Synthesis of novel heteropentacenes containing nitrogen, sulfur and oxygen or selenium†

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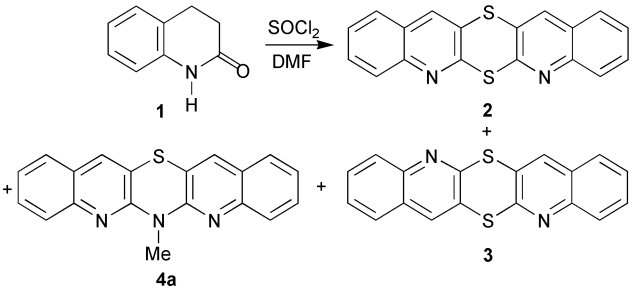
Reactions of 2,2′-dichloro-3,3′-diquinolinyl sulfide with selected S-, O-, Se-, C- and N-nucleophiles proceeded as a hetero-ring closure to form six linear annelated pentacyclic heterocycles with a sulfur-containing central ring (1,4-dithiin, 1,4-thiazine, 1,4-thiaselenin, 1,4-oxathiin and thiopyran) in moderate to good yields. The X-ray study of selected heteropentacenes revealed that heteropentacenes, in contrast to homopentacene, are non-planar and folded along the central sulfur-heteroatom axis. The central six-membered ring is in a boat conformation.

Considerable recent interest has focused on organic materials with interesting electronic, optoelectronic or magnetic properties. The basic strategy is the investigation of the molecular donors and acceptors. The incorporation of polarizable heteroatoms within the donor framework is regarded as one important aspect to design new polyheterocyclic donor molecules.[1] Very few papers have appeared in the literature about fused pentacyclic heterocycles (linear heteropentacenes and angular heteropentaphenes). The synthesis of these compounds is fatiguing and the yields (from very low, 2%, to good, 80%) depend mainly on the heteroatom to be incorporated into the ring system.[1–5] Some azathiapentaphenes and diazadithiapentacenes show photoelectric properties[6] and some diazapentacenes are considered as photodynamic therapeutic agents against cancer cell lines, bacteria and viruses.[7] Very recent studies demostrated the remarkable potential of homopentacene for device applications.[8,9]

Results and discussion

In continuation of our studies on 1,4-dithiinodiquinolines[10–12] we tried to synthesize and improve the yield (6%)[13] of heteropentacene **2** from the reaction of 3,4-dihydro-2(1*H*)-quinolone **1** with thionyl chloride in DMF at higher temperature (152 °C instead of 100 °C) and we obtained dithiin **2** in 13% yield, its isomeric dithiin **3** in 4% yield and unexpectedly the novel heteropentacene, 6-methyl-1,4-thiazinodiquinoline **4a** in 21% yield (Scheme 1). The formation of thiazine **4a** can be explained by an action of DMF on the substrate or intermediates. This result prompted us to try to obtain other 1,4-thiazinodiquinoline and generally choose a strategy for the construction of other heteropentacenes. Since we found 4,4′-dichloro-3,3′-diquinolinyl sulfide to be a very useful substrate to get selected heteropentaphenes,[14–16] its isomer, 2,2-dichloro-3,3′-diquinolinyl sulfide **7**, should be appropriate for the synthesis of heteropentacenes. This sulfide can be isolated from the reaction of 3,4-dihydro-2(1*H*)-quinolone **1** with thionyl chloride in DMF at room temperature in 23% yield[13] but the described procedure is not quite so simple because, beside sulfide **7**, not only 2,2′-dichloro-3,3′-diquinolinyl disulfide[13] but small amounts of dithiins **2** and **3** are also formed. Thus, we decided not only to isolate these from the reaction mixture but also transform dithiin **2** into sulfide **7**. For this purpose we carried out the 1,4-dithiin ring opening in dithiin **2** with sodium methanethiolate in DMSO followed by *S*-methylation with methyl iodide to form 2,2′-dimethylthio-3,3′-diquinolinyl sulfide **5** (in 89% yield). The latter compound was hydrolyzed using an ethanol–hydrochloric acid mixture to give diquinolonyl sulfide **6** (in 94% yield), which underwent reaction with phosphoryl chloride to form the required dichloro compound **7** (in 94% yield). The total yield of this transformation is 79% (Scheme 2).



Scheme 1

Reactions of sulfide **7** with selected divalent Z-reagents (S-, O-, Se-, C- and N-nucleophiles) under various conditions led to heteropentacenes containing nitrogen, sulfur and oxygen or selenium in moderate to good yields. In all cases these reagents did not substitute the sulfur atom, as was observed in a similar reaction of diquinoxalinyl sulfide with butylamine.[4] Reaction of sulfide **7** with boiling DMF in the presence of sodium hydroxide confirmed our supposition on the action of DMF, giving thiazine **4a** in 68% yield (Scheme 3). The same product was obtained in 51% yield when sulfide **7** reacted with

† Part LXX in the series of Azinyl Sulfides. Part LXIX: B. Morak, K. Pluta and K. Suwińska, *Heterocycl. Commun.*, in press.

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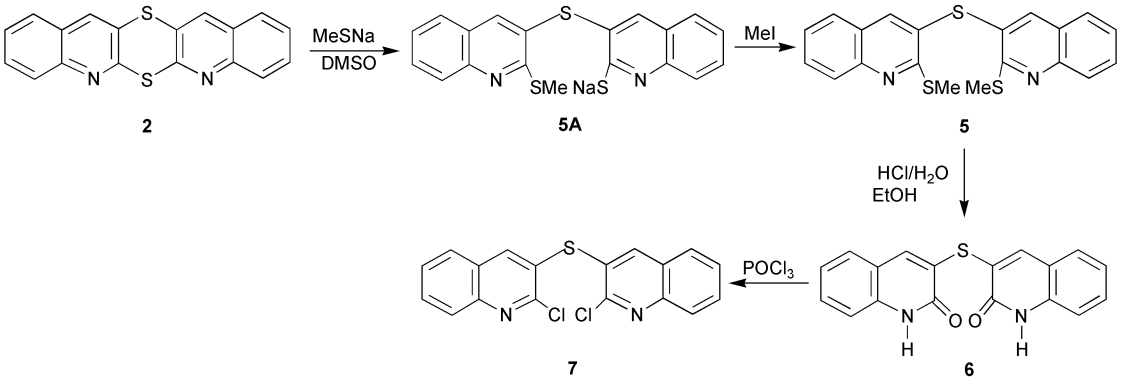
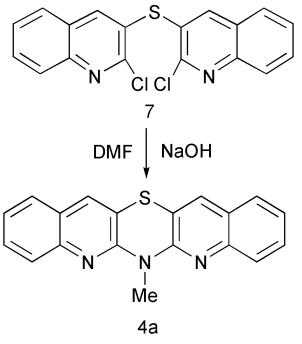


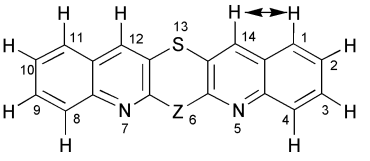
2 5A 5 7 6

Scheme 2



7 4a

Scheme 3



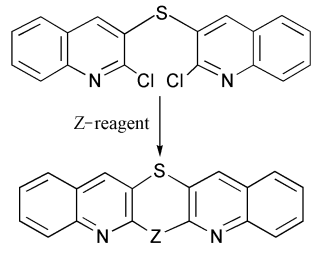
Scheme 5

methylamine using the phenolic procedure.[15] Thiazines with aryl substituents, for example 6-phenylthiazinodiquinoline **4b**, can be easily obtained in 82% yield in the reaction of sulfide **7** with aniline in boiling MEDG (methyl ether of diethylene glycol), using the reported procedure[14,15] (Scheme 4).

Reaction of sulfide **7** with thiourea in boiling MEDG gave the already known heteropentacene **2** in 91% yield. Similar reaction with selenourea gave the novel heteropentacene **8** in 81% yield. Since the reaction of sulfide **7** with sodium hydroxide in MEDG gave no cyclization product, and that with acetic acid and acetic anhydride in pyridine gave only 7% of oxathiinodiquinoline **9**, we changed the substrate. Cyclization of diquinolonyl sulfide **6** in the presence of phosphorus pentoxide gave the required heteropentacene **9** in 53% yield.

Reaction of the dichloro compound **7** with a selected C-nucleophile, a carbanion generated from phenylacetonitrile, in DMSO in the presence of sodium hydroxide led to the novel heteropentacene **10** in 82% yield.

The ^{1}H NMR spectra of the obtained heteropentacenes **2**, **4**, **8–10**, recorded in deuteriochloroform at 500 MHz, showed four multiplets (two doublet-shaped multiplets with one ortho-coupling and two triplet-shaped multiplets with two ortho-couplings, J = 7–8.5 Hz) of an ABCD system of the benzene ring protons and a singlet of the pyridine ring protons (*i.e.*, H-12 and H-14). In order to assign unqestionably all of the benzene protons, homonuclear NOE experiments and ^{1}H-^{1}H correlations (COSY) were used. Irradiation of the singlet protons caused a slight enhancement (1.3–4.9%) of one of the doublet-shaped multiplet signals, being more upfield than the another, which was attributed to the H-1 and H-11 protons due to *peri* interactions (Scheme 5). The COSY spectra permitted the complete assignment of the remaining proton signals. All the ^{1}H NMR spectra showed the spectral equivalency of the left and right parts of heteropentacenes **2**, **4**, **8–10**, which implies that all these reactions ran without cleavage of the C–S bond and all these heteropentacenes have C_{2v} symmetry.



	Z		Z
2	S	**8**	Se
4a	NMe	**9**	O
4b	NPh	**10**	C(CN)Ph

Scheme 4

To avoid any discussions that the ring closure reaction is preceded by a Smiles rearrangement stage and that the spectral identity is fortuitous, and above all to determine the conformation and configuration of these novel heteropentacenes, we carried out X-ray structural determinations of thiazine **4b** (published separately[17]), thiaselenin **8** and thiopyran **10** (we were not able to prepare appropriate single crystals of oxathiin **9**). In contrast to homopentacene,[18] heteropentacenes **4b**, **8** and **10** are nonplanar (Figs. 1 and 2). The central heterocyclic ring is in a boat conformation with the S(1) and Z atoms [N(3), Se(1) or C(21)] out of the basal plane formed by the C(2), C(3), C(2′), C(3′) plane. The heteropentacene ring system is folded mainly along the S(1)–Z axis and slightly along the C(2)–C(3) and C(2′)–C(3′) axes. The butterfly angle between two quinoline planes and the dihedral angles between the planes determined by the atoms of the two halves of the central heterocyclic rings [*i.e.*, S(1), Z, C(2), C(3) and S(1), Z, C(2′), C(3′)] are different depending on the nature of the central ring (Table 1). The quinoline ring system is quite planar, the dihedral angles between the pyridine and benzene rings are less than 1.9°. In contrast to the phenyl group in heteropentacene **4b**, which is in the quasi-equatorial location [S···N–C_{phenyl} angle of 163.0(2)°],[17] the same group in heteropentacene **10** is in the quasi-axial location with a S···C–C_{phenyl} angle of 86.3(1)°. The plane of the phenyl group nearly bisects the pentacene ring system in **4b**[17] and **10** with dihedral angles of 73.4(1)° and 89.1(1)° between the phenyl plane and the C(2),

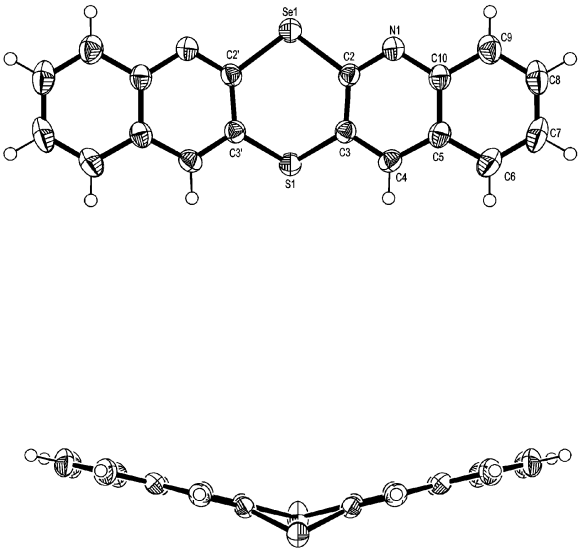


Fig. 1 ORTEP drawing of heteropentacene **8**.

C(3), C(2′), C(3′) plane. The nature of the heteroatom Z affects not only the Z bond angle but also the sulfur bond angle and to a lesser degree the C(2) and C(3) bond angles. In contrast to this, the S–C bond lengths are nearly unchanged (Table 1).

Conclusions

We report here an efficient synthesis of novel heteropentacenes, possessing different central 6-membered rings (*i.e.*, a dithiin, a thiopyran, a thiazine, an oxathiin and a thiaselenin ring), in the annulation reactions of 2,2-dichloro-3,3′-diquinolinyl sulfide with various divalent Z-reagents (selected S-, O-, Se-, C- and N-nucleophiles).

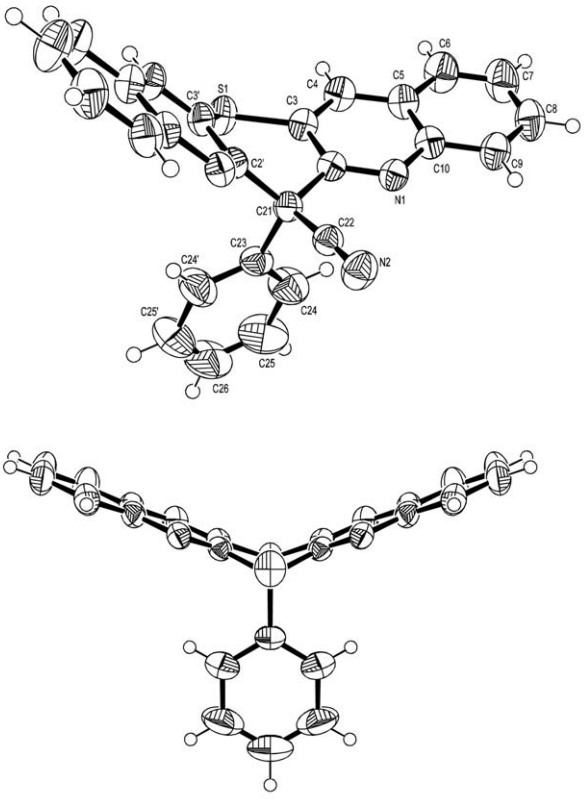


Fig. 2 ORTEP drawing of heteropentacene **10**.

Table 1 Comparison of geometrical features of selected novel heteropentacenes

Geometrical feature	**8**	**10**	**4b**[17]
C–S bond length/Å	1.763(3)	1.7546(15)	1.70(3) 1.761(4)
C–Z bond length/Å	1.906(3)	1.5297(18)	1.395(4) 1.410(4)
C–S–C angle/°	104.25(18)	98.88(10)	100.1(2)
C–Z–C angle/°	120.20(17)	110.53(16)	123.8(2)
Dihedral angle between quinoline moieties/°	26.80(7)	44.73(3)	20.5(1)
Angle between the halves of the central ring/°	41.03(7)	47.47(5)	30.6(1)
Displacement of the S(1) atom from C(2),C3),C(2′),C(3′) plane/Å	0.645(5)	0.580(3)	0.481(1)
Displacement of the Z atom from C(2),C3),C(2′),C(3′) plane/Å	0.423(5)	0.563(3)	0.247(4)

Experimental

Melting points were determined in open capillary tubes on a Boetius melting point apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on Bruker AM 500 and Varian Unity Inova 300 spectrometers at 500.13 and 300 MHz in deuteriochloroform and dimethyl sulfoxide-d_6 with tetramethylsilane as the internal standard. Electron impact mass spectra (EI MS) were run on a LKB 9000S at 70 eV.

Synthesis

5,7-Diaza-6,13-dithiapentacene **2**, 5,12-diaza-6,13-dithiapentacene **3** and 2,2′;-dichloro-3,3′-diquinolinyl sulfide **7** were obtained by reported procedures[13] and by the procedures described below. Additionally, heteropentacene **2** was obtained by isomerization of heteropentacene **3**.[19]

5,7-Diaza-6,13-dithiapentacene 2. A solution of sulfide **7** (0.36 g, 1 mmol) and thiourea (0.15 g, 2 mmol) in 20 mL of MEDG was stirred for 30 min at ambient temperature and then refluxed for 1 h. After cooling pale yellow needles precipitated, which were filtered off to give heteropentacene **2** (0.29 g, 91%); mp 257–258 °C, lit.[13] mp 258–259 °C. ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 2H, H-2, H-10), 7.69 (m, 2H, H-3, H-9), 7.73 (m, 2H, H-1, H-11), 8.02 (m, 2H, H-4, H-8), 8.17 (s, 2H, H-12, H-14).

6-Methyl-5,6,7-triaza-13-thiapentacene 4a. (*a*) To a boiling solution of 3,4-dihydro-2(1*H*)-quinolone (4.41 g, 30 mmol) in anhydrous DMF (50 mL) thionyl chloride (6.6 mL, 90 mmol) was added over 15 min and then the solution was boiled for 1 h. After cooling the resulting solid was filtered off, washed with water and air-dried. Separation by column chromatography (silica gel 60, chloroform) gave (1) heteropentacene **2** (0.10 g, 2%); mp 257–258 °C, lit.[13] mp 258–259 °C and (2) 5,12-diaza-6,13-dithiapentacene **3** (0.20 g, 4%); mp 285–286 °C, lit.[13] mp 287–289 °C.

The filtrate was poured into water (300 mL) and the resulting solid was filtered off, washed with water and air-dried. The solid was stirred with chloroform (4 × 8 mL), the insoluble material was filtered off and the filtrate was concentrated and separated by column chromatography (silica gel 60, chloroform) to give (1) heteropentacene **4a** (0.98 g, 21%); mp 200–201 °C. ^{1}H NMR ($CDCl_3$): δ 3.90 (s, 3H, CH_3), 7.31 (m, 2H, H-2, H-10), 7.54 (m, 2H, H-1, H-11), 7.55 (m, 2H, H-3,

H-9), 7.73 (s, 2H, H-12, H-14), 7.82 (m, 2H, H-4, H-8). MS: m/z 315 (M^+, 100). Anal. calcd for $C_{19}H_{13}N_3S$: C 72.36, H 4.15, N 13.32. Found: C 72.17, H 4.24, N 13.18. (2) Heteropentacene **3** (0.54 g, 11%); mp 257–258 °C, lit.[13] mp 258–259 °C.

(*b*) A mixture of sulfide **7** (0.36 g, 1 mmol), sodium hydroxide (0.04 g, 1 mmol) and DMF (10 mL) was refluxed for 2 h. After cooling the reaction mixture was poured into water (15 mL) and the resulting solid was filtered off, washed with water, air-dried and purified by column chromatography (silica gel 60, chloroform) to give heteropentacene **4a** (0.21g, 68%); mp 200–201 °C.

(c) To a solution of sulfide **7** (0.36 g, 1 mmol) in phenol (2 g) at 180 °C methylamine [generated from methylamine hydrochloride (0.35 g, 5 mmol) and 5% sodium hydroxide solution] was added by portions during 1 h. After cooling water (20 mL) was added and phenol was distilled off. The crude product was filtered off, washed with water, air-dried and purified by column chromatography (silica gel 60, chloroform) to give heteropentacene **4a** (0.16 g, 51%).

6-Phenyl-5,6,7-triaza-13-thiapentacene 4b. A solution of sulfide **7** (0.36 g, 1 mmol) and aniline (0.18 mL, 2 mmol) in MEDG (10 mL) was refluxed for 4 h. After cooling pale yellow needles precipitated, which were filtered off to give heteropentacene **4b** (0.31 g, 82%); mp 262–263 °C. ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 2H, H-2, H-10), 7.42 (m, 2H, H-3, H-9), 7.47 (d, 2H, *o*-C_6H_5), 7.51 (d, 1H, *p*-C_6H_5), 7.52 (m, 2H, H-1, H-11), 7.54 (m, 2H, H-4, H-8), 7.60 (d, 2H, *m*-C_6H_5), 7.78 (s, 2H, H-12, H-14). MS: m/z 377 (M^+, 100). Anal. calcd for $C_{24}H_{15}N_3S$: C 76.37, H 4.01, N 11.13. Found: C 76.19, H 4.11, N 11.06.

2,2′-Dimethylthio-3,3′-diquinolinyl sulfide 5. To a suspension of dithiin **2** (0.32 g, 1 mmol) in dry DMSO (10 mL) at 70 °C sodium methanethiolate (0.08 g, 1.2 mmol) was added. The mixture was stirred for 15 min. After cooling the reaction mixture was poured into 15% aqueous sodium hydroxide (30 mL) and stirred with methyl iodide (0.1 mL, 1.6 mmol). The resulting solid was filtered off, washed with water, air-dried and purified by column chromatography (silica gel 60, chloroform) to give heteropentacene **5** (0.34 g, 89%); mp 188–189 °C. ^{1}H NMR ($CDCl_3$): δ 2.69 (s, 6H, $2SCH_3$), 7.41 (m, 2H, 2H-6), 7.61 (m, 2H, 2H-5), 7.65 (m, 2H, 2H-7), 7.87 (s, 2H, 2H-4), 7.97 (m, 2H, 2H-8). MS: m/z 380 (M^+, 88.6), 333 ($M^+ - CH_3S$, 100), 318 ($M^+ - (CH_3)_2S$, 27.6]. Anal. calcd for $C_{20}H_{16}N_2S_3$: C 63.13, H 4.24, N 7.36. Found: C 63.04, H 4.29, N 7.25.

3,3′-Bis(2-oxo-1,4-dihydroquinolinyl) sulfide 6. A mixture of sulfide **5** (0.38 g, 1 mmol), ethanol (10 mL) and concentrated hydrochloric acid (10 mL) was refluxed for 72 h. After cooling the resulting solid was filtered off and dissolved in a mixture of DMSO (1 mL) and 15% aqueous sodium hydroxide (3 mL). Acidification with 10% hydrochloric acid to pH ~9 yielded a solid, which was filtered off, washed with water and air-dried to give sulfide **6** (0.30 g, 94%); mp 290–292 °C. ^{1}H NMR (DMSO-d_6): δ 7.17 (m, 2H, 2H-6), 7.36 (m, 2H, 2H-8?), 7.50 (m, 2H, 2H-7), 7.65 (m, 2H, 2H-5?), 7.90 (s, 2H, 2H-4), 12.1 (s, 2H, 2NH). MS: m/z 320 (M^+, 100), 303 ($M^+ - OH$, 10.0), 287 ($M^+ - SH$, 16.7). Anal. calcd for $C_{18}H_{12}N_2O_2S$: C 67.48, H 3.78, N 8.74. Found: C 67.33, H 3.88, N 8.62.

2,2′-Dichloro-3,3′-diquinolinyl sulfide 7. Sulfide **6** (0.32 g, 1 mmol) was refluxed in phosphoryl chloride (4 mL) for 1 h. After cooling the reaction mixture was carefully poured on ice (40 g) and alkalized with concentrated ammonia to pH ~10. The resulting solid was filtered off, washed with water and crystallized from ethanol to give sulfide **7** (0.34 g, 94%); mp 197–198 °C, lit.[13] mp 198–200 °C. ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 2H, H-6), 7.71 (m, 2H, 2H-5), 7.77 (m, 2H, 2H-7), 8.01 (s, 2H, 2H-4), 8.06 (m, 2H, 2H-8).

5,7-Diaza-6-selena-13-thiapentacene 8. A solution of sulfide **7** (0.36 g, 1 mmol) and selenourea (0.25 g, 2 mmol) in MEDG (20 mL) was stirred for 30 min at ambient temperature and then refluxed for 1 h. After cooling pale yellow needles precipitated, which were filtered off to give heteropentacene **8** (0.30 g, 81%); mp 283–284 °C. ^{1}H NMR ($CDCl_3$): δ 7.56 (m, 2H, H-2, H-10), 7.73 (m, 2H, H-3, H-9), 7.77 (m, 2H, H-1, H-11), 8.09 (m, 2H, H-4, H-8), 8.28 (s, 2H, H-12, H-14). MS: m/z 365 (M^+, 100), 286 ($M^+ - Se$, 85.2), 285 ($M^+ - SeH$, SeH, 13.9). Anal. calcd for $C_{18}H_{10}N_2SSe$: C 59.18, H 2.76, N 7.67. Found: C 59.02, H 2.84, N 7.58.

5,7-Diaza-6-oxa-13-thiapentacene 9. (*a*) A solution of sulfide **7** (0.36 g, 1 mmol) in a mixture of solvents: pyridine (16 mL), acetic anhydride (14 mL) and acetic acid (2 mL), was refluxed for 3 h. After cooling the solution was diluted with cold water (4 mL). The resulting solid was filtered off and crystallized from MEDG to give heteropentacene **9** (0.02 g, 7%).

(*b*) Sulfide **6** (0.32 g, 1 mmol) was mixed with phosphorus pentoxide (0.99 g, 7 mmol) and heated at 200 °C for 15 h. After cooling water (10 mL) was added very carefully and the resulting suspension was alkalized with ammonia. The precipitated solid was filtered off, washed with water, air-dried and purified by column chromatography (silica gel 60, chloroform) to give heteropentacene **9** (0.16g, 53%); mp 252–253 °C. ^{1}H NMR ($CDCl_3$): δ 7.47 (m, 2H, H-2, H-10), 7.64 (m, 2H, H-3, H-9), 7.68 (m, 2H, H-1, H-11), 7.95 (m, 2H, H-4, H-8), 7.99 (s, 2H, H-12, H-14). MS: m/z 302 (M^+, 100), 270 ($M^+ - S$, 19.2). Anal. calcd for $C_{18}H_{10}N_2OS$: C 71.51, H 3.33, N 9.27. Found: C 71.39, H 3.40, N 9.19.

14-Cyano-14-phenyl-5,7-diaza-13-thiapentacene 10. A mixture of sulfide **7** (0.36 g, 1 mmol), phenylacetonitrile (0.23 g; 2 mmol), potassium hydroxide (0.08 g, 2 mmol) and dry DMSO (10 mL) was stirred at 80 °C for 1 h. After cooling the reaction mixture was poured into water (40 mL). The resulting solid was filtered off and crystallized from MEDG to give heteropentacene **10** (0.33 g, 82%); mp 269–270 °C. ^{1}H NMR ($CDCl_3$): δ 6.92 (d, 2H, *o*-C_6H_5), 7.15(t, 2H, *m*-C_6H_5), 7.22 (t, 1H, *p*-C_6H_5), 7.64 (m, 2H, H-2, H-10), 7.78 (m, 2H, H-3, H-9), 7.80 (m, 2H, H-1, H-11), 8.26 (s, 2H, H-12, H-14), 8.35 (m, 2H, H-4, H-8). MS: m/z 401 (M^+, 100), 376 ($M^+ - CN$, 29.1), 324 ($M^+ - C_6H_5$, 17.3). Anal. calcd for $C_{26}H_{15}N_3S$: C 77.78, H 3.77, N 10.47. Found: C 77.67, H 3.74, N 10.48.

X-Ray analysis

The intensity data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-86)[20] and refined by full-matrix least-squares based on all unique F^2 (SHELXL-93).[21] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were 'riding' on their carbon atoms ($d_{C\text{-}H}$) = 0.93 Å, $U_{iso} = 1.2U_{eq}$ of the attached C atom.

Crystal data for **8**: $C_{18}H_{10}N_2SSe$, $M_r = 365.30$, orthorhombic, $a = 14.3960(1)$, $b = 16.1410(4)$, $c = 6.1360(6)$ Å, space group *Pnma*, $Z = 4$, $u = 1425.8$ Å^3, $T = 293(2)$, μ(Mo Kα) = 2.776 cm^{-1}. 3139 reflections were collected of which 1673 were unique and 1379 with $I \geqslant 2\sigma(I)$ ($R_{int} = 0.022$). The structure was refined to $R = 0.0449$, $R_w = 0.1006$.

Crystal data for **10**: $C_{26}H_{15}N_3S$, $M_r = 401.47$, orthorhombic, $a = 9.8440(3)$, $b = 15.5250(3)$, $c = 13.2510(6)$ Å, space group *Pnma*, $Z = 4$, $u = 2025.1$ Å^3, $T = 293(2)$, μ(Mo Kα) = 0.178 cm^{-1}. 4485 reflections were collected of which 2397 were unique and 1776 with $I \geqslant 2\sigma(I)$ ($R_{int} = 0.023$). The structure was refined to $R = 0.0459$, $R_w = 0.1078$.

CCDC reference numbers 190255 and 190256. See http://www.rsc.org/suppdata/nj/b2/b202107m/ for crystallographic files in CIF or other electronic format.

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