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N,*N*′-Disubstituted phenanthrene-9,10-diimines: synthesis and NMR spectroscopic study

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ABSTRACT

Novel aryl-aryl, alkyl-alkyl, aryl-alkyl *N*,*N*′-disubstituted phenanthrene-9,10-diimines were synthesized by condensation of 9,10-phenanthrenequinone with primary amines. The novel two-stage method of synthesis of disubstituted phenanthrene-9,10-diimines with identical or different aryl and alkyl substituents at the nitrogen atom was established. The investigated compounds undergo slow *Z*-*E*/*E*-*Z* interconversion which was studied by NMR spectroscopy. Thermodynamic parameters of interconversion were obtained by variable temperature NMR spectroscopy.

1. Introduction

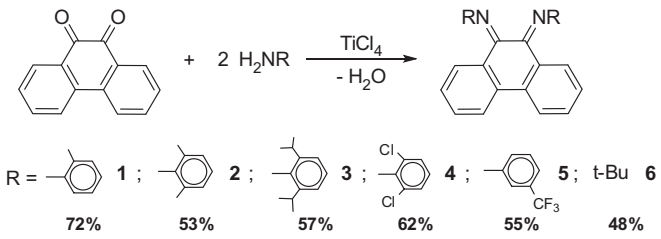
There is a considerable interest in molecules with an N═C–C═N moiety due to their versatile coordination behavior and the interesting properties of their complexes with metals. For example, bis(imino)acenaphthenes (BIAN) are widely employed as ligands and feature the rigidity and strain of the diazabutadiene moiety, the stereoelectronic tunability of the substituents at nitrogen, and facile ability to accept electrons.[1]

Recently a number of articles concerning complexes of transition and non-transition metals with unsubstituted[2] and substituted phenanthrene-9,10-diimine ligands—structural analogues of R-BIAN, has been published. These complexes show biological activity,[3] act as a DNA photocleavage agent,[4] are employed as a catalysts in the olefin polymerization[5] and have interesting spectral and redox[6] properties, which can be used for building molecules with intriguing electronic properties. Most of the investigations in this field were carried out with unsubstituted or *N*,*N*′-diphenyl-substituted phenanthrene-9,10-diimines, but there are also some investigations dedicated to synthesis and complexes of *N*,*N*′-di-(2-methylphenyl)-, *N*,*N*′-di-(2,6-dimethylphenyl)-, *N*,*N*′-di-(2,6-diisopropylphenyl)-substituted phenanthrene-9,10-diimines.[5,7,8]

2. Results and discussion

In this work we report the synthesis of novel *N*,*N*′-disubstituted phenanthrene-9,10-diimine compounds with identical and different substituents at the nitrogen atom and evaluation of some thermodynamic parameters of their *Z*-*E*/*E*-*Z* interconversion.

The majority of previously reported *N*,*N*′-disubstituted phenanthrene-9,10-diimines was synthesized by reductive cyclodehydrogenation of benzyl-bis(arylimines).[8] Prof. Li and coworkers reported[5] the synthesis of a new disubstituted phenanthrene-9,10-diimine by interaction of 9,10-phenanthrenquinone with 2,6-dimethylaniline by treatment of reagents with $TiCl_4$/DABCO at 140 °C. We have established that this reaction can be carried out under mild conditions with good yields. Compounds **1**–**6** were obtained by condensation of 9,10-phenanthrenequinone with 6-fold excess of primary amines in the presence of equimolar quantity of $TiCl_4$ in toluene at 70 °C (Scheme 1). The obtained phenanthrene-9,10-diimines were isolated with 54–72% yields. All compounds are yellow-red crystals, which are soluble in organic solvents.



Scheme 1.

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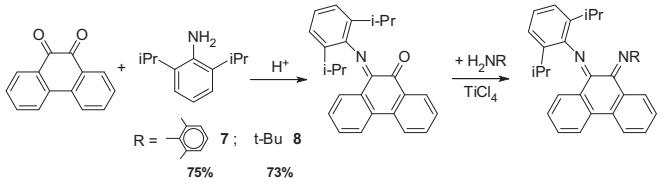
In our earlier studies it was shown that mono-substituted phenanthreneiminoquinones can be synthesized by condensation of substituted anilines with 9,10-phenanthrenquinone in boiling methanol in the presence of catalytic formic acid.[9] No formation of phenanthrene-9,10-diimines has been observed under these conditions. Applying this and the aforementioned methods step-by-step we have synthesized phenanthrene-9,10-diimines having different aryl-aryl (**7**) and aryl-alkyl (**8**) substituents in the imine groups (Scheme 2).



Scheme 2.

This two-stage process can be also used for the synthesis of phenanthrene-9,10-diimines with identical substituents in order to increase yield. The yield of compound **3** obtained by the two-stage reaction reaches 82%, whereas yield of **3** obtained by the one-stage process is 57%.

The diimines **2** and **8** were investigated by X-ray crystallography (Fig. 1). According to it both diimines are *E*-*Z* isomers in the crystals. The lengths of N=C double bonds in **2** and **8** vary in the range of 1.270(1)–1.277(1) Å, which are typical for this type of compound. The phenanthrene and N=C–C=N fragments in both molecules are not planar as a result of steric repulsion between the 2,6-dimethylphenyl substituents in **2** as well as 2,6-di-methylphenyl and *tert*-butyl in **8**. The torsion N(1)C(1)C(14)N(2) and N(1)C(1)C(2)N(2) angles are −44.9° and −66.3°. The deviations of C(1), C(14) and C(1), C(2) atoms in **2** and **8** from the phenanthrene fragments mean plane are 0.289, 0.309 Å and 0.406, 0.454 Å, respectively. The dihedral angles between C(2)–C(7) and C(8)–C(13) as well as C(3)–C(8) and C(9)–C(14) fragments are 11.3° and 21.5°, respectively, in **2** and **8**.

The NMR spectra of **2**,**3**,**6**–**8** are rather complicated and features two times more signals than expected for symmetrical structures with identical *N*,*N*′ substituents at nitrogens. In order to explain the obtained spectra we assume that investigated substances exist as a mixture of *E*,*Z* and *Z*,*E* isomers (Scheme 3). In the case of slow interconversion (according to NMR timescale) of **2**,**3**,**6**–**8** molecules *N*,*N*′ substituents and all protons of phenanthrene fragment became unequivalent. The greatest difference of the chemical shifts was observed for protons H-1 and H-8 (Scheme 3, Fig. 2) in **2**,**3**,**6**–**8**; this occurs due to the influence of the aryl substituents ring currents.

It is interesting to note that *N*,*N*′-(diphenyl)phenanthrene-9,10-diimine, **1** and **5** exist in a form of symmetrical *Z*-*Z* isomers both in solution and in the solid-state according to NMR spectra and X-ray data[7c] of *N*,*N*′-diphenyl compound. In contrast compounds **2**,**3**,**6**–**8** provide NMR spectra of unsymmetrical compounds at room temperature. Exchange between *E*-*Z* and *Z*-*E* forms is slow (in NMR timescale) in a chloroform or DMSO solution at room temperature for **2**,**3**,**6**–**8** and at 253 K for **4**. Presence of exchange between *E*-*Z* and *Z*-*E* isomers is confirmed by 2D NOESY NMR spectra. In the NOESY spectra of phenanthrene-9,10-diimines intense 'exchange' cross-peaks due to *Z*-*E*/*E*-*Z* interconversion are observed (Scheme 3, Fig. 2).

The chemical shifts of *Z*-*E* and *E*-*Z* isomers signals and the ratio of isomers is equal for compounds with identical *N*,*N*′ substituents **2**,**3**,**6** and differ for compounds with different substituents **7**,**8** (Table 1). The content of symmetrical *Z*-*Z* isomer reaches only 1–5% for **2**,**3**,**6**–**8**.

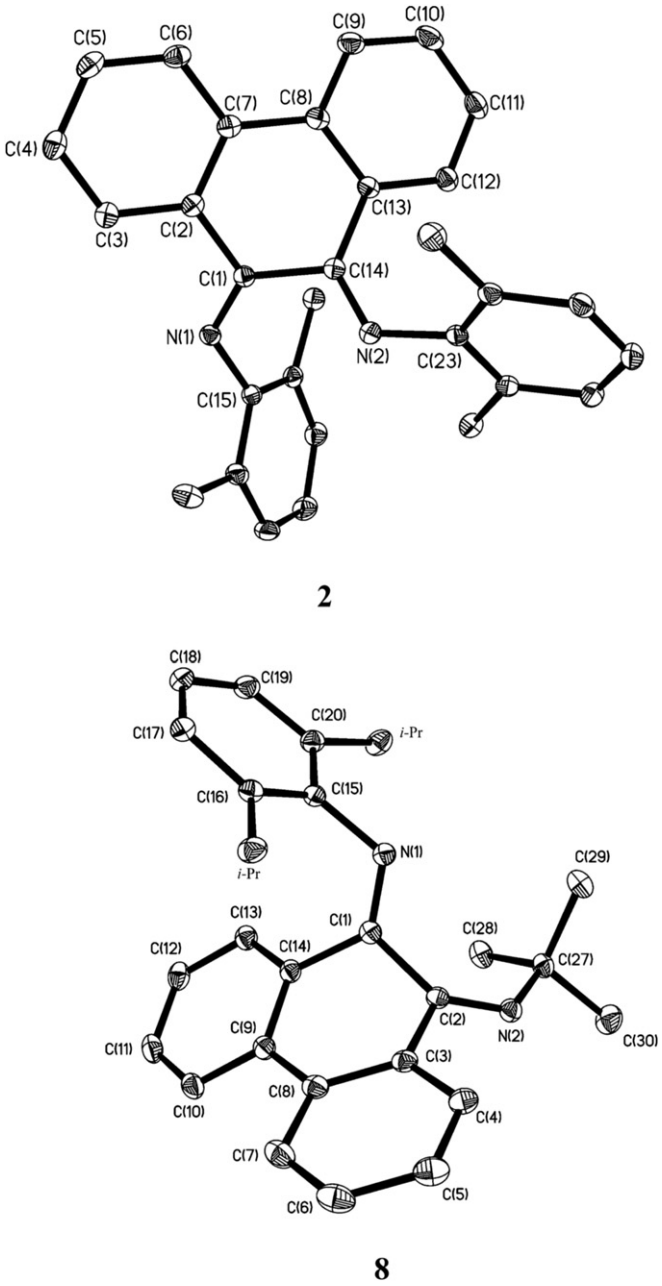
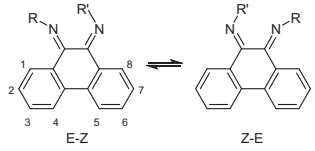


Fig. 1. Molecular structure of **2** and **8**.



Scheme 3.

Warming of solution of **2**–**4**,**6**–**8** leads to simplification of their NMR spectra. Heating of **2**–**4** in DMSO results in NMR spectrum of symmetrical diimine (*E*-*Z* and *Z*-*E* became indistinguishable) (Fig. 3).

In order to determine thermodynamic parameters of interconversion we have conducted the series of NMR experiments with variable temperature. The obtained parameters are shown in Table 1. The rate constant of exchange for each temperature was determined by lineshape analysis.[10] Standard errors of estimations were calculated from parameters of linear regressions.

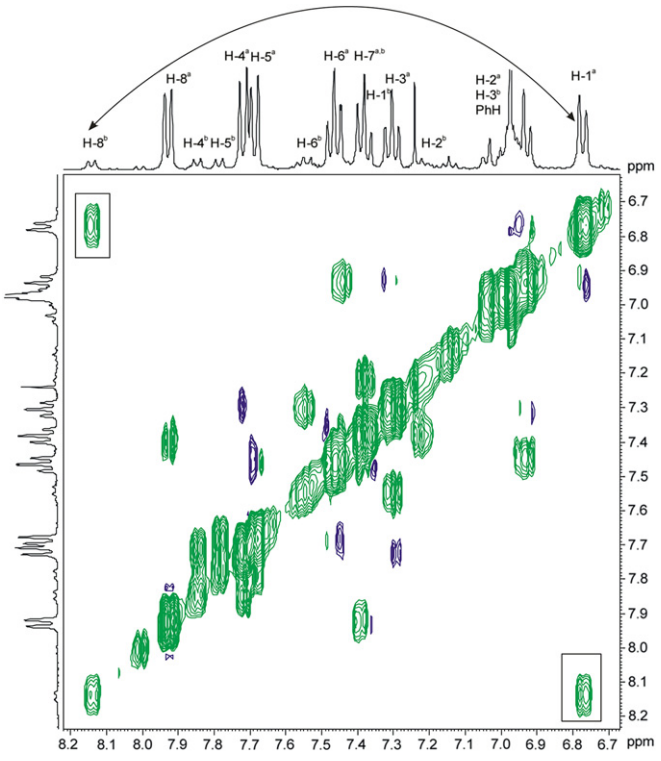


Fig. 2. NOESY spectrum of compound **8** (region of aryl protons). Peaks due to exchange and diagonal are green, NOE peaks are blue. Some NOE peaks are suppressed due to exchange. T_{mix}=250 ms. One of the exchanging pairs is marked by boxes and arrow.

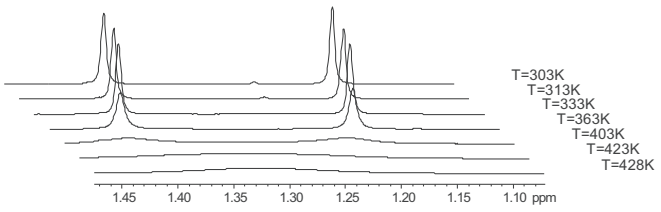


Fig. 3. Temperature dependence of **6** *tert*-butyl NMR signals. Signal with the chemical shift 1.25 ppm belongs to *Z-Z* isomer.

3. Conclusion

Some novel *N*,*N*′-disubstituted phenanthrene-9,10-diimines were synthesized and a new two-stage method for their synthesis was established. Applying this method allowed the synthesis of disubstituted phenanthrene-9,10-diimines with not only identical substituents but also with different aryl and alkyl groups at nitrogen atom. The investigated compounds undergo *Z-E*/*E-Z* interconversion, which was studied by NMR spectroscopy. Thermodynamic parameters of interconversion were obtained by variable temperature NMR spectroscopy. Further investigations of *Z-E* interconversion mechanism and applying the obtained ligands for the synthesis of complexes are being explored.

4. Experimental

4.1. General

9,10-Phenantrenequinone, substituted anilines, and *tert*-butylamine are commercially available products. Substituted phenanthrene-9,10-diimines **1**–**3**[5,8] were prepared by already known[5] modified method. The NMR spectra were recorded on a Bruker 'Avance III' NMR spectrometer (400 MHz—^{1}H, 100 MHz—^{13}C) using DMSO or $CDCl_3$ as the solvents and tetramethylsilane as the internal standard. IR-spectra were recorded by FTIR spectrometer 'Bruker Vertex 70'. Elemental analyses were obtained on 'EuroEA-3028-HT'. The X-ray data were collected on an SMART APEX diffractometer (graphite-monochromated, Mo Kα-radiation, ω- and θ-scan technique, λ=0.71073 Å) at 100 K. The structures were solved by direct methods and were refined on F^2 using SHELXTL[11] package. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. The H atoms in **2** were found from Fourier syntheses of electron density and were refined isotropically, whereas in **8** the H atoms were placed in calculated positions and were refined in the riding model. SADABS[12] was used to perform area-detector scaling and absorption corrections. The details of crystallographic, collection, and refinement data are shown in the Supplementary data. CCDC-832612 (**2**) and 832613 (**8**) contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

Table 1
Thermodynamic parameters of exchange obtained by variable temperature NMR. Energy of activation (*Ea*) was determined from Arrhenius plot ($k=A^*e^{-Ea/RT}$), $\Delta H^{\#}$, $\Delta S^{\#}$—from Eyring plot ($\ln(k/T)=-\Delta H^{\#}/(RT)+\Delta S^{\#}/R+23.7600$). $\Delta G^{\#}=RT(23.760+\ln(T/k))$

Compd	*Tc*, K	Δ*ν*, Hz	*Ea*, kCal/mol	$\Delta G^{\#}$, kCal/mol	$\Delta H^{\#}$, kCal/mol	$\Delta S^{\#}$, cal/(mol K)	*ZE*/*EZ* ratio	*ZZ*/*EZ* ratio
2	375	263	16.9±0.8	17.4±1.2	16.2±0.8	−1.3±1.3	1:1	5:100
3	380	371	18.5±0.3	17.3±0.6	17.8±0.3	1±0.7	1:1	3:100
6	423	81.5	17.9±0.5	20.7±1.0	17.2±0.5	−6.7±1.3	1:1	2:100
7	378	267	18.7±0.4	17.5±0.8	18.0±0.4	2.4±1.0	1:0.75	2:100
8	384	249	17.2±0.4	17.4±1.1	16.5±0.4	−0.6±1.4	1:0.14	3:100

4.2. Phenanthrene-9,10-diimines with identical substituents 1–6 were synthesized using the general procedure

To stirred suspension of 9,10-phenantrenquinone (1.0 g; 4.8 mmol) and 6-fold excess of aniline or *tert*-butylamine in toluene (30 mL) $TiCl_4$ (0.5 mL; 4.8 mmol) was added dropwise. The stirring was continued at ambient temperature during 10–20 h. Completeness of reaction was monitored by TLC. Resulting solution was washed out to the neutral medium by water and then organic part was separated and filtered. After removal of the solvent the crude product was recrystallized from acetonitrile.

4.2.1. ***1****. (N,N′-(2-Methyl)phenyl)phenanthrene-9,10-diimine.* Orange crystals. Mp=150–151 °C. Yield: 1.4 g (72%). Found (%): C, 87.16; H, 5.85; N, 7.20. Calculated for $C_{28}H_{22}N_2$ (%): C 87.01; H, 5.74; N, 7.25. IR (Nujol, ν/cm^{-1}): 1630m, 1614m, 1591s, 1574w, 1484m, 1324w, 1286m, 1220m, 1191w, 1181w, 1166w, 1154w, 1123m, 1115m, 1046m,

1022w, 957m, 944m, 929w, 872w, 854w, 846w, 760s, 666m, 615s. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 1.59 (s, 3H, Me); 6.33–6.35 (m, 2H, PhH); 6.86–6.94 (m, 6H, PhH); 7.48 (m, 2H, H-3 and H-6); 7.60 (m, 2H, H-2 and H-7); 7.94 (d, 2H, H-4 and H-5, J=8.1); 8.09 (d, 2H, H-1 and H-8, J=7.6).

4.2.2. ***2****. (N,N′-(2,6-Dimethyl)phenyl)phenanthrene-9,10-diimine.* Cherry red crystals, yield: 1.06 g (53%); mp=166 °C. Found (%): C, 86.92; H, 6.25; N, 6.71. Calculated for $C_{30}H_{26}N_2$ (%): C, 86.92; H, 6.32. IR (Nujol, ν/cm^{-1}): 1646m, 1624m, 1591m, 1490w, 1324w, 1287w, 1241w, 1206m, 1176w, 1093w, 955w, 939w, 761s, 726s. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 1.37, 2.04 (s., both 3H, PhMe); 6.70 (d, 1H, H-1, J=7.8); 6.75–6.85 (m, 2H+1H, *m*-PhH, *p*-Ph′H); 6.86 (m, 1H, *p*-PhH); 6.92 (m, 1H, H-2); 6.98 (d, 2H, *m*-Ph′H, J=7.5); 7.40 (m, 1H, H-3); 7.51 (m, 1H, H-7); 7.62 (m, 1H, H-6); 7.90 (d, 1H, H-4, J=7.9); 7.93 (d, 1H, H-5, J=7.9); 8.32 (d, 1H, H-8, J=7.8). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 17.2, 18.4 PhMe; 122.5, 123.1 *p*-Ph, *p*-Ph′; 123.5C(5)H, 124.6C(4)H; 124.9, 125.2, 126.8C; 126.9C(8)H; 127.4C(2)H; 127.6, 127.9 *m*-Ph, *m*-Ph′; 127.7C(1)H; 129.1C(7)H; 131.4C(3)H; 131.8C(6)H; 133.4, 134.0, 134.5C; 147.5, 148.9 PhN; 158.2, 159.9 C=N. Ph and Ph′ belongs to nonequivalent *N*,*N*′ substituents.

4.2.3. ***3****. (N,N′-(2,6-Diisopropyl)phenyl)phenanthrene-9,10-diimine.* Red crystals, yield: 1.44 g (57%); mp=159 °C. Found (%): C, 86.47; H, 8.11. Calculated for $C_{38}H_{42}N_2$ (%): C, 86.65; H, 8.04. IR (Nujol, ν/cm^{-1}): 1644m, 1619m, 1597m, 1589m, 1435s, 1360m, 1325m, 1294m, 1285m, 1253m, 1220w, 1190w, 1169w, 1122w, 1104w, 1057w, 1042w, 1034w, 954m, 942m, 807w, 796w, 778m, 760s, 754s, 727s, 665m. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.59, 0.75, 1.02, 1.14 (d, all 6H, Ph–CH(CH_3)$_2$, J=6.7), 1.85, 2.81 (sept, both 2H, PhCH(CH_3)$_2$, J=6.7), 6.67 (d, 1H, H-1, J=7.8), 6.80–6.98 (2H+1H+1H, *m*-PhH, *p*-Ph′H, *p*-PhH), 7.04 (m, 1H, H-2), 7.10 (d, 2H, m-Ph′H, J=7.5), 7.35 (m, 1H, H-3), 7.52 (m, 1H, H-7), 7.63 (m, 1H, H-6), 7.90 (d, 1H, H-4, J=7.9), 7.94 (d, 1H, H-5, J=7.9), 8.30 (d, 1H, H-8, J=7.8). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 22.5, 22.6, 23.5, 24.7, 27.3, 28.7, 122.4, 123.2, 123.3, 123.3, 124.0, 124.4, 127.0, 127.3, 128.7, 129.0, 129.4, 131.0, 131.7, 133.6, 134.0, 135.1, 135.3, 135.6, 144.9, 146.6, 158.9, 159.7.

4.2.4. ***4****. (N,N′-(2,6-Dichloro)phenyl)phenanthrene-9,10-diimine.* Red crystals, yield: 1.48 g (62%); mp=172–173 °C. Found (%): C, 63.03; H, 2.81; Cl, 28.63. Calculated for $C_{26}H_{14}Cl_4N_2$ (%): C, 62.93; H, 2.84; Cl, 28.58. IR (Nujol, ν/cm^{-1}): 1648m, 1628s, 1595m, 1557m, 1434s, 1330m, 1298m, 1290m, 1264w, 1256w, 1226m, 1204w, 1193w, 1170w, 1149w, 1121w, 1098w, 1078w, 1062w, 1037w, 955w, 942m, 839w, 823w, 787m, 766s, 755s, 733m, 722s, 666m, 622m. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 6.76–6.96 (m, 3H, PhH); 6.97–7.20 (m, 3H, PhH); 7.21–7.37 (m, 2H); 7.39–7.72 (m, 3H); 7.90–8.01 (m, 2H); 8.17–8.58 (m, 1H). ^{13}C NMR (400 MHz, $CDCl_3$, δ/ppm): 123.9, 124.4, 127.3–129.8, 132.0–133.4, 134.6, 161.9–162.6. ^{1}H and ^{13}C signals are widened. There are two sets of signals observed in the PMR spectrum at 253 K—one belongs to *Z-E* isomer and another to *ZZ* isomer. The ratio of *ZZ*/*EZ* isomers is 77:100.

4.2.5. ***5****. (N,N′-(3-Trifluoromethyl)phenyl)phenanthrene-9,10-diimine.* Orange crystals. Yield: 1.33 g (55%). Decomposed at 146 °C. Found (%): C, 68.19; H, 3.41. Calculated $C_{24}H_{12}F_6N_2$ (%): C, 68.02; H, 3.26. IR (Nujol, ν/cm^{-1}): 1630m, 1617m, 1595s, 1483m, 1453s, 1328s, 1285s, 1226w, 1204w, 1177s, 1159s, 1116s, 1096s, 1066s, 1024m, 1001w, 982w, 958w, 947m, 890s, 802s, 764s, 752s, 742w, 699s, 669w, 659w, 640w, 617w, 596w, 542w, 528w, 517w, 474w, 461w. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 6.51 (d, 2H, PhH, J=7.8); 6.58 (m, 2H, PhH); 7.17 (m, 2H, PhH); 7.25 (m, 2H, PhH); 7.52 (m, 2H, H-3 and H-6); 7.66 (m, 2H, H-2 and H-7); 7.95 (d, 2H, H-4 and H-5, J=7.9); 8.09 (d, 2H, H-1 and H-8, J=6.0). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 117.1; 121.6; 121.7; 122.7; 123.9; 125.0; 126.6; 129.3; 129.4; 132.5; 134.5; 134.7; 149.2; 161.1.

4.2.6. ***6****. (N,N′-Di-tert-butyl)phenanthrene-9,10-diimine.* Yellow crystals, yield: 0.74 g (48%); mp=126 °C. Found (%): C, 83.02; H, 8.15. Calculated for $C_{22}H_{26}N_2$ (%): C, 82.97; H, 8.23. IR (Nujol, ν/cm^{-1}): 1650s, 1636s, 1597m, 1360s, 1287w, 1264w, 1230s, 1207s, 1193m, 1162w, 1119w, 1074w, 1040w, 1027w, 1005w, 978w, 955m, 943w, 913w, 889w, 878w, 862w, 776m, 767m, 748s, 741m, 729s, 697m, 671m, 665m, 615m. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 1.25, 1.47 (s, both 9H, *t*-Bu), 7.24 (m, 1H, H-3), 7.32 (m, 1H, H-7), 7.37–7.48 (m, 3H, H-1, H-2, H-6), 7.66, 7.68 (both d, 1H+1H, H-4, H-5, J=7.5), 7.85 (d, 1H, H-8, J=7.5). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 31.50, 31.52 (C(CH_3)$_3$), 57.9, 58.2 (C(CH_3)$_3$), 122.9, 124.7 (C(4)H, C(5)H), 126.2, 126.3 (C(3)H, C(8)H), 127.7, 129.9, 130.1 (C(1)H, C(2)H, C(6)H), 128.6 (C(7)H), 134.3, 134.4, 135.9, 137.0 (C), 162.7, 164.7 (C=N).

4.3. Phenanthrene-9,10-diimines with different substituents 7,8 were synthesized using the general procedure

In the first stage was obtained *N*-(2,6-di-*iso*-propylphenyl)-phenanthren-*o*-iminoquinone by known method.[9] In the second stage reaction of *N*-(2,6-di-*iso*-propylphenyl)-phenanthren-*o*-iminoquinone with a 3-fold excess of amine in the presence of $TiCl_4$ was carried out during 3–5 h. Isolation and purification of products were performed by method described above.

4.3.1. ***7****. (N-(2,6-Dimethyl)phenyl-N′-(2,6-diisopropyl)phenyl) phenanthrene-9,10-diimine.* Red crystals, yield: 1.69 g (75%); mp=174 °C. Found (%): C, 86.63; H, 7.21. Calculated for $C_{34}H_{34}N_2$ (%): C, 86.77; H, 7.28. IR (Nujol, ν/cm^{-1}): 1647m, 1615s, 1593s, 1463s, 1435s, 1361w, 1328m, 1288m, 1257w, 1245w, 1237w, 1217w, 1198m, 1168w, 1158w, 1120w, 1090w, 1058w, 1042w, 1033w, 986w, 954w, 940w, 922w, 835w, 820w, 804w, 780m, 758s, 727s, 688w, 665w. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.59, 0.79 (d, both 6H, CH(CH_3)$_2^a$, J=6.7); 1.00, 1.14 (d, CH(CH_3)$_2^b$, J=6.7); 1.35 (s, PhMe^b); 2.04 (s, 6H, PhMe^a); 1.81 (sept, 2H, CH(CH_3)$_2^a$, J=6.7); 2.81 (sept, 2H, CH(CH_3)$_2^b$, J=6.7); 6.66 (d, 1H, H-1^b, J=7.8); 6.72 (d, 1H, H-1^a, J=7.8); 6.75–7.01 (*m*-PhH^{a,b}, *p*-PhH^{a,b}, H-2^{a,b}) 7.33–7.42 (m, H-3^{a,b}), 7.51 (m, H-7^{a,b}), 7.62 (m, H-6^{a,b}); 7.91, 7.94 (m, H-4^{a,b},H-5^{a,b}); 8.29 (d, H-8^b, J=7.8); 8.35 (d, H-8^a, J=7.8). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 17.3^a, 18.5^b, 22.6^b, 22.8^a, 23.5^b, 24.1^a, 27.4^a, 28.8^b, 122.5^a, 122.5^a, 122.9^b, 123.1^b, 123.3, 123.4, 123.5, 124.1, 124.5, 124.6, 125.0, 127.1, 127.2, 127.3, 127.4, 127.7, 127.9, 128.6, 128.8, 129.0, 129.7, 131.2^a, 131.3^b, 131.7^b, 131.9^a, 133.6, 134.1, 134.6, 135.2, 135.4, 135.6, 145.3^a, 146.7^b, 147.5^a, 149.0^b, 157.9^b, 158.7^b, 159.2^a, 159.8^a.

4.3.2. ***8****. (N-tert-Butyl-N′-(2,6-di-iso-propyl)phenyl) phenanthrene-9,10-diimine.* Yellow crystals, yield: 1.48 g (73%); mp=109–110 °C. Found (%): C, 85.33; H, 8.15. Calculated for $C_{30}H_{34}N_2$ (%): C, 85.26; H, 8.11. IR (Nujol, ν/cm^{-1}): 1648m, 1618m, 1597m, 1435w, 1360w, 1321m, 1289s, 1268s, 1255s, 1233m, 1210m, 1175s, 1156s, 1121s, 1007s, 1070s, 1055s, 1034s, 946s, 933m, 894s, 820s, 803s, 773m, 759w, 744w, 725w, 694m, 665w. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm, J/Hz): 0.86, 0.97 (d, both 6H, CH(CH_3)$_2^a$, J=6.7), 0.96 (s, *t*-Bu^b), 1.11, 1.12 (d, both 6H, CH(CH_3)$_2^b$, J=6.7); 1.61 (s, 9H, *t*-Bu^a); 2.70–2.85 (m, CH(CH_3)$_2^{a,b}$); 6.77 (d, 1H, H-1^a, J=7.8); 6.93 (m, 1H, H-2^a); 6.95–7.06 (m, PhH^{a,b}); 7.19 (m, 1H, H-2^b); 7.31 (m, 1H, H-3^a); 7.37* (d, 1H, H-1^b); 7.38 (m, 1H, H-7^{a,b}); 7.40* (H-3^b); 7.44* (H-7^b); 7.47 (m, 1H, H-6^a); 7.55 (m, 1H, H-6^b); 7.72 (d, 1H, H-5^a, J=7.9); 7.78 (d, 1H, H-4^a, J=7.9); 7.84 (d, 1H, H-5^b, J=7.9); 7.87 (d, 1H, H-4^b, J=7.9); 7.93 (d, H-8^a, J=7.8); 8.00 (d, 1H H-8^b, J=7.8). Signals assigned to isomers a or b are marked by letters. Ratio of isomers is 1:0.14 (a/b). Chemical shifts obtained from HSQC

spectrum are marked by asterisk. ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 22.3, 24.6 $CH(CH_3)_2$; 27.8 $CH(CH_3)_2$; 31.4C$(CH_3)_3$; 57.6 $C(CH_3)_3$; 122.9C(5)H; 123.3 PhH; 124.2C(4)H; 124.3 PhH; 126.6C(8)H; 127.0C(2)H, 127.3C(1)H; 129.0C(7)H; 130.4C(6)H; 130.6C(3)H; 132.1, 133.1, 136.2, 137.1, 144.9C; 161.0, 169.7 (C=N). This spectrum is for isomer a only.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.12.028.

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