Stepwise Synthesis of Substituted Dicyanotriazolehemiporphyrazines. A Regioselective Approach to Unsymmetrically Substituted Hemiporphyrazines†

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Received April 17, 1996

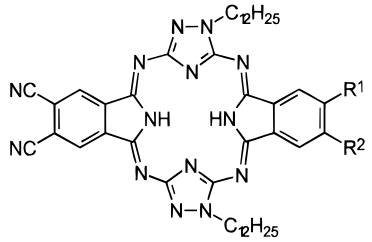
Introduction

Hemiporphyrazines,[1] two-dimensional π-conjugated macrocycles related to phthalocyanines,[2] have been proposed as targets for the construction of semiconducting[1c,d,3] and nonlinear optical materials.[4]

Recently, we have reported the synthesis of highly soluble crowned-triazolehemiporphyrazines[5] and related triazolephthalocyanines,[6] both able to self-organize in Langmuir−Blodgett films.[7,8] The long-range goal of our research is to develop substances and processable organic materials with unusual physical properties.[9]

Although symmetrically substituted hemiporphyrazines are well documented,[1,5] there are no reports on the selective preparation of unsymmetrically substituted compounds.[10] Thus, for example, the one-step statistical condensation of two differently substituted diiminoisoindolines with an adequate diaminoheteroaromatic compound (e.g., 2,5-diamino-1,2,4-triazole) affords a mixture of the corresponding statistical distribution compounds.[11] Moreover, hemiporphyrazines are obtained as regioisomer mixtures difficult to separate if one or the two reagents are unsymmetrically substituted.[5]

Herein we describe a stepwise general method for the preparation of substituted dicyanotriazolehemiporphyrazines **1**. The method represents the first regioselective approach to unsymmetrically substituted hemiporphyrazines. The preparation of these compounds is interesting, not only from a preparative point of view but also because this kind of non-centrosymmetric conjugated macrocycles with a "push−pull" substitution pattern are targets for the study of second-order nonlinear optical properties.[12] On the other hand, the functionalization of the compounds with *o*-cyano groups allows their use as building blocks for the stepwise assembly of ladder oligomers.[1c,d,13]



1 **1a, 2a**: R^1, R^2 = CN
1b, 2b: R^1 = ^{t}Bu; R^2 = H
1c, 2c: R^1 = OC_8H_{17}; R^2 = H
1d, 2d: R^1 = NO_2; R^2 = H

Results and Discussion

The reaction of 5,6-dicyano-1,3-diiminoisoindoline (**2a**)[14] with an excess of 1-dodecyl-3,5-diamino-1,2,4-triazole (**3**)[1a] afforded, as major components, a mixture of two isomeric three-unit compounds **4a** (*syn*) and **4b** (*anti*) in a 7:1 molar ratio in 55% yield,[15] as well as a mixture of hemiporphyrazines **1a** and **5** in 5% yield. The compounds were separated by column chromatography. Only traces (<0.5%) of the third possible isomer **4c** were isolated from the reaction mixture (Scheme 1).

The relative ratios of compounds **4a**−**c** are consistent with the differential reactivity of the amino groups in the precursor **3**, which would be originated by the steric hindrance of the dodecyl chain over the neighboring amino moiety. In this way, the formation of the major isomer **4a** involves a nucleophilic attack of the less hindered amino group of two triazole units on the iminic double bonds of the diiminoisoindoline.

The structural assignment of the three-unit compounds **4a**−**c** was made by ^{1}H NMR spectroscopy. The *syn*-isomer **4a** shows in the spectrum taken in $CDCl_3$ a single signal for the aromatic protons and an only triplet for the first methylene group of the aliphatic chains linked to the triazole, due to its C_{2v} symmetry. On the other hand, the *anti*-isomer **4b** exhibits two singlets for the aromatic protons and also two triplets corresponding to two kinds of methylene groups. The downfield-shifted

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† Dedicated to Professor Michael Hanack on the occasion of his 65th birthday.

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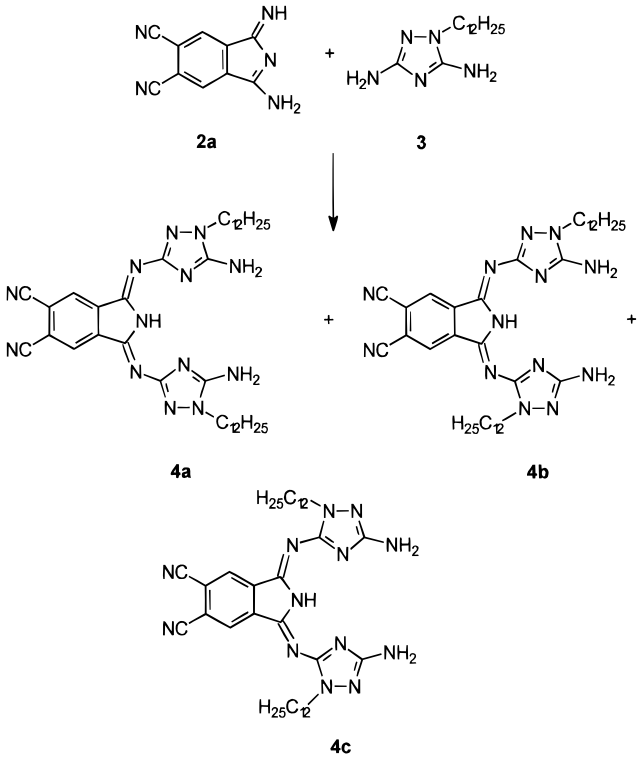
(14) Ouyang, J; Shigehara, K.; Yamada, A.; Anson, F. C. *J. Electroanal. Chem.* **1991**, *297*, 489.

(15) Three-unit compounds related to **4** having two pyridine units instead of the triazole ones have been described; see, for example: (a) Siegl, W. O. *J. Org. Chem.* **1977**, *42*, 1872. (b) Siegl, W. O. *J. Heterocycl. Chem.* **1981**, *18*, 1613.

S0022-3263(96)00704-9 CCC: $12.00

Scheme 1. Synthesis of Three-Unit Compounds 4a−c



triplet has to be assigned to the methylene linked to the triazole, which is in a position adjacent to that occupied by an imino group. The same chemical shift is observed for the only triplet that appears in the ^{1}H NMR spectra in $CDCl_3$ of **4c** and of hemiporphyrazines **1a** and **5** (see below) for the same kind of protons. In these compounds, both methylene groups of the two lipophilic chains are adjacent to imino moieties. Nuclear Overhauser experiments were carried out over compound **4a** in order to support the structural assignment. However, the results did not give conclusive evidence due to the small effects observed.

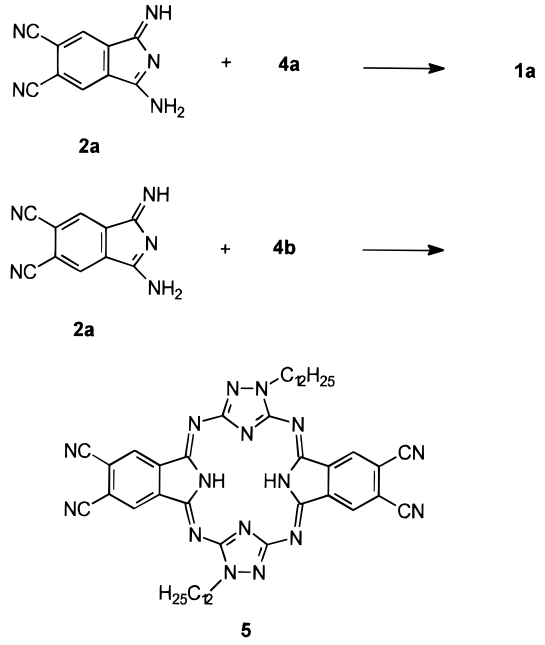
Compounds **4a** and **4b** were reacted with diiminoisoindoline **2a** in 2-ethoxyethanol at 100 °C to afford, respectively, triazolehemiporphyrazines **1a** and **5** as the only reaction product in each case, in ca. 70% yield (Scheme 2). Both hemiporphyrazines **1a** and **5** exhibit in the ^{1}H NMR spectra taken in *d*-TFA two singlets for the aromatic protons. The three-unit compounds **4** are stable under the reaction conditions. However, when these compounds are heated at higher temperatures (e.g., refluxing 2-ethoxyethanol) in the absence of diiminoisoindoline, decomposition takes place in each case giving rise to some amount of a mixture of the macrocycles **1a** and **5**.[3,16]

On the other hand, the one-pot statistical condensation of **2a** and **3** in equimolar amounts afforded a mixture of **1a** and **5** in a 4:1 ratio in 50% yield, as was pointed out by the presence of four aromatic signals in the ^{1}H NMR spectrum registered in *d*-TFA and the corresponding integrals' evaluation.

The three-unit compound **4a** was also reacted with a variety of monosubstituted diiminoisoindolines **2b**−**d**[17] in the same conditions mentioned above to afford the

(16) Rodríguez-Morgade, S.; Torres, T. *Inorg. Chim. Acta* **1995**, *230*, 153.

Scheme 2. Synthesis of Triazolehemiporphyrazines 1 and 5



corresponding unsymmetrically substituted triazolehemiporphyrazines **1b**−**d** in good yield (65−85%). The asymmetry of the triazolehemiporphyrazines **1b**−**d** is reflected in the ^{1}H NMR spectra in $CDCl_3$, which show two different singlets for the aromatic protons of the dicyanoisoindole subunit in the case of hemiporphyrazines **1b**,**c**. This difference in chemical shifts cannot be appreciated in the case of **1d**. It is noticeable that two signals for compounds **1** and one for compound **5** appear between 15−16 ppm, which can be assigned to the two protons of the central core.[18] Their chemical shifts depend on the electronic character of the substituents on the isoindoline moieties. Hence, in the case of **1a** and **5** having four electron-withdrawing substituents, a deshielding of ca. 1 ppm is experienced by the mentioned protons, with respect to the shifts observed for the same kind of signals in the ^{1}H NMR spectra of hemiporphyrazines bearing four donor groups.[5]

The UV−vis spectra in $CHCl_3$ of triazolehemiporphyrazines **1** and **5** are similar to those already described by us for related compounds.[5] As a function of the kind of peripheral substitution remarkable changes of the wavelength values of the absorption bands are observed. Thus, for example, crowned triazolehemiporphyrazines bearing four alkoxy groups on the isoindole moieties[5] show the highest wavelength band at ca. 380 nm, whereas this band undergoes a batochromic shift in compounds **1a** (425 nm) and **1d** (419 nm) substituted, respectively, by four and three electron-withdrawing groups. Intermediate values are obtained for "push−pull" substituted compounds **1b** (406 nm) and **1c** (405 nm) (Figure 1).

(17) (a) For 5-*tert*-butyl-1,3-diiminoisoindoline (**2b**): Larner, B. W.; Peters, A. T. *J. Am. Chem. Soc.* **1952**, 680. (b) For 5-(octyloxy)-1,3-diimnoisoindoline (**2c**): Leznoff, C. C.; Marcuccio, S. M.; Greenberg, S.; Lever, A. B. P. *Can. J. Chem.* **1985**, *63*, 623. (c) For 5-nitro-1,3-diiminoisoindoline (**2d**): Young, J. G.; Onyebuagu, W. *J. Org. Chem.* **1990**, *55*, 2155.

(18) The very low-field resonance of the inner protons of the triazolehemiporphyrazine core is consistent with the antiaromaticity of these compounds.[1a] The same kind of protons appear in the ^{1}H NMR spectra of structurally related aromatic phthalocyanines at very high field (ca. −3 to −5 ppm).

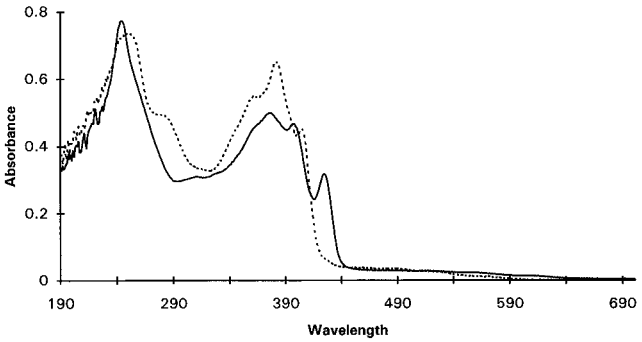


Figure 1. UV/vis spectra of hemiporphyrazines **1a** (continuous line) and **1c** (dashed line) in chloroform at ca. 9×10^{-6} mol L^{-1}.

In summary, we have developed the first selective synthetic method for preparing unsymmetrically substituted triazolehemiporphyrazines. The NLO properties of these compounds as a function of the electronic character of the substituents are being presently studied. Efforts are being also made for the preparation of mixed hemiporphyrazine−phthalocyanine systems, starting from compounds **1**.

Experimental Section

Preparation of 5,6-Dicyano-1,3-bis[[(5′-amino-1′-dodecyl)-1′,2′,4′-triazol-3′-yl]imino]isoindoline (4a), 5,6-Dicyano-1-[[(5′-amino-1′-dodecyl)-1′,2′,4′-triazol-3′-yl]imino]-3-[[(3′′-amino-1′′-dodecyl)-1′′,2′′,4′′-triazol-5′′-yl]imino]-isoindoline (4b), and 5,6-Dicyano-1,3-bis[[(3′-amino-1′-dodecyl)-1′,2′,4′-triazol-5′-yl]imino]isoindoline (4c). A mixture of **2a**[14] (0.23 g, 1.18 mmol) and **3**[1a] (1.26 g, 4.71 mmol) in butanol (20 mL) was refluxed for 24 h. After vacuum evaporation of the solvent, the crude reaction mixture was chromatographed on deactivated alumina (5%) (CH_2Cl_2/MeOH 100:1). The first eluted component was identified as a mixture of hemiporphyrazines **1a** and **5** (described below) (yield < 5%). Afterwards, compounds **4c** and **4b** were eluted, and subsequently, the amount of MeOH was gradually changed to CH_2Cl_2/MeOH 50:1 in order to separate **4a**. Some amount of starting compound **3** was eluted in the final fractions. Trituration with hot methanol afforded the pure products.

Data for **4c**: second eluted component; yield < 0.5%, orange-reddish powder; mp > 250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.40 (s, 2H), 4.2 (m, 4H), 1.9 (m, 4H), 1.2 (m, 36H), 0.87 (m, 6H) ppm; FAB-MS (3-NOBA) *m*/*z* 696 [(M + H)$^+$, 100].

Data for **4b**: third eluted component; yield 7%, orange-reddish powder; mp > 250 °C; ^{1}H NMR (200 MHz, d_6-DMSO) δ 12.6 (bs, 1H), 8.74 (s, 1H), 8.66 (s, 1H), 6.5 (bs, 2H), 5.6 (bs, 2H), 4.16 (t, J = 6.5 Hz, 2H), 3.93 (t, J = 6.5 Hz, 2H), 1.7 (m, 4H), 1.2 (m, 36H), 0.81 (m, 6H) ppm; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.36 (s, 1H), 4.5 (bs, 4H), 4.20 (t, J = 7.5 Hz, 2H), 3.94 (t, J = 7.5 Hz, 2H), 1.9 (m, 4H), 1.3 (m, 36H), 0.87 (m, 6H) ppm; ^{13}C NMR (75 MHz, d_6-DMSO) δ 162.0, 159.3, 154.8, 151.9, 148.8, 147.5, 138.6, 138.0, 128.3, 128.1, 117.5, 117.2, 115.7, 45.9, 45.3, 31.4−14.1 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 696 [(M + H)$^+$, 100]; IR (KBr) ν 3414−3378 (NH_2), 2920, 2850, 2239 (C≡N), 1648, 1630 (C═N), 1558, 1532, 1499, 1469, 1372, 1277 cm^{-1}. Anal. Calcd for $C_{38}H_{57}N_{13}\cdot H_2O$: C, 63.92; H, 8.33; N, 25.50. Found: C, 64.19; H, 7.94; N, 25.64.

Data for **4a**: fourth eluted component; yield 47%, orange powder; mp > 250 °C; ^{1}H NMR (200 MHz, d_6-DMSO) δ 12.51 (s, 1H), 8.63 (s, 2H), 6.4 (bs, 4H), 3.92 (t, J = 6.5 Hz, 4H), 1.7 (m, 4H), 1.2 (m, 36H), 0.81 (m, 6H) ppm; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.43 (s, 2H), 4.4 (bs, 4H), 3.92 (t, J = 7.5 Hz, 4H), 1.9 (m, 4H), 1.3 (m, 36H), 0.87 (m, 6H) ppm; ^{13}C NMR (75 MHz, d_6-DMSO) δ 158.2, 154.0, 148.6, 138.3, 128.0, 117.4, 115.7, 46.1, 31.4−14.1 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 696 [(M + H)$^+$, 100]; IR (KBr) ν 3435−3375 (NH_2), 2920, 2850, 2238 (C≡N), 1647, 1630 (C═N), 1558, 1505, 1465, 1370, 1277 cm^{-1}. Anal. Calcd for $C_{38}H_{57}N_{13}\cdot H_2O$: C, 63.92; H, 8.33; N, 25.50. Found: C, 64.06, H, 7.99; N, 25.25.

General Procedure for the Preparation of Triazolehemiporphyrazines 1a−d and 5. A mixture of **4a** or **4b** (0.10 g, 0.14 mmol) and the corresponding diiminoisoindoline **2** (0.16 mmol) in 2-ethoxyethanol (1 mL) was stirred at 100 °C for 24 h. Methanol (30 mL) was added, and after centrifugation, the isolated solid was triturated with hot methanol and filtered.

Data for **8,21-Didodecyl-2,3,14,15-tetracyano-5,24:12,17-diimino-7,10:19,22-dinitrilo-8*H*,20*H*-dibenz[*f*,*p*][1,2,4,9,11,-12,14,19]octaazacycloeicosine** (**1a**): yield 74%, brown powder; mp > 250 °C; ^{1}H NMR (200 MHz, *d*-TFA) δ 8.74 (s, 2H), 8.57 (s, 2H), 4.5 (m, 4H), 2.0 (m, 4H), 1.3 (m, 36H), 0.9 (m, 6H) ppm; ^{1}H NMR (200 MHz, $CDCl_3$) δ 15.9 (bs, 1H), 15.6 (bs, 1H), 8.26 (s, 2H), 8.24 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 1.9 (m, 4H), 1.2 (m, 36H), 0.87 (m, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.0, 154.8, 150.8, 138.3, 137.9, 128.1, 128.0, 119.5, 118.7, 114.6, 114.2, 47.6, 31.9−14.1 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 857 [(M + H)$^+$, 100]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 244 (4.92), 364 sh, 376 (4.73), 397 (4.70), 425 (4.53) nm; IR (KBr) ν 3280, 2923, 2852, 2232 (C≡N), 1662 (C═N), 1483, 1294, 761, 685 cm^{-1}. Anal. Calcd for $C_{48}H_{56}N_{16}\cdot H_2O$: C, 65.88; H, 6.68; N, 25.60. Found: C, 66.07, H, 6.30; N, 25.56.

Data for **1b**: yield 87%, brown-reddish powder; mp > 250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 15.7 (bs, 1H), 15.2 (bs, 1H), 8.02 (s, 1H), 7.99 (s, 1H), 7.7−7.5 (m, 3H), 4.1 (m, 4H), 1.9 (m, 4H), 1.45 (s, 9H), 1.3 (m, 36H), 0.89 (m, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 162.3, 157.9, 155.4, 154.6, 154.2, 150.1, 138.3, 133.9, 131.1, 130.7, 127.3, 122.5, 119.7, 117.6, 114.5, 47.0, 35.9, 31.9−14.1 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 863 [(M + H)$^+$, 100]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 243 (4.97), 279 (4.68), 345 sh, 360 (4.85), 379 (4.85), 406 (4.62) nm; IR (KBr) ν 3295, 2924, 2853, 2234 (C≡N), 1656 (C═N), 1487, 1294, 762, 675 cm^{-1}. Anal. Calcd for $C_{50}H_{66}N_{14}\cdot H_2O$: C, 68.15; H, 7.78; N, 22.25. Found: C, 68.06; H, 7.72; N, 22.16.

Data for **1c**: yield 86%, brown-reddish powder; mp > 250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 15.7 (bs, 1H), 15.2 (bs, 1H), 7.87 (s, 1H), 7.77 (s, 1H), 7.39 (d, J = 8 Hz, 1H), 6.98 (d, J = 8 Hz, 1H), 6.77 (s, 1H), 4.1 (m, 6H), 1.9 (m, 4H), 1.7 (m, 2H), 1.3 (m, 48H), 0.9 (m, 9H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.3, 162.2, 162.0, 155.5, 155.2, 153.6, 149.8, 137.7, 135.8, 126.9, 125.0, 124.2, 117.9, 117.2, 114.4, 108.5, 69.4, 46.9, 31.9−14.1 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 935 [(M + H)$^+$, 100]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 251 (4.93), 282 sh, 362 sh, 382 (4.88), 405 (4.72) nm; IR (KBr) ν 3293, 2923, 2852, 2233 (C≡N), 1666 (C═N), 1488, 1295, 759, 678 cm^{-1}. Anal. Calcd for $C_{54}H_{74}N_{14}O\cdot H_2O$: C, 68.03; H, 8.03; N, 20.57. Found: C, 68.40; H, 7.70; N, 20.58.

Data for **1d**: yield 66%, brown powder; mp > 250 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 15.7 (bs, 1H), 15.6 (bs, 1H), 8.63 (s, 1H), 8.50 (d, J = 8.5 Hz, 1H), 8.26 (s, 2H), 8.00 (d, J = 8.5 Hz, 1H), 4.2 (m, 4H), 1.9 (m, 4H), 1.2 (m, 36H), 0.9 (m, 6H) ppm; ^{13}C NMR (50 MHz, *d*-TFA) δ 159.1, 159.0, 158.6, 157.4, 154.0, 153.9, 153.7, 141.1, 137.4, 137.0, 131.9, 131.1, 127.1, 123.2, 121.2, 118.3, 114.5, 50.3, 33.7−14.7 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 852 [(M + H)$^+$, 100]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 247 (4.84), 361 sh, 369 (4.72), 391 (4.67), 419 (4.42) nm; IR (KBr) ν 3283, 2923, 2852, 2233 (C≡N), 1665 (C═N), 1540, 1483, 1346 (NO_2), 1296, 759, 681 cm^{-1}. Anal. Calcd for $C_{46}H_{57}N_{15}O_2\cdot H_2O$: C, 63.50; H, 6.83; N, 24.14. Found: C, 63.80, H, 6.42, N, 24.15.

Data for **5**: yield: 68%, brown powder; mp > 250 °C; ^{1}H NMR (200 MHz, *d*-TFA) δ 8.75 (s, 2H), 8.63 (s, 2H), 4.5 (m, 4H), 2.0 (m, 4H), 1.3 (m, 36H), 0.9 (m, 6H) ppm; ^{1}H NMR (200 MHz, $CDCl_3$) δ 15.8 (bs, 2H), 8.30 (s, 2H), 8.22 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 1.9 (m, 4H), 1.2 (m, 36H), 0.87 (m, 6H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 163.0, 154.8, 150.8, 138.3, 137.9, 128.1, 128.0, 119.5, 118.7, 114.6, 114.2, 47.6, 31.9−14.1 ppm, several signals; FAB-MS (3-NOBA) *m*/*z* 857 [(M + H)$^+$, 100]; UV/vis ($CHCl_3$) λ_{max} (log ϵ/L mol^{-1} cm^{-1}) 244 (4.86), 359 (4.58), 375 (4.63), 398 (4.62), 426 (4.46) nm; IR (KBr) ν 3291, 2921, 2851, 2233 (C≡N), 1661 (C═N), 1485, 1469, 1296, 762, 687 cm^{-1}. Anal. Calcd for $C_{48}H_{56}N_{16}\cdot H_2O$: C, 65.88; H, 6.68; N, 25.60. Found: C, 66.18; H, 6.41; N, 25.32.

Statistical Condensation of 2a and 3. Regioisomeric Mixture of Triazolehemiporphyrazines 1a and 5. A mixture of **2a**[14] (0.12 g, 0.61 mmol) and **3**[1a] (0.16 g, 0.61 mmol) was refluxed in 2-ethoxyethanol (20 mL) for 24 h. The solid was isolated by centrifugation and purified by column chromatography on deactivated alumina (5%) (CH_2Cl_2/MeOH, 100:1): yield 51%, brown powder; mp >250 °C. By analytical and spectro-

scopical data (^{1}H NMR, ^{13}C NMR, FAB-MS, UV/vis), the compound showed to be a mixture of hemiporphyrazines **1a** and **5** in a 4:1 ratio.

Acknowledgment. This work was supported by the Dirección General de Investigación Científica y Técnica (MAT-93-0075), the Community of Madrid (TEC-AE-00333/95), Spain, and the European Community (HCM programme, ERB CHRXCT 940558).

Supporting Information Available: Assignment of the ^{13}C NMR signals of the tree-unit compounds **4a** and **4b** and triazolehemiporphyrazines **1** and **5** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960704K