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Syntheses of chiral fused 4,5-diazafluorene–bis(nopinane) derivatives

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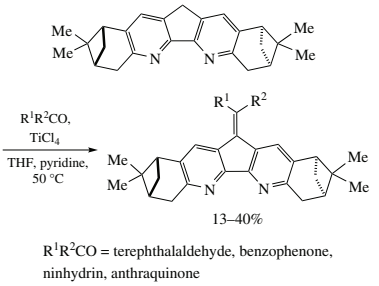
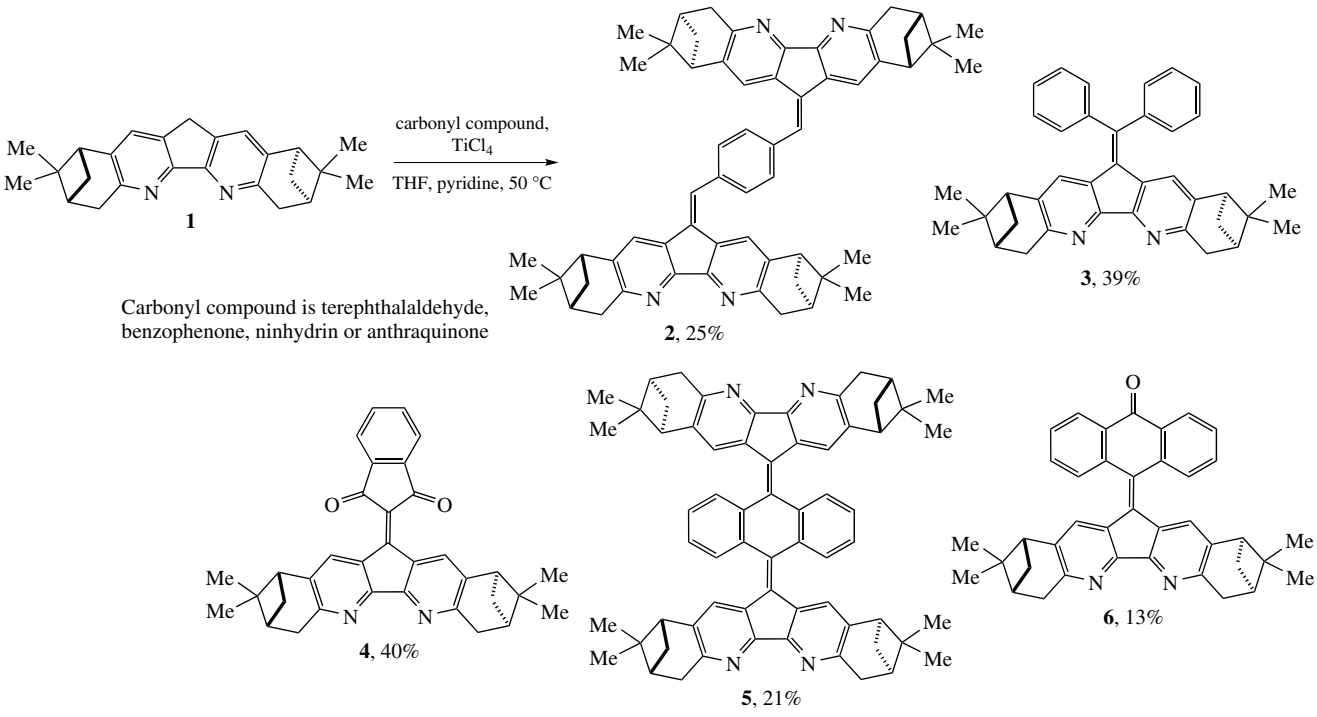
Reaction of fused 4,5-diazafluorene–bis(nopinane) with terephthalaldehyde, benzophenone, ninhydrin or anthraquinone in THF in the presence of $TiCl_4$ and pyridine results in a formation of new chiral condensation products, which exhibit solvatochromism and pleochroism. Crystal structure of the key products has been determined by X-ray crystallography, and unusual colour behavior has been explained by DFT calculations.



4,5-Diazafluorene derivatives,[1–4] including the sterically hindered alkylidene ones,[5,6] have been investigated as promising ligands for the biologically active transition metal complexes, fluorescence chemosensors and light-driven molecular motors. Available synthetic methods for these compounds are based on the oxidation of substituted 1,10-phenanthrolines with central ring contraction, affording the 4,5-diazafluorenone derivatives.[7] Subsequent preparation of the corresponding alkylidene derivatives from the ketones is typically achieved through the Barton–Kellogg reaction,[8] cross-coupling with 1,3-dithiole-2-thiones[9] or the Knoevenagel condensation with CH-active compounds.[10]

In this work, we used chiral fused 4,5-diazafluorene–bis(nopinane) **1**,[11] prepared from natural (1*S*)-(–)-α-pinene *via* (+)-pinocarvone oxime,[12] as a CH-active component in a condensation with aromatic aldehydes and ketones. This research area is in line with the recent extensive investigations of chiral fused nopinane–pyridine and pinane–pyridine functionalities.[13,14]



Scheme 1

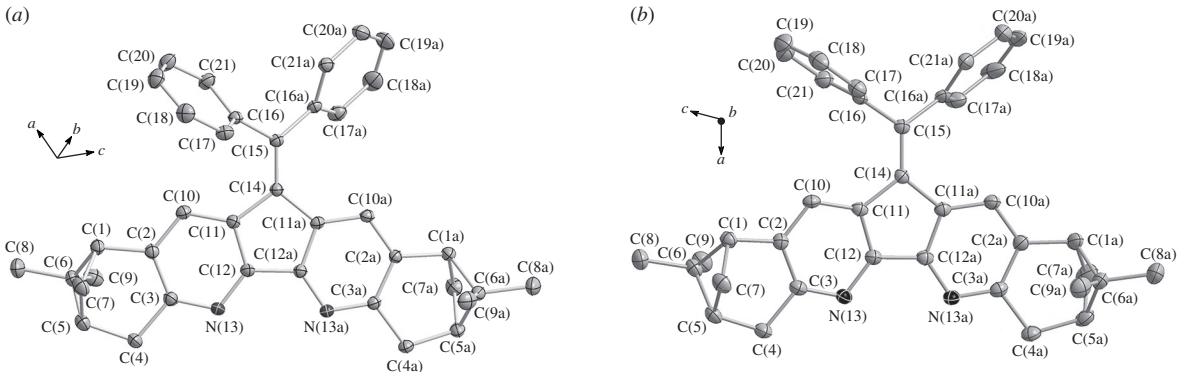


Figure 1 Thermal ellipsoid plot for the crystal structures of polymorphs (*a*) **3′** and (*b*) **3″** showing 50% probability. Hydrogen atoms are omitted for clarity.

We found that the condensation of compound **1** with carbonyl compounds, namely terephthalaldehyde, benzophenone, ninhydrin and anthraquinone, occurred in THF in the presence of $TiCl_4$ and pyridine at 50 °C for 4 days. The corresponding reaction products **2–6** were isolated by column chromatography on silica gel with benzene–THF in 20–40% yields (Scheme 1, Online Supplementary Materials). All the compounds **2–6** were formed as crystalline solvates upon slow evaporation of their solutions in MeCN–$CHCl_3$ at room temperature. The solvates were unstable and rapidly decomposed, therefore it was not possible to obtain reproducible results of elemental analysis and melting points.

Compound **3** forms a mixture of two crystalline phases, namely **3′** and **3″**, both of them being solvates with one acetonitrile molecule† (Scheme 1). The brown-yellow solvate **3′** and its light-yellow counterpart **3″** are polymorphs of the same composition and, importantly, they have very close parameters of unit cells, but notably distinct molecular conformations (Figure 1) with different deviations of the C(16)–C(14)–C(16a) plane from the plane of the 4,5-diazafluorene moiety as well as with diverse angles between benzene rings and the plane of the C(14)–C(15) double bond.

Reaction of compound **1** with anthraquinone resulted in the mixture of products **5** and **6**, corresponding to 2 : 1 and 1 : 1 condensation ratios. Compound **6** demonstrates solvatochromism with red, purple and yellow colours for benzene, chloroform and acetonitrile solutions, respectively. The purple colour of the chloroform solution originates from the band with $\lambda_{max} = 530$ nm in the electronic absorption spectrum. Crystalline phase prepared from derivative **6** (Figure 2)† exhibits pleochroism with colour change from lemon-yellow to red-orange when it is observed at different angles. In the crystalline phase its molecule has the so called folded conformation with the angle of 43.6(1)° between

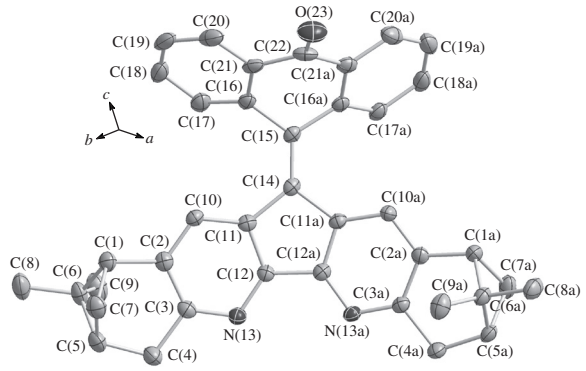


Figure 2 Thermal ellipsoid plot for the crystal structure of compound **6** showing 50% probability. Hydrogen atoms are omitted for clarity.

† *(1*R*,3*R*,8*R*,10*R*)-12-Diphenylmethylidene-2,2,9,9-tetramethyl-2,3,4,7,8,9,10,12-octahydro-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b*′]diquinoline* **3**. Single crystals of compound **3** were obtained by crystallization from acetonitrile as a mixture of two phases **3′** and **3″**.

Crystal data for **3′**. $C_{38}H_{36}N_2$·MeCN, M = 561.74, monoclinic, space group $P2_1$, 150(2) K, a = 11.7645(3), b = 10.1314(2) and c = 14.1240(4) Å, β = 109.5310(10)°, Z = 2, Z' = 1, V = 1586.59(7) Å^3, d_{calc} = 1.176 g cm^{-3}, μ(MoKα)$_{calc}$ = 0.068 mm^{-1}, 3.674° < 2θ < 63.074° for data collection, index ranges –16 ⩽ h ⩽ 16, –14 ⩽ k ⩽ 14, –20 ⩽ l ⩽ 19; 25676 reflections collected, 9704 independent reflections, R_{int} = 0.0272, R_σ = 0.0370. Data/restraints/parameters 9704/1/393, GOF 1.034. Final R indexes for $I \geqslant 2\sigma(I)$: R_1 = 0.0436, wR_2 = 0.1087, for all data: R_1 = 0.0502, wR_2 = 0.1137, largest diff. peak/hole: 0.35/–0.22 e Å^{-3}, Flack parameter 0.3(7).

Crystal data for **3″**. $C_{38}H_{36}N_2$·MeCN, M = 561.74, monoclinic, space group $P2_1$, 150(2) K, a = 11.6611(4), b = 10.0899(5) and c = 14.1166(7) Å, β = 109.386(2)°, Z = 2, Z' = 1, V = 1566.78(12) Å^3, d_{calc} = 1.191 g cm^{-3}, μ(MoKα)$_{calc}$ = 0.069 mm^{-1}, 3.702° < 2θ < 59.364° for data collection, index ranges –15 ⩽ h ⩽ 16, –14 ⩽ k ⩽ 14, –19 ⩽ l ⩽ 19; 19621 reflections collected, 8813 independent reflections, R_{int} = 0.0330, R_σ = 0.0563. Data/restraints/parameters 8813/1/393, GOF 1.049. Final R indexes for $I \geqslant 2\sigma(I)$: R_1 = 0.0472, wR_2 = 0.1019, for all data: R_1 = 0.0632, wR_2 = 0.1105, largest diff. peak/hole: 0.23/–0.23 e Å^{-3}, Flack parameter 0.6(10).

*10-{(1*R*,3*R*,8*R*,10*R*)-2,2,9,9-Tetramethyl-2,3,4,7,8,9,10,12-octahydro-1,3:8,10-dimethanocyclopenta[1,2-*b*:5,4-*b*′]diquinolin-12-ylidene}anthracen-9(10*H*)-one* **6**. Single crystals of compound **6** were obtained by crystallization from acetonitrile.

Crystal data for **6**. $C_{39}H_{34}N_2O$·MeCN, M = 587.73, orthorhombic, space group $P2_12_12_1$, 150(2) K, a = 10.6467(4), b = 13.0734(4) and c = 22.9617(9) Å, Z = 4, Z' = 1, V = 3196.0(2) Å^3, d_{calc} = 1.221 g cm^{-3}, μ(MoKα)$_{calc}$ = 0.073 mm^{-1}, 4.216° < 2θ < 54.26° for data collection, index ranges –10 ⩽ h ⩽ 13, –16 ⩽ k ⩽ 16, –28 ⩽ l ⩽ 28; 14782 reflections collected, 6859 independent reflections, R_{int} = 0.0324, R_σ = 0.0586. Data/restraints/parameters 6859/12/411, GOF 1.021. Final R indexes for $I \geqslant 2\sigma(I)$: R_1 = 0.0505, wR_2 = 0.1122, for all data: R_1 = 0.0657, wR_2 = 0.1190, largest diff. peak/hole: 0.48/–0.19 e Å^{-3}, Flack parameter 1.4(9).

Suitable crystals were investigated on a Bruker Apex DUO diffractometer equipped with a 4K CCD area detector using graphite monochromated MoKα radiation (λ =0.71073 Å). The φ- and ω-scan techniques were employed to measure the intensities. The crystal structures were solved by direct methods and refined by full-matrix least squares technique using the SHELXTL package[15] assisted with OLEX2 graphical user interface.[16] Atomic displacement parameters for non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model.

CCDC 1893703–1893705 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

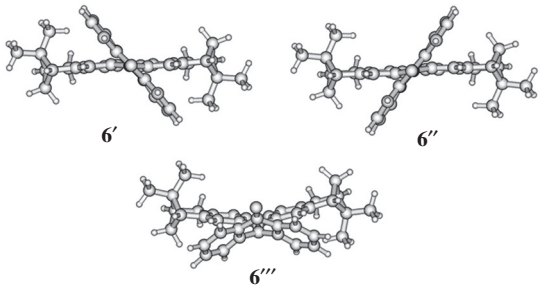


Figure 3 Structures of the stable conformations of the 1 : 1 condensation product **6** in $CHCl_3$, based on quantum chemical calculations at the DFT level B3LYP/def2-TZVP.

the planes of the two benzene rings. As is known, the crystals of bianthrone and related compounds have yellow colour in the folded conformation as well.[17,18]

According to the quantum chemical calculations at DFT level using the ORCA program system[19] with B3LYP/def2-TZVP,[20] there are three stable conformations of compound **6** in a chloroform solution (Figure 3, Online Supplementary Materials). Conformations **6′** and **6″** slightly differ in their heat of formation with $\Delta\Delta H_f^0$ = 0.07 kcal mol^{-1} in favor to the form **6″**, whereas conformation **6‴** is *ca*. 0.6 kcal mol^{-1} more stable. According to the calculations, the electronic absorption spectra of the twisted forms **6′** and **6″** should significantly differ from the spectra of the folded conformation **6‴** by the presence of a long-wave band with λ_{max} = 510–520 nm (Figure 4). Estimation of the population at room temperature gives the values of 19, 21 and 60% for the conformations **6′**, **6″** and **6‴**, respectively. Thus, the purple colour of compound **6** in chloroform can be explained by the presence of twisted forms **6′** and **6″**.

In summary, the investigated condensation of fused 4,5-diazafluorene–bis(nopinane) with aromatic carbonyl compounds opens the way to a new group of hybrid chiral derivatives, whose molecules have specific conformations and demonstrate a promising combination of spectral, optical and chiroptical properties.

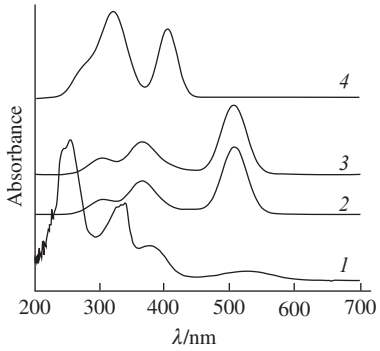


Figure 4 (*1*) Experimental UV–VIS absorption spectrum in $CHCl_3$ for compound **6** and simulated spectra for its conformers (*2*) **6′**, (*3*) **6″** and (*4*) **6‴** using quantum chemical calculations at the DFT level B3LYP/def2-TZVP.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.036.

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