isomers. The filtrate was evaporated, giving a mixture of isomers (1.3 g). The precipitates were combined, the isomers were separated by column chromatography (eluting with a gradient from petroleum ether to a 30:1 mixture of petroleum ether – EtOAc) and then by recrystallization from petroleum ether.

Isomer **9**. Yield 5.5 g (35%), white powder, mp 93–95°C (mp 100–102°C[24]). R_f 0.65 (petroleum ether – EtOAc, 4:1).

Isomer **10**. Yield 5.9 g (37%), white powder, mp 105–107°C (mp 100–102°C[24]). R_f 0.52.

Preparation of bromo-3-[(*E*)-4-(dimethylamino)-phenylethenyl]quinoxalines 11–14 (General method). Method I. Methylquinoxaline **7**–**10** (1 mmol) and 4-(dimethylamino)benzaldehyde (1 mmol) were mixed in an open test tube, then Ac_2O (2 drops) and pyridine (1 drop) were added. The reaction mixture was fused for 1.5 h at 220°C, cooled, and purified by silica gel column chromatography (eluent petroleum ether – EtOAc, gradient from 100:1 to 20:1).

Method II. A mixture of methylquinoxaline **9**, **10** (1 mmol) and 4-(dimethylamino)benzaldehyde (1 mmol) was treated with 20 M NaOH (15 ml) and Aliquat 336 (1 drop). The reaction mixture was heated for 15 h at 100°C, cooled, the solid precipitate was washed with water, dried, and purified by silica gel column chromatography (eluent petroleum ether – EtOAc, gradient from 100:1 to 20:1).

6-Bromo-3-{(*E*)-[4-(dimethylamino)phenyl]ethenyl}-1-propylquinoxalin-2(1*H*)-one (11) was obtained according to method I. Yield 0.28 g (68%), red powder, mp 170–172°C. R_f 0.44 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 464. IR spectrum, ν, cm^{-1}: 2928, 2799, 1652, 1598, 1565, 1514, 1475, 1429, 1359, 1312, 1248, 1223, 1179, 1165, 1113, 1094, 977, 943, 919, 866, 800, 782. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.08 (3H, t, *J* = 7.5, CH_3); 1.77–1.87 (2H, m, CH_2); 3.06 (6H, s, $2CH_3$); 4.23 (2H, t, *J* = 7.7, NCH_2); 6.73 (2H, d, *J* = 8.8, H Ar); 7.14 (1H, d, *J* = 8.9, H-8); 7.53 (1H, dd, *J* = 2.2, *J* = 8.9, H-7); 7.57 (1H, d, *J* = 16.0, –CH=); 7.61 (2H, d, *J* = 8.8, H Ar); 8.00 (1H, d, *J* = 2.2, H-5); 8.10 (1H, d, *J* = 16.0, –CH=). ^{13}C NMR spectrum, δ, ppm: 11.4; 20.6; 40.2; 44.0; 112.0; 114.9; 116.0; 116.7; 124.5; 129.8; 131.0; 131.1; 131.9; 135.0; 139.7; 151.4; 154.1; 154.7. Mass spectrum, *m*/*z* (I_{rel}, %): 412 [M(^{79}Br)+H]$^+$, 414 [M(^{81}Br)+H]$^+$.

7-Bromo-3-{(*E*)-[4-(dimethylamino)phenyl]ethenyl}-1-propylquinoxalin-2(1*H*)-one (12) was obtained according to the method I. Yield 0.25 g (61%), red powder, mp 176–177°C. R_f 0.46 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 462. IR spectrum, ν, cm^{-1}: 2961, 2877, 2804, 1652, 1595, 1561, 1526, 1508, 1475, 1434, 1365, 1326, 1295, 1228, 1165, 1109, 1077, 1035, 1001, 979, 947, 817. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 (3H, t, *J* = 7.4, CH_3); 1.75–1.85 (2H, m, CH_2); 3.02 (6H, s, $2CH_3$); 4.19 (2H, t, *J* = 7.8, NCH_2); 6.70 (2H, d, *J* = 8.8, H Ar), 7.38 (1H, d, *J* = 1.9, H-8); 7.39 (1H, dd, *J* = 8.3, *J* = 1.9, H-6); 7.53 (1H, d, *J* = 16.0, –CH=); 7.57 (2H, d, *J* = 8.8, H Ar); 7.66 (1H, d, *J* = 8.3, H-5); 8.07 (1H, d, *J* = 16.0, –CH=). ^{13}C NMR spectrum, δ, ppm: 11.4; 20.6; 40.2; 44.0; 112.0; 116.4; 116.8; 122.4; 124.6; 126.7; 130.0; 130.8; 132.8; 132.9; 139.3; 151.3; 153.2; 154.7. Mass spectrum, *m*/*z* (I_{rel}, %): 412 [M(^{79}Br)+H]$^+$, 414 [M(^{81}Br)+H]$^+$.

6-Bromo-3{(*E*)-[4-(dimethylamino)phenyl]ethenyl}-2-phenylquinoxaline (13). Yield 0.13 g (29%) (method I), 0.33 g (77%) (method II), red powder, mp 165–167°C. R_f 0.67 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 454. IR spectrum, ν, cm^{-1}: 2893, 2805, 1605, 1519, 1431, 1392, 1363, 1328, 1273, 1236, 1183, 1149, 1128, 1053, 1013, 974, 944, 873, 805, 697. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.00 (6H, s, $2CH_3$); 6.68 (2H, d, *J* = 8.9, H Ar); 7.15 (1H, d, *J* = 15.5, –CH=); 7.42 (2H, d, *J* = 8.8, H Ar); 7.52–7.58 (3H, m, H Ph); 7.69–7.75 (2H, m, H Ph, H-7); 7.92 (1H, d, *J* = 8.9, H-8); 8.01 (1H, d, *J* = 15.5, –CH=); 8.27 (1H, d, *J* = 2.1, H-5). ^{13}C NMR spectrum, δ, ppm: 40.2; 112.0; 119.1; 123.6; 124.5; 128.6; 129.1; 129.2; 129.6; 130.4; 130.9; 132.1; 138.0; 138.5; 139.6; 142.4; 150.6; 151.1; 154.5. Mass spectrum, *m*/*z*: 430 [M(^{79}Br)+H]$^+$, 432 [M(^{81}Br)+H]$^+$.

7-Bromo-3-{(*E*)-[4-(dimethylamino)phenyl]ethenyl}-2-phenylquinoxaline (14). Yield 25% (method I), 70% (method II), red powder, mp 163–165°C. R_f 0.70 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 456. IR spectrum, ν, cm^{-1}: 3059, 2888, 2797, 1600, 1520, 1433, 1391, 1361, 1330, 1303, 1234, 1185, 1149, 1121, 1051, 1014, 969, 946, 935, 878, 827, 788, 767. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.00 (6H, s, $2CH_3$); 6.68 (2H, d, *J* = 8.8, H Ar); 7.15 (1H, d, *J* = 15.5, –CH=); 7.42 (2H, d, *J* = 8.8, H Ar); 7.51–7.58 (3H, m, H Ph); 7.71–7.75 (2H, m, H Ph); 7.78 (1H, dd, *J* = 8.9, *J* = 2.2, H-6); 7.94 (1H, d, *J* = 8.9, H-5); 8.01 (1H, d, *J* = 15.5, –CH=); 8.24 (1H, d, *J* = 2.2, H-8). ^{13}C NMR spectrum, δ, ppm: 40.2; 112.2; 119.3; 122.3; 124.6; 128.6; 129.1; 129.2; 129.6; 129.9; 131.4; 133.2; 137.6; 138.4; 140.6; 141.4; 150.2; 151.1; 154.9. Mass spectrum, *m*/*z*: 430 [M(^{79}Br)+H]$^+$, 432 [M(^{81}Br)+H]$^+$.

Preparation of (*E*)-[4-(dimethylamino)phenyl]ethenyl-3-methylquinoxalines 15–18 (General method). A mixture of the appropriate bromoquinoxaline **7–10** (1 mmol), *N*,*N*-dimethyl-4-vinylaniline (0.15 g, 1 mmol), tri(*o*-tolyl)-phosphine (3 mg, 0.01 mmol), $Pd(OAc)_2$ (1 mg, 0.005 mmol), Et_3N (25 mg, 0.25 mmol), and anhydrous DMF (1 ml) was stirred for 24 h at 100°C. The reaction mixture was cooled, poured into water, and extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, filtered, the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent petroleum ether – EtOAc, gradient from 100:1 to 10:1).

6-{(*E*)-[4-(Dimethylamino)phenyl]ethenyl}-3-methyl-1-propylquinoxalin-2(1*H*)-one (15). Yield 0.17 g (50%), yellow powder, mp 160–162°C. R_f 0.22 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 363. IR spectrum, ν, cm^{-1}: 2961, 2875, 2801, 1659, 1607, 1558, 1522, 1495, 1443, 1351, 1285, 1250, 1219, 1195, 1162, 1120, 1061, 1002, 964, 896, 854, 817. ^{1}H NMR spectrum, δ, ppm (*J*, Hz):

1.03 (3H, t, J = 7.4, CH_3); 1.57–1.63 (2H, m, CH_2); 2.48 (3H, s, CH_3); 3.00 (6H, s, $2CH_3$); 4.23 (2H, t, J = 7.7, NCH_2); 6.76 (2H, d, J = 8.5, H Ar); 7.06 (1H, d, J = 16.2, –CH=); 7.20 (1H, d, J = 16.2, –CH=); 7.47 (2H, d, J = 8.5, H Ar); 7.48 (1H, d, J = 8.1, H-8); 7.74 (1H, dd, J = 8.3, J = 1.4, H-7); 7.84 (1H, d, J = 1.4, H-5). ^{13}C NMR spectrum, δ, ppm (J, Hz): 11.5; 21.4; 21.6; 40.5; 44.1; 113.2; 115.2; 123.3; 126.4; 127.1; 128.0; 128.5; 130.0; 132.3; 134.0; 134.6; 151.4; 155.2; 159.1. Mass spectrum *m*/*z*: 348 $[M+H]^+$.

7-{(*E*)-[4-(Dimethylamino)phenyl]ethenyl}-3-methyl-1-propylquinoxalin-2(1*H*)-one (16). Yield 0.21 g (61%), orange powder, mp 164–165°C. R_f 0.24 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 402. IR spectrum, ν, cm^{-1}: 3019, 2959, 2929, 2874, 2802, 1652, 1599, 1557, 1522, 1495, 1445, 1355, 1285, 1219, 1190, 1164, 1117, 1062, 1002, 962, 948, 892, 816. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.03 (3H, t, J = 7.5, CH_3); 1.76–1.82 (2H, m, CH_2); 2.44 (3H, s, CH_3); 2.99 (6H, s, $2CH_3$); 4.29 (2H, t, J = 7.7, NCH_2); 6.75 (2H, d, J = 8.8, H Ar); 7.13 (1H, d, J = 16.3, –CH=); 7.30 (1H, d, J = 16.3, –CH=); 7.47 (2H, d, J = 8.8, H Ar); 7.55 (1H, dd, J = 8.3, J = 1.4, H-6); 7.56 (1H, s, H-8); 7.66 (1H, d, J = 8.7, H-5). ^{13}C NMR spectrum, δ, ppm: 11.6; 21.4; 21.5; 40.4; 43.9; 112.3; 113.2; 121.2; 126.0; 126.9; 128.8; 130.4; 132.1; 132.7; 134.1; 140.9; 151.6; 155.6; 157.4. Mass spectrum, *m*/*z*: 348 $[M+H]^+$.

6-{(*E*)-[4-(Dimethylamino)phenyl]ethenyl}-3-methyl-2-phenylquinoxaline (17). Yield 0.18 g (48%), orange powder, mp 155–157°C. R_f 0.33 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 414. IR spectrum, ν, cm^{-1}: 3060, 3017, 2923, 2850, 2803, 1601, 1555, 1521, 1486, 1443, 1347, 1271, 1229, 1180, 1166, 1061, 1006, 995, 949, 911, 887, 826, 800. ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.77 (3H, s, CH_3); 3.01 (6H, s, $2CH_3$); 6.73 (2H, d, J = 8.6, H Ar); 7.10 (1H, d, J = 16.1, –CH=); 7.27 (1H, d, J = 16.1, –CH=); 7.45–7.50 (3H, m, *o*,*p*-H Ph); 7.53 (2H, dd, J = 7.4, J = 7.2, *m*-H Ph); 7.66 (2H, d, J = 8.6, H Ar); 7.92 (1H, d, J = 8.7, H-7); 8.00 (1H, s, H-5); 8.03 (1H, d, J = 8.7, H-8). ^{13}C NMR spectrum, δ, ppm: 24.4; 40.4; 112.3; 123.2; 124.7; 125.2; 127.3; 128.1; 128.5; 128.9; 129.0; 129.2; 131.6; 139.3; 140.0; 140.5; 141.9; 150.6; 152.7; 153.7. Mass spectrum, *m*/*z*: 366 $[MH]^+$.

7-{(*E*)-[4-(Dimethylamino)phenyl]ethenyl}-3-methyl-2-phenylquinoxaline (18). Yield 0.17 g (46%), orange powder, mp 160–163°C. R_f 0.41 (petroleum ether – EtOAc, 4:1). UV spectrum, λ_{max}, nm: 367, 407. IR spectrum, ν, cm^{-1}: 2929, 2874, 2802, 1601, 1554, 1522, 1488, 1443, 1425, 1348, 1224, 1188, 1168, 1132, 1062, 1005, 996, 958, 949, 826, 808. ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.76 (3H, s, CH_3); 3.01 (6H, s, $2CH_3$); 6.73 (2H, d, J = 8.8, H Ar); 7.09 (1H, d, J = 16.2, –CH=); 7.25 (1H, d, J = 16.2, –CH=); 7.47 (2H, d, J = 8.8, H Ar); 7.48–7.58 (3H, m, *m*,*p*-H Ph); 7.66 (2H, dd, J = 1.5, J = 8.2, *o*-H Ph); 7.92–8.02 (2H, m, H-5,6); 8.07 (1H, d, J = 1.4, H-8). ^{13}C NMR spectrum, δ, ppm: 24.2; 40.4; 112.4; 123.2; 125.2; 125.6; 127.9; 128.0; 128.3; 128.5; 128.9; 129.0; 131.3; 139.3; 139.4; 140.7; 141.6; 150.5; 151.3; 155.1. Mass spectrum, *m*/*z*: 366 $[M+H]^+$.

X-ray diffraction analysis of compounds 7–10 was performed on a Bruker AXS SMART APEX II diffractometer using MoKα radiation (λ 0.71073 Å) at room temperature. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization of compounds from hexane. Compound **7**: rhombic syngony, space group *Pca2*. Compound **8**: monoclinic syngony, space group $P2_1/c$. Compound **9**: monoclinic syngony, space group $C2/c$. Compound **10**: rhombic syngony, space group *Pbca*. The following software was used: APEX2[19] (data acquisition), SAINT[20] (data processing), SADABS Version 2.10[21] (accounting for absorption), SHELXS[22] (solving of structures), SHELXL[22] (refinement of structures by the least squares method). The structures were visualized by using the Mercury 3.0 program.[23] The positions and temperature parameters of non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atom positions were calculated geometrically and refined according to the "rider" model. The complete X-ray diffraction data sets for compounds **7**–**10** were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1523877, CCDC 1523876, CCDC 1523879, CCDC 1523878, respectively).

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