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

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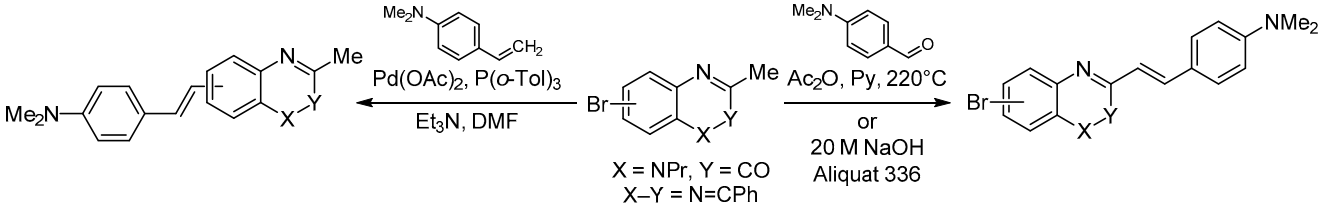

Methods are presented for the preparation of isomeric (*E*)-3-, (*E*)-6-, (*E*)-7-[4-(dimethylamino)phenylethenyl]quinoxalin-2-ones and 2-phenylquinoxalines – compounds of "donor–π-bridge" type, which serve as precursors for new nonlinear optical chromophores with potentially high first hyperpolarizability 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

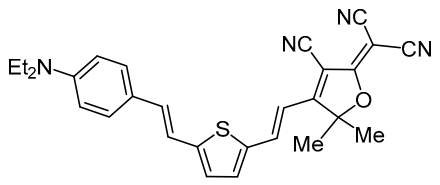

Figure 1. The structure of FTC chromophore.

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