

## New Bifunctional Luminophors. Synthesis of (*p*-*N,N*-Dimethylaminophenyl)cyanoperylene

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**Abstract**—Synthesis was developed of perylene series luminophors containing in the perylene core simultaneously a cyano group and *N,N*-dimethylaniline residue.

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*N,N*-Dimethylaniline (**I**) is known to efficiently quench the fluorescence of perylene (**II**) and of a number of its derivatives by the mechanism of electron transfer [1, 2]. Yet the intramolecular electron transfer in systems containing a residue of arylamine **I** and the framework of arene **II** was not investigated till recently. This opportunity appeared after our successful synthesis of substituted perylenes containing in the molecule *para*-*N,N*-dimethylaminophenyl group linked directly or through a carbon bridge to the framework of compound **II** [3]. We described in [3] the spectral luminescence properties of compounds obtained and presented the findings proving the possibility of the intramolecular electron transfer in these systems.

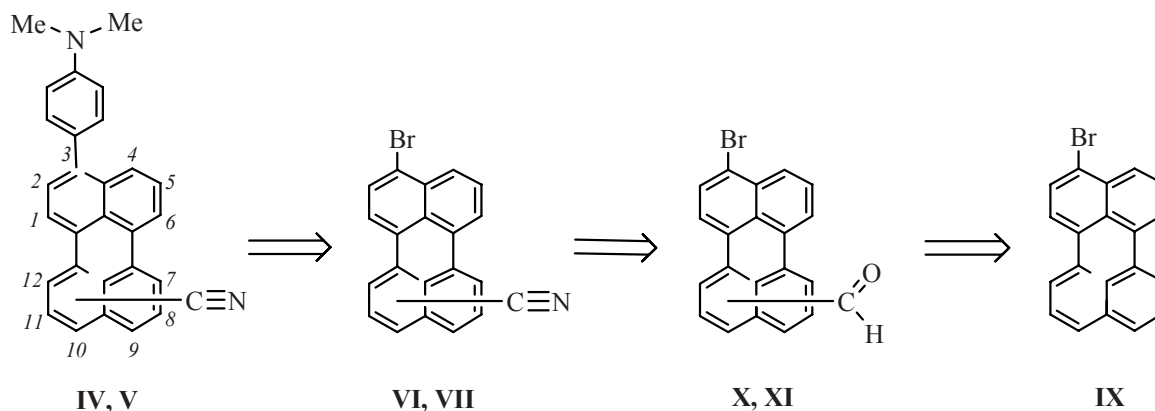
It was found lately [1, 2] that the quenching of the fluorescence of 3-cyanoperylene (**III**) dissolved in *N,N*-dimethylaniline (**I**) occurred abnormally fast [compared

to perylene (**II**) and a series of its derivatives]. The more detailed understanding of this phenomenon requires the study of the effect of the cyano substituent on the intramolecular electron transfer. To this end we attempted to synthesize a molecule containing a *para*-*N,N*-dimethylaminophenyl substituent directly at the framework of 3-cyanoperylene (**III**).

The most accessible from the synthetic viewpoint compounds of the like structure are 3-(*p*-*N,N*-dimethylaminophenyl)-10-cyanoperylene (**IV**) or its isomer 3-(*p*-*N,N*-dimethylaminophenyl)-9-cyanoperylene (**V**) (Scheme 1).

It was presumed that arylcyanoperylene **IV** or **V** would be obtained by a cross-coupling of 3-bromo-10-cyano- (**VI**) or 3-bromo-9-cyanoperylene (**VII**) with 3-(*p*-*N,N*-dimethylaminophenyl)magnesium bromide (**VIII**) [4] in the presence of a catalyst Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (Kumada

Scheme 1.



reaction [5]). We formerly demonstrated the suitability of this reaction for introducing the *p*-*N,N*-dimethylaminophenyl group into the perylene framework [3]. The preparation of arenes by this method with the conservation of a cyano group in the aromatic ring was also previously described [6].

No data were published on the synthesis of bromo-(cyano)perylene **VI** and **VII**. We presumed that bromo-(cyano)perylene **VI** and **VII** may be prepared from available 3-bromoperylene (**IX**) [7] by formylation in keeping with the procedure of Vilsmeier–Haack followed by conversion of the aldehyde group into a cyano group (Scheme 1). Although the formylation of bromoperylene **IX** was not studied before, its possibility and direction could be forecasted based on the chemical properties of unsubstituted perylene (**II**). Actually, perylene (**II**) is readily involved into the electrophilic substitution reactions [8], including the formylation [9], giving products of mono- and polysubstitution mainly in the *peri*-position. In the formation of disubstituted perylene the second substituent enters mainly into the *peri*-position of the unsubstituted naphthalene fragment of the molecule, and as a rule two *peri*-isomeric compounds are obtained in comparable quantity [10]. The attempts at separation of isomer mixtures of 3,10- and 3,9-disubstituted perylene of various structure are commonly unsuccessful [11, 12]. It was expectable that the formylation product of 3-bromoperylene **IX** would also be an inseparable mixture of 3-bromo-10-formyl- (**X**) and 3-bromo-9-formylperylene (**XI**). We planned in this case to carry out the cross-coupling of *p*-*N,N*-dimethylaminophenylmagnesium bromide (**VIII**) with the isomers mixture **VI** and **VII** (Scheme 1).

We obtained key 3-bromoperylene (**IX**) by a selective bromination of perylene (**II**) with *N*-bromosuccinimide in DMF [7, 13]. It was found that haloarene **IX** treated with *N*-methylformanilide (**XII**) in the presence of POCl<sub>3</sub> in chlorobenzene was converted into a chromatographically individual product. The rate of this product formation became suitable only at heating and at an excess of the formylating agent. At 100°C and the molar ratio of the reagents **IX**, **XII**, POCl<sub>3</sub>, and solvent equal 1:6.4:6.4:7.5 the materially complete consumption of compound **IX** in the reaction mixture was attained within 7 h. The reaction was accompanied by a considerable tarring.

In the <sup>1</sup>H NMR spectrum of the formylation product characteristic signals of the aldehyde proton are present at ~10.3 ppm, and the signal of the proton in the perylene core located in the *peri*-position to this substituent, at

~9.2 ppm. Therewith the aldehyde proton appears like two close singlets, and the signal of the *peri*-aromatic proton, as two superimposed doublets of the close chemical shifts. The ratio of intensity of two signals is ~3:1. These findings show that the formylation of perylene **IX** yields a mixture of perylenecarboxaldehydes. A similar abnormally strong downfield shift of the signal from the *peri*-aromatic proton (~9.2 ppm) compared to the other perylene protons (7.45–8.40 ppm) was also observed in the spectra of perylene-3-carboxaldehyde (**XIII**) [14] and of 1-formylnaphthalene [15]. It is striking that in the <sup>1</sup>H NMR spectrum of 2-formylnaphthalene the signals of all aromatic protons appeared in the region 7.52–8.30 ppm [15]. Therefore the NMR data show that the bromoperylene **IX** formylation is *peri*-directed into the unsubstituted naphthalene fragment resulting in the formation of two perylenecarboxaldehydes (possibly **X** and **XI**).

However the elemental analysis of the reaction product revealed the reduced bromine content, and in the high-resolution mass spectrum alongside the peaks of two possible Br-isotope molecular ions of the target bromo(formyl)perylene (*M* 358 and 360) a strong signal appeared with *M* 280 corresponding by the molecular mass to perylene-3-carboxaldehyde (**XIII**). Apparently the formylation of 3-bromoperylene (**IX**) is accompanied by a partial dehydrobromination to provide a mixture of bromoperylenecarboxaldehyde (**X** and/or **XI**) and perylenecarboxaldehyde **XIII** in a molar ratio ~3:1 (Scheme 2).

Regrettably, we failed to preparatively separate the presumed mixture into individual components and also to analyze it by GC-MS procedure. Therefore we decided to convert further the aldehyde groups of the mixture into a cyano group and to examine the products of this transformation.

From the numerous known ways of converting the aldehyde group into the cyano group we chose a simple one-stage preparative procedure of treating the corresponding aldehyde with NH<sub>2</sub>OH·HCl in ethanol in the presence of concn. HCl at heating [16]. This method was developed for aliphatic nitriles [16]. The reaction with NH<sub>2</sub>OH·HCl was carried out in a mixture of ethanol, dioxane, and concn. HCl at a volume ratio 5:5:1. At the initial concentrations of perylenecarboxaldehydes and NH<sub>2</sub>OH·HCl ~21.6 and ~300 mmol l<sup>-1</sup> respectively the complete conversion of aldehydes into a chromatographically individual product was attained by heating the reaction mixture on a bath at ~110°C for ~16 h. The final

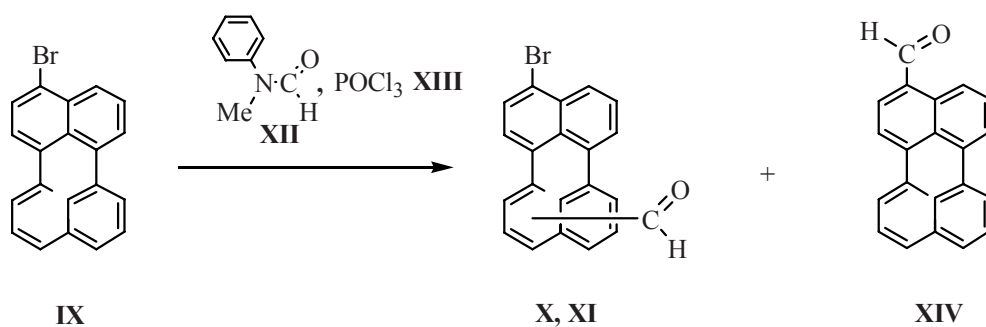
product, like its precursor, aldehydes mixture, was inseparable at the column chromatography on various adsorbents. Still the GC-MS analysis of the compound obtained demonstrated the presence therein of two main components of different molecular masses that were cleanly separated in the course of the analysis and appeared as two narrow peaks with the area ratio ~3:1. The component corresponding to the stronger signal proved to be cyano-substituted 3-bromoperylene, the other compound was 3-cyanoperylene (**III**) (Scheme 3).

In the mass spectrum of bromo(cyano)perylene a characteristic doublet signal is present of a bromosubstituted isotope molecular ions of masses  $M_{355}$  and  $M_{357}$

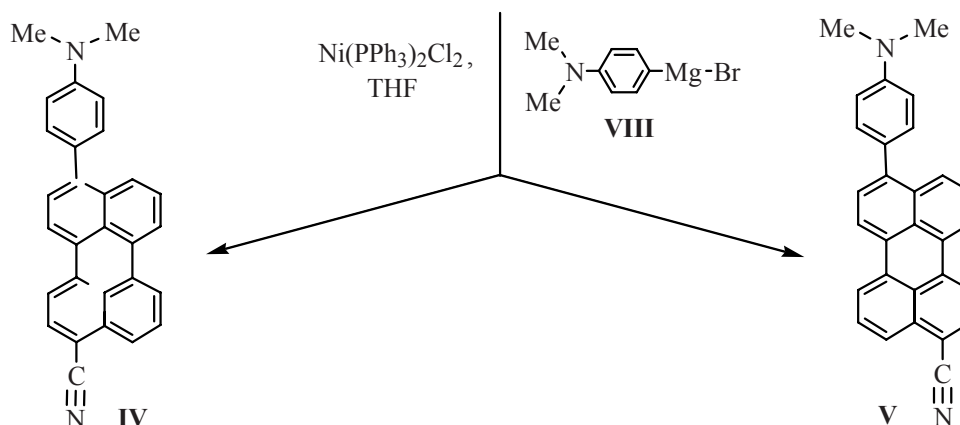
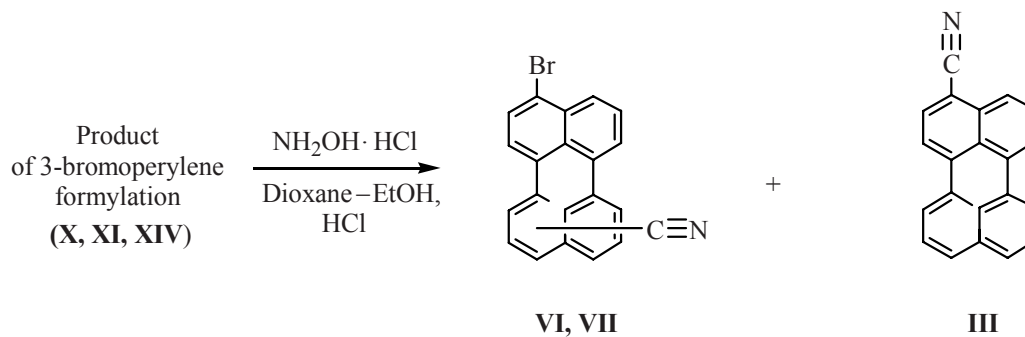
whereas in the spectrum of cyanoperylene (**III**) a singlet signal of the molecular ion appears with the mass  $M_{277}$  [17]. The analysis performed failed to establish the isomeric composition of the cyanoderivative of bromoperylene (**VI** and/or **VII**).

Thus actually under the conditions of Vilsmeier–Haack reaction 3-bromoperylene (**IX**) yielded the expected *peri*-formyl derivative of 3-bromoperylene, but the process was complicated by the formation of perylene-3-carboxaldehyde (**XIII**). The overall yield of perylene-carboxaldehydes amounts to ~67% with respect to initial 3-bromoperylene (**IX**). The  $^1\text{H}$  NMR spectrum of the reaction product unfortunately does not allow to

Scheme 2.



Scheme 3.



estimate the isomeric composition of the bromocyanoperylene.

Inasmuch as we failed to obtain in a pure state the *peri*-cyanoderivative of the 3-bromoperylene with a known isomeric composition we used in the cross-coupling reaction the mixture of bromocyano- and 3-cyanoperylene. We hoped that thus synthesized *peri*-(*p*-*N,N*-dimethylaminophenyl)ciano derivatives of perylene would be easily separated from the products mixture by chromatography and, in particular, would be separated from the cyanoperylene (**III**) impurity.

Actually, under the conditions of preparation of 3-(*p*-*N,N*-dimethylaminophenyl)perylene [3] by treating with excess *p*-*N,N*-dimethylaminophenylmagnesium bromide (**VIII**) in the presence of Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> in THF at ~65°C we succeeded to isolate from the mixture of cyano derivatives of 3-bromoperylene and perylene (reaction time 35 min) the expected aminoarylcyano derivative of perylene (Scheme 3). The reaction involved the formation of quite a number of side products. The yield of the target product after the chromatographic purification on silica gel and the recrystallization from hexane–toluene mixture was ~15%. The compound obtained was inseparable both by TLC and column chromatography. The chemical composition of the (aminoaryl)cyanoperylene was proved by the results of high resolution mass spectrometry and by <sup>1</sup>H NMR and IR spectra. Its mass spectrum contains a strong peak of the molecular ion of the mass *M* 396. In the IR spectrum of the (aminoaryl)cyanoperylene a strong absorption band of cyano group appears at 2230 cm<sup>-1</sup>, and in the <sup>1</sup>H NMR spectrum a characteristic singlet of protons from the dimethylamino group is present at 3.06 ppm and also the signals of all 14 aromatic protons. It is difficult to estimate reliably the isomeric composition of the product based on the <sup>1</sup>H NMR spectrum. However the presence in the spectrum of broadened doublet signals from individual protons of the perylene framework apparently indicates the existence in the compound synthesized of a mixture of two inseparable isomers, 3-(*p*-*N,N*-dimethylaminophenyl)-10-cyanoperylene (**IV**) and 3-(*p*-*N,N*-dimethylaminophenyl)-9-cyanoperylene (**V**) in a molar ratio ~1:1.

Hence we accomplished for the first time a synthesis of difficultly available perylene derivative containing a *p*-*N,N*-dimethylaminophenyl substituent and a cyano group attached to the perylene framework. The formylation of 3-bromoperylene by Vilsmeier–Haack was performed for the first time, and the potential value of this reaction for the synthesis of previously unknown

perylene derivatives was demonstrated. At present the team of Professor Vauthey is studying the fluorescence dynamics on the obtained (*p*-*N,N*-dimethylaminophenyl)ciano derivative of perylene.

## EXPERIMENTAL

<sup>1</sup>H NMR spectra of compounds synthesized were registered on a spectrometer Bruker DPX-200 in CDCl<sub>3</sub> at room temperature. High resolution mass spectrometry and GC-MS analyses were performed on spectrometers Finnigan MAT-8200 and HP 6890N/5973 respectively. IR spectra were recorded on a spectrophotometer Bruker Vector 22 from solutions in CHCl<sub>3</sub>. The reaction progress was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates, spots visualized under UV radiation, eluents benzene or its mixture with hexane.

3-Bromoperylene (**IX**) [7] was formylated by procedure [9]. The mixture of 3-(*p*-*N,N*-dimethylaminophenyl)-10-cyano- and 3-(*p*-*N,N*-dimethylaminophenyl)-9-cyanoperylene (**IV**), (**V**) was synthesized by Kumada reaction [5] along the procedure we had previously described for preparation of 3-(*p*-*N,N*-dimethylaminophenyl)perylene [3].

**Mixture of 3-bromo-10-cyano- and 3-bromo-9-cyanoperylene (**VI**, **VII**).** Mass spectrum, *m/z* (*I*<sub>rel.</sub>, %): 357 [*M*]<sup>+</sup> (95), 355 [*M*]<sup>+</sup> (100), 275 (75), 248 (11), 178 (26), 137 (34), 124 (81), 111 (11).

**3-Cyanoperylene (**III**)** [9]. Mass spectrum, *m/z* (*I*<sub>rel.</sub>, %): 277 [*M*]<sup>+</sup> (100), 248 (5), 138 (21), 124 (22), 112 (6).

**Mixture of 3-(*p*-*N,N*-dimethylaminophenyl)-10-cyano- and 3-(*p*-*N,N*-dimethylaminophenyl)-9-cyanoperylene (**IV**), (**V**).** mp 253–255°C (from the mixture of toluene and hexane). IR spectrum, ν, cm<sup>-1</sup>: 2230 (C≡N). <sup>1</sup>H NMR spectrum, δ, ppm: 3.06 s (6H, NMe<sub>2</sub>), 6.87 d (2H, H<sub>Ph</sub><sup>m</sup>), 7.36–7.54 m (4H), 7.61–7.73 m (1H), 7.86 d (1H), 7.98 br.d (1H), 8.07 br.d (1H), 8.17 br.d (1H), 8.22–8.37 m (3H). Mass spectrum, *m/z* (*I*<sub>rel.</sub>, %): 396.1 [*M*]<sup>+</sup> (100), 380.1 (16.60), 351.1 (44.46), 197.6 (17.42), 175.5 (29.49), 162.0 (21.53), 148.0 (6.64), 91.1 (7.19). Found *M* 396.16188. C<sub>29</sub>H<sub>20</sub>N<sub>2</sub>. Calculated *M* 396.16264.

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