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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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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.

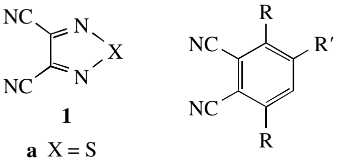
Unsymmetrically substituted porphyrazines combining electron-donor and electron-acceptor moieties capable of inducing strong π-electron intramolecular polarization ('push-pull' porphyrazines) are of special interest because they might exhibit second-order non-linear optical properties.[1] Recently, we 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.

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)



1
a X = S
b X = Se

2

a R = R′ = H
b R = OAm, R′ = H
c R = H, R′ = Bu^t

Scheme 1

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.

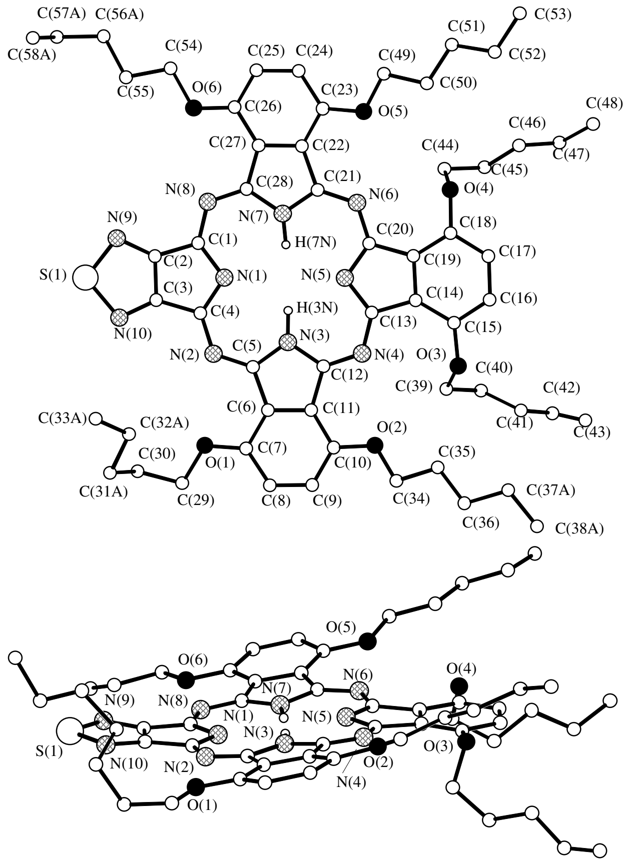

Figure 1 Top and side views of compound **3**. Disorder associated to some alkyl chains has been omitted for clarity.

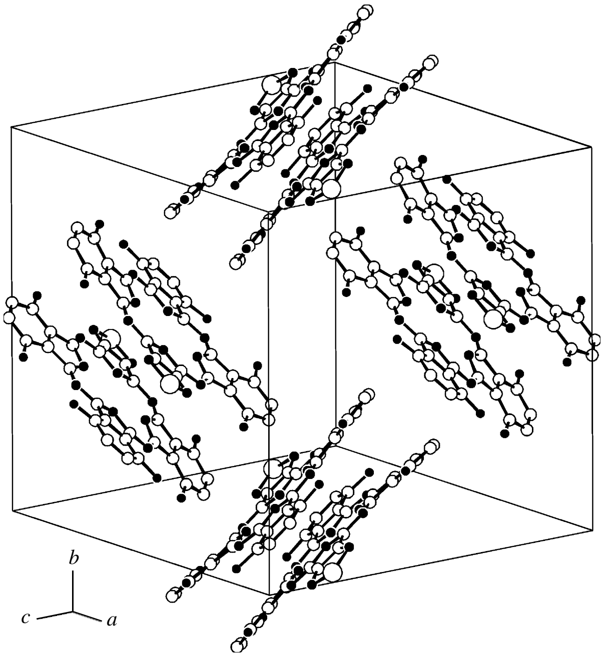

Figure 2 Crystal packing in **3**. Alkyl chains are omitted for clarity.

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_4N_2S 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_4N_2S 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 $H_2Pc(OAm^i)_8$ (ref. 7) and $H_2Pc(OAm)_8$.[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

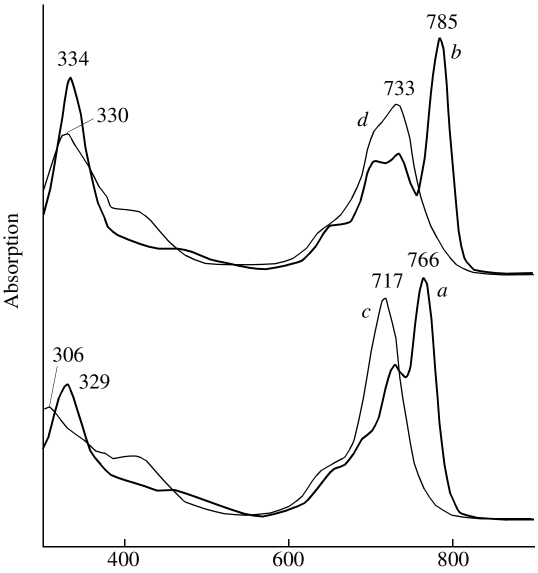

Figure 3 UV–VIS spectra of (*a*) **3** and (*b*) **4** and their deprotonated species (*c* and *d*, respectively) in CH_2Cl_2 (*a*, *b*), in the presence of 1% tbaOH in CH_2Cl_2 (*c*, *d*).

[‡] *Crystal data for* **3**: $C_{58}H_{74}N_{10}O_6S$, $M = 1039.3$, 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, $Z = 4$, $d_{calc} = 1.203$ 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**: $C_{58}H_{74}N_{10}O_6Se$, $M = 1086.2$, 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, $Z = 4$, $d_{calc} = 1.253$ 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 ($U_{iso} = 0.12$ 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.

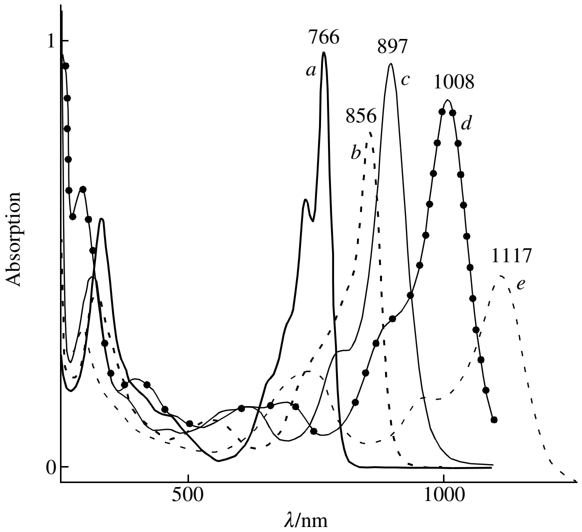

Figure 4 UV–VIS spectra of (*a*) $H_2\{SN_2\}\{3,6\text{-}(OAm)_2Bz\}_3Pz$ (6×10^{-6} mol dm^{-3}) and (*b*)–(*e*) protonated species in: (*a*) CH_2Cl_2, (*b*) 5% HCOOH in CH_2Cl_2, (*c*) HCOOH, (*d*) 35% H_2SO_4 in AcOH, (*e*) 96% H_2SO_4. The Q-band maxima are indicated on the graph, the B-band maxima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

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