Unsymmetrical porphyrazines with annulated 1,2,5-thia(seleno)diazole and 3,6-diamyloxybenzene rings: synthesis, characterization and X-ray crystal structure of $H_2\{XN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ (X = S, Se)

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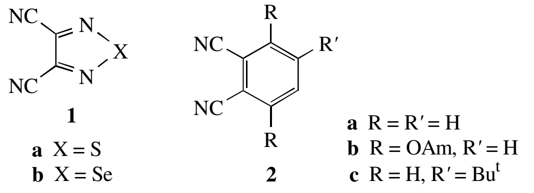
10.1070/MC2001v011n02ABEH001372

Cyclotetramerization of a mixture of 3,4-dicyano-1,2,5-thiadiazole or 3,4-dicyano-1,2,5-selenodiazole with 3,6-diamyloxyphthalodinitrile gives new unsymmetrical porphyrazines with annulated 1,2,5-thia(seleno)diazole and 3,6-diamyloxybenzene rings; the structures of the 1:3 products $H_2\{XN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ (X = S, Se) has been elucidated by single-crystal X-ray diffraction.

Unsymmetrically substituted porphyrazines combining electron-donor and electron-acceptor moieties capable of inducing strong π-electron intramolecular polarization ('push-pull' porphyrazines) are of special interest because they might exhibit second-order non-linear optical properties.[1] Recently, we have used S- and Se-containing monomeric precursors 1,2,5-thia(seleno)diazole-3,4-dicarbonitriles **1**, for the synthesis of new symmetrical phthalocyanine-like macrocycles having peripherally annulated five-membered electron-deficient heterocycles, *i.e.*, tetrakis(1,2,5-thiadiazole)porphyrazines ($\{M[(SN_2)_4Pz]\}$, M = 2H, Mg, Mn, Co, Fe, Ni, Cu and Zn)[2,3] and their Se analogues ($\{M[(SeN_2)_4Pz]\}$, M = 2H, Mg and Cu).[4]

In an extension of our work, efforts have successfully been directed to the synthesis of a new series of low-symmetry porphyrazines using mixtures of species **1** and 2,3-dicyano-5,7-diphenyl-6*H*-1,4-diazepine with phthalodinitriles **2**.[5] We report here on the synthesis and structural and spectroscopic characterization of the novel 1:3 species $H_2\{XN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ (**3** X = S, **4** X = Se) obtained from 3,4-dicyano-1,2,5-thiadiazole **1a** or 3,4-dicyano-1,2,5-selenodiazole **1b** and 3,6-diamyloxyphthalodinitrile **2b**. To our knowledge, these species are the first porphyrazine macrocycles with annulated thia- and selenodiazole rings whose structure has been elucidated by single-crystal X-ray diffraction analysis.



Scheme 1

The reaction of **1a** or **1b** with **2b** in boiling *n*-amyl alcohol in the presence of lithium or magnesium amylate gives an olive-green mixture of Li or Mg complexes of unsymmetrical porphyrazines and octa-substituted phthalocyanine, which were then demetallated with either acetic acid (Li) or trifluoroacetic acid (Mg). Column chromatography was used for the isolation of pure 1:3 compounds **3** and **4**.[†] Well-shaped black crystals of these species for X-ray analysis were obtained by the slow diffusion of acetone in a $CHCl_3$ solution. Unsymmetrical 2:2 and 3:1 species were also isolated and investigated.

Table 1 Selected bond lengths (Å) and bond angles (°) for compounds **3** and **4**.

Geometric parameter	**3** X = S	**4** X = Se
X(1)–N(9)	1.611(4)	1.774(4)
X(1)–N(10)	1.656(4)	1.840(4)
N(9)–C(2)	1.332(6)	1.336(6)
N(10)–C(3)	1.289(6)	1.273(6)
C(1)–C(2)	1.432(6)	1.427(6)
C(2)–C(3)	1.413(7)	1.435(7)
C(3)–C(4)	1.457(6)	1.462(6)
N(1)–C(1)	1.388(6)	1.396(6)
N(1)–C(4)	1.355(5)	1.357(5)
N(3)–C(5)	1.352(6)	1.345(6)
N(3)–C(12)	1.390(6)	1.412(6)
N(5)–C(13)	1.391(6)	1.393(5)
N(5)–C(20)	1.344(5)	1.344(5)
N(7)–C(21)	1.354(5)	1.337(6)
N(7)–C(28)	1.387(6)	1.388(6)
N(9)–X(1)–N(10)	102.0(2)	96.4(2)
C(1)–N(1)–C(4)	109.7(3)	110.1(4)
C(5)–N(3)–C(12)	111.6(4)	111.9(4)
C(13)–N(5)–C(20)	107.4(4)	107.3(4)
C(21)–N(7)–C(28)	111.9(4)	111.9(4)

Crystal data for two macrocycles **3** and **4** show strong similarities.[‡] Thus, the top and side views of S-containing species **3** are shown in Figure 1. Bond distances and angles within the macrocycle indicate an extended π-electron delocalization and are consistent with the presence of the internal H atoms directly localized on N(3) and N(7) as shown by a difference Fourier map. The structural data (Table 1) of the annulated heterocycles in **3** and **4** are close to the average values found for other quasi-aromatic systems containing 1,2,5-thiadiazole and 1,2,5-seleno-

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[†] *Synthetic procedures.* $H_2\{SN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ **3**: the refluxing of **1a** (0.9 g, 6.6 mmol) and **2b** (1.8 g, 6 mmol) with lithium amylate (40 mmol, from 0.28 g of Li) in *n*-amyl alcohol (30 ml) leads to an olive-green mixture, which, after addition of acetic acid (5 ml), was poured into acetone (150 ml) to give a dark green precipitate. It was filtered off, washed with acetone and extracted with benzene in a Soxhlet apparatus. The volume of the benzene extract was reduced, and it was chromatographed on aluminium oxide (Reakhim, chromatographic grade). The octaamyloxy substituted phthalocyanine $H_2Pc(OAm)_8$ was eluted with benzene, and 1:3 compound $H_2\{SN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ **3** with tetrachloroethane, from which it was precipitated with acetone (yield 46 mg, 2.2%). ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ: 7.66 (s, 2H), 7.65 (s, 2H, arom.) and 7.51 (s, 2H, arom.), 4.82 (t, 4H, α-CH_2), 4.78 (t, 4H, α-CH_2) and 4.67 (t, 4H, α-CH_2), 2.42 (m, 4H, β-CH_2) and 2.22 (m, 8H, β-CH_2), 1.75–1.40 (m, 24H, γ-CH_2, δ-CH_2), 1.11 (t, 6H, Me), 0.97 (t, 6H, Me) and 0.86 (t, 6H, Me), –0.25 (s, 2H, NH). UV-VIS [CH_2Cl_2, λ_{max}/nm (log ε)]: 329 (4.96), 408 sh, 458 (4.29), 520 sh, 663 sh, 699 sh, 730 (5.02), 766 (5.21). MS (FAB) *m/z*: 1040 $[M + H]^+$ (100%). Found (%): C, 66.70; H, 7.33; N, 13.47; S, 2.56. Calc. for $C_{58}H_{74}N_{10}O_6S$ (%): C, 67.03; H, 7.18; N, 13.48; S, 3.08.

$H_2\{SeN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ **4**: the synthetic procedure for **4** is similar to that used for **3** with the use of Mg amylate as a tetramerising agent and CF_3COOH for demetallation. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ: 7.51 (s, 2H, arom.), 7.50 (s, 2H, arom.) and 7.45 (s, 2H, arom.), 4.81 (m, 8H, α-CH_2) and 4.68 (t, 4H, α-CH_2), 2.40 (m, 4H, β-CH_2) and 2.21 (m, 8H, β-CH_2), 1.80–1.40 (m, 24H, γ-CH_2, δ-CH_2), 1.10 (t, 6H, Me), 0.94 (t, 6H, Me) and 0.87 (t, 6H, Me), –0.11 (s, 2H, NH). UV-VIS [CH_2Cl_2, λ_{max}/nm (log ε)]: 334 (5.11), 458 (4.26), 527 sh, 657 (4.52), 709 (4.88), 735 (4.90), 785 (5.19). MS (FAB) *m/z*: 1086 $[M + H]^+$ (100%). Found (%): C, 63.85; H, 7.06; N, 12.95. Calc. for $C_{58}H_{74}N_{10}O_6Se$ (%): C, 64.13; H, 6.87; N, 12.89.

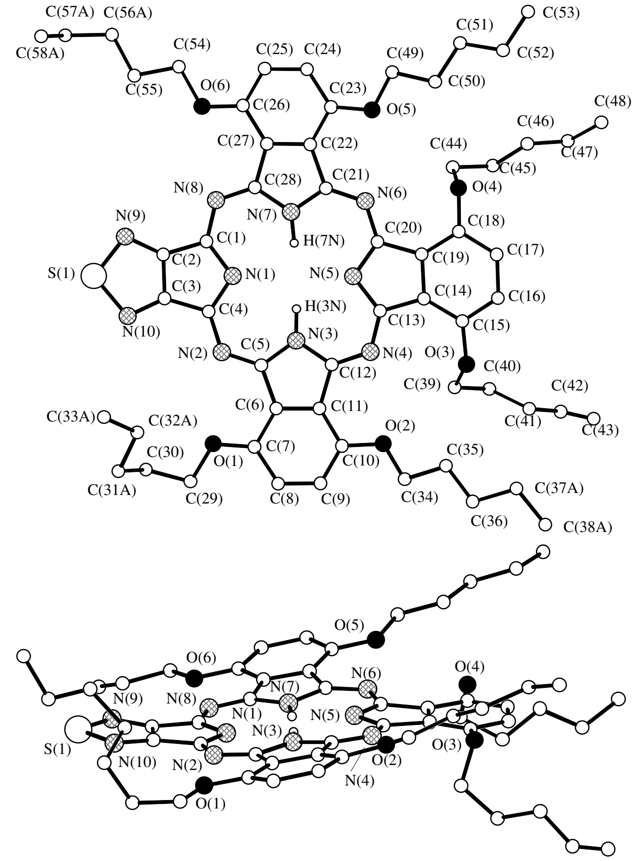

Figure 1 Top and side views of compound **3**. Disorder associated to some alkyl chains has been omitted for clarity.

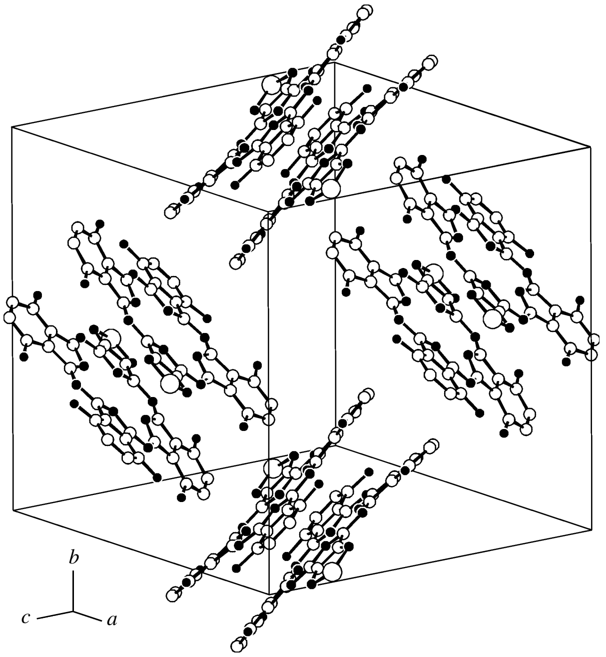

Figure 2 Crystal packing in **3**. Alkyl chains are omitted for clarity.

diazole rings.[6] As to species **3** (the following observations are also valid for species **4**), the internal substantially planar N$_4$ core shows significantly different distances for the opposite N atoms, N(1)···N(5) [3.861(4) Å] and N(3)···N(7) [4.100(5) Å]. The observed planarity is consistent with the presence of two bifurcated hydrogen bonds involving H(3N) [N(1)···H(3N), 2.30 Å N(5)···H(3N), 2.09 Å; N(1)···H(3N)···N(5), 123°] and H(7N) atoms [N(1)···H(7N), 2.22 Å; N(5)···H(7N), 2.19 Å; N(1)···H(7N)···N(5), 122°]. The NC$_4$N$_2$S moiety and three isoindole units, distinguishable as containing N(1) and N(3), N(5) and N(7) atoms, respectively, although singly nearly planar, form, in the order given, dihedral angles with the N$_4$ plane of 10.1(1), 4.7(1), 8.0(1), and 13.5(1)°. Noticeably, the NC$_4$N$_2$S moiety and the opposite isoindole ring, being nearly coplanar [dihedral angle of 10.6(1)°], show a definite separation between their planes (*ca.* 0.66 Å). The distortion from planarity of the entire macrocycle is its most interesting structural feature. Such a type of distortion is much less evident in the octa-substituted phthalocyanines H$_2$Pc(OAm^i)$_8$ (ref. 7) and H$_2$Pc(OAm)$_8$.[8] Hence, the observed distortion in the above species cannot be related to the steric interaction between adjacent alkoxy chains; rather, it might be assigned to the strong dipole polarization of the π-electron system of the macrocycle arising from the 'push-pull' interaction between the electron-deficient thiadiazole ring and the strongly electron-donating alkoxy-substituted benzene rings. The intermolecular dipole–dipole interaction determines the crystal packing

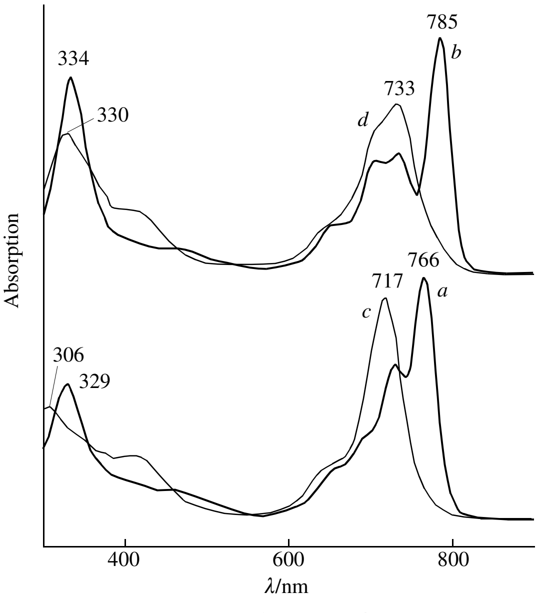

Figure 3 UV–VIS spectra of (*a*) **3** and (*b*) **4** and their deprotonated species (*c* and *d*, respectively) in CH$_2$Cl$_2$ (*a*, *b*), in the presence of 1% tbaOH in CH$_2$Cl$_2$ (*c*, *d*).

[‡] *Crystal data for* **3**: C$_{58}$H$_{74}$N$_{10}$O$_6$S, $M = 1039.3$, monoclinic, space group $P2_1/c$, $a = 17.314(1)$ Å, $b = 19.122(2)$ Å, $c = 17.794(1)$ Å, $\beta = 103.07(1)°$, $V = 5738.6(8)$ Å^3, $Z = 4$, $d_{\text{calc}} = 1.203$ g cm^{-3}, $F(000) = 2224$, λ(MoKα) = 0.71073 Å, μ(MoKα) = 1.08 cm^{-1}. For 5354 unique observed reflections [$I > 2\sigma(I)$] collected at 295 K on a Bruker AXS Smart 100 CCD ($5 < 2\theta < 58°$), the final R is 0.079 ($wR_2 = 0.188$).

Crystal data for **4**: C$_{58}$H$_{74}$N$_{10}$O$_6$Se, $M = 1086.2$, monoclinic, space group $P2_1/c$, $a = 17.305(2)$ Å, $b = 19.084(3)$ Å, $c = 17.882(2)$ Å, $\beta = 102.90(2)°$, $V = 5756.5(14)$ Å^3, $Z = 4$, $d_{\text{calc}} = 1.253$ g cm^{-3}, $F(000) = 2296$, λ(CuKα) = 1.54178 Å, μ(CuKα) = 13.35 cm^{-1}. For 3419 unique observed reflections [$I > 2\sigma(I)$] collected at 295 K on an Enraf-Nonius CAD-4 diffractometer ($5 < 2\theta < 140°$), the final R is 0.062 ($wR_2 = 0.170$ for 8357 unique reflections having $I > 0$ used in the refinement). The structures of **3** and **4** were solved by direct methods and anisotropically refined for all non-hydrogen atoms except for the disordered ones. Some carbon atoms of the alkyl chains showed rather high thermal parameters indicating the presence of a disorder. The best fit was obtained by splitting the C(31)–C(33), C(37), C(38), C(56)–C(58) carbon atoms over two positions (called A and B) isotropically refined with site occupation factors for **3** of 0.5 for C(31)–C(33), C(56)–C(58); 0.6 and 0.4 for the A and B positions, respectively, of C(37), C(38); and for **4** of 0.5 for C(31)–C(33); 0.7 and 0.3 for the A and B positions, respectively, of C(56), C(57); 0.65 and 0.35 for the A and B positions, respectively, of C(56)–C(58). The hydrogen atoms associated to the nitrogen atoms and to the isoindole units were located from a difference Fourier map, while those associated to the aliphatic chains were put in geometrically calculated positions. All the H atoms were introduced as fixed contributors at the last stage of refinement ($U_{\text{iso}} = 0.12$ Å^2 for **3** and 0.10 Å^2 for **4**). Atomic coordinates, bond lengths, bond angles and thermal parameters for both **3** and **4** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/80.

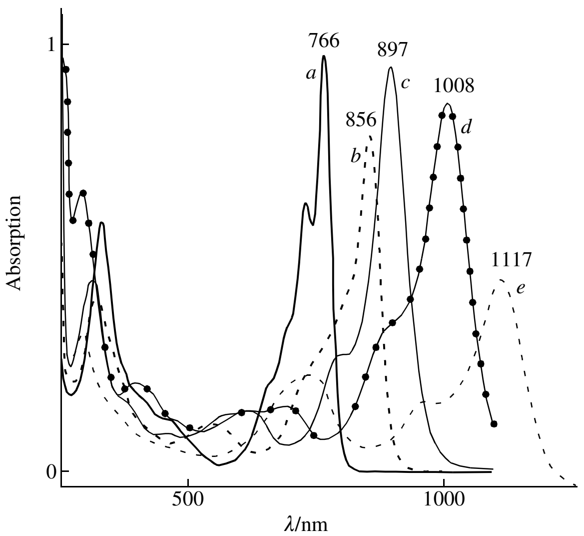

Figure 4 UV–VIS spectra of (*a*) $H_2\{SN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ (6×10^{-6} mol dm^{-3}) and (*b*)–(*e*) protonated species in: (*a*) CH_2Cl_2, (*b*) 5% HCOOH in CH_2Cl_2, (*c*) HCOOH, (*d*) 35% H_2SO_4 in AcOH, (*e*) 96% H_2SO_4. The Q-band maxima are indicated on the graph, the B-band maxima are 329, 317, 312, 293 and 296 nm for spectral curves (*a*)–(*e*), respectively.

— the molecules are arranged in centrosymmetric parallel pairs (Figure 2). As a consequence, the thiadiazole ring of one molecule in the pair is located over the centrosymmetric isoindole unit. The sterically less crowded conformation allows the N_4 cores of the molecules in a pair to approach at an average interplanar distance of 3.273(15) Å [3.265(11) Å for the Se analogue].

The UV–VIS spectra of **3** and **4** in CH_2Cl_2 [Figure 3(*a*),(*b*)] are characteristic for highly conjugated porphyrazine chromophores with unsymmetrically attached strongly electron-donating substituents: in addition to the B-band in the UV region (329 nm for **3** and 334 nm for **4**), intense split Q-bands are observed in the near IR region (700–800 nm). In the case of **3**, the maximum of the long-wave Q_x component is found at 766 nm, whereas for **4**, owing to the presence of the less electronegative Se atom, the corresponding absorption is shifted bathochromically to 785 nm. Deprotonation of **3** and **4** and formation of the corresponding dianions occurring in the presence of tetrabutylammonium hydroxide, (tbaOH), whilst leaving unchanged the C_{2v} symmetry of the chromophore, results [Figure 3(*c*),(*d*)] in a hypsochromic shift of the Q_x component (to 717 nm for **3** and 733 nm for **4**) and associated decrease of the splitting of the Q-band (especially for **3**). In the UV region, along with the B-band (306 nm for **3** and 330 nm for **4**), a better resolved less intense band due to the $n \rightarrow \pi^*$ transition appears at *ca.* 405 nm. A progressive increase in the acidity of the medium results, as is illustrated for **3** in Figure 4, in the gradual bathochromic shifts of the Q-band maxima (766 → 856 → 897 → 1008 → 1117 nm) due to the consequent acid–base interaction with all four *meso*-nitrogens and appearence of four corresponding acid forms.

We are grateful to A. D'Arcangelo ('Tor Vergata', Rome) for the assistance in measuring the mass spectra. This work was supported by the Ministry of Education of the Russian Federation (grant no. SPb 97-0-9.4-362) and by the Italian grant Murst 9903263473.

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Received: 7th September 2000; Com. 00/1698