Approaches towards the synthesis of a 2,9,16,23-tetrasubstituted phthalocyanine as a pure isomer

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SHAFRIRA GREENBERG, A. B. P. LEVER, and CLIFFORD C. LEZNOFF. Can. J. Chem. **66**, 1059 (1988).

Treatment of 4-neopentoxyphthalonitrile with hydrogen sulfide gas yielded 1-imino-6-neopentoxy-3-thioisoindoline and 1-imino-5-neopentoxy-3-thioisoindoline, which on alkylation with iodomethane gave 1-imino-3-methylthio-6-neopentoxyiso-indolenine and 1-imino-3-methylthio-5-neopentoxyisoindolenine. The methylthioisoindolenines readily condensed at room temperature to a mixture of tetrasubstituted phthalocyanines and a series of linear open-chained purple compounds characteristic of isoindigos, while condensation at −20°C in the presence of zinc acetate gave, in at least one experiment, 2,9,16,23-tetraneo-pentoxyphthalocyanine as a pure isomer. The low temperature formation of phthalocyanines is remarkable and the syntheses described herein provide guidelines for the synthesis of pure isomers of 2,9,16,23-tetrasubstituted phthalocyanines. The purple and red compounds are shown to have isoindigo structures rather than a ring-opened phthalocyanine structure as previously reported.

SHAFRIRA GREENBERG, A. B. P. LEVER et CLIFFORD C. LEZNOFF. Can. J. Chem. **66**, 1059 (1988).

La réaction du néopentoxy-4 phtalonitrile et du sulfure d'hydrogène gazeux conduit à l'imino-1 néopentoxy-6 thio-3 isoindoline et à l'imino-1 néopentoxy-5 thio-3 isoindoline qui, par alkylation avec l'iodométhane, conduisent à l'imino-1 méthylthio-3 néopentoxy-6 isoindoline et à l'imino-1 méthylthio-3 néopentoxy-5 isoindoline. À la température ambiante, les méthylthioisoindolines se condensent facilement pour donner un mélange de phtalocyanines tétrasubstituées et une série de composés linéaires pourpres caractéristiques des isoindigos; par ailleurs, une condensation à −20°C, en présence d'acétate de zinc, a conduit—au moins dans une expérience—à la tétranéopentoxy-2,9,16,23 phtalocyanine sous la forme d'un isomère pur. La formation de phtalocyanines à basse température est remarquable et les synthèses décrites dans ce travail fournissent des indications sur les méthodes de synthèse des isomères purs des phtalocyanines substituées en 2,9,16,23. On a démontré que les composés pourpre et rouge possèdent des structures reliées à celle de l'isoindigo plutôt que des structures reliées à celle de la phtalocyanine qui avaient été suggérées antérieurement.

[Traduit par la revue]

Tetrasubstituted phthalocyanines having one substituent on each of the four benzo rings of phthalocyanine have been known for some time (1) but have received more attention recently due to their importance in electrocatalytic studies (2, 3). Most tetrasubstituted phthalocyanines are prepared by self-condensation of a suitable 3 or 4-substituted phthalonitrile or derivative (4, 5). For example, the isoindoline of 4-neopentoxyphthalo-nitrile will, upon condensation, give not only 2,9,16,23-tetra-neopentoxyphthalocyanine (**1**) but also the 2,10,16,24-, 2,9,17,24-, and 2,9,16,24-tetraneopentoxyphthalocyanine iso-mers (6, 7). Indeed, we have shown that the 2,9,16,23-tetra-neopentoxyphthalocyanine zinc(II) (**2**) derivative exhibited peaks in its ^{1}H nmr spectrum, indicating the presence of seven of the possible eight environments collectively present in the four isomers (7). A full discussion of this phenomenon was also recently demonstrated for some quaternized tetra-2,3-pyridino-porphyrazines (8). In this latter example, it was suggested that steric considerations favoured the symmetrical isomer, having C_{4h} symmetry, but that the other isomers were present in lesser amounts. Virtually all tetrasubstituted phthalocyanines known in the literature (1) exist as a mixture of the four possible isomers, and in the case of substituents at the 2 position are usually referred to as the 2,9,16,23-tetrasubstituted isomer. On the other hand, in a very recent paper, Gaspard and Maillard (9) have succeeded in preparing the pure isomer 2,9,17,24-tetra-*tert*-butylphthalocyanine zinc(II), using metallic zinc as the condensing agent.

In connection with our studies on multinuclear phthalocya-nine (6, 7, 10) and with the possibility of obtaining one pure isomer of a binuclear phthalocyanine for X-ray diffraction studies, we were interested in exploring synthetic methods of

phthalocyanine formation that could give rise exclusively to the 2,9,16,23-tetrasubstituted phthalocyanines as one isomer. In a previous paper we showed that dithioamides do form phthalocy-anines with diiminoisoindolines at modest temperatures (11). We envisioned that a 5-substituted iminothioamide should self-condense in one direction to form exclusively a 2,9,16,23-tetrasubstituted phthalocyanine as one isomer, because the imino group on one side of the molecule should displace selectively the methythio group on the other side of a second molecule. It turns out that treatment of phthalonitrile (**3**) with hydrogen sulfide gas gives 1-imino-3-isoindoline (**4**) directly, as reported by Baguley and Elvidge (12), but **4** does not readily condense to phthalocyanine under normal conditions (4, 5). Despite the fact that we were unable to successfully *S*-alkylate dithioamides (11) under a variety of conditions, we found that the iminothioamide **4** is readily alkylated to a separable mixture of *N*-methyl-2,3-dihydro-3-thioxo-1*H*-isoindol-1-one (**5**) and 1-imino-3-methylthioisoindolenine (**6**). The *S*-alkyl derivative **6** readily condenses to phthalocyanine (**7**) under the usual con-ditions but *at room temperature* instead of 150°C (Scheme 1).

This encouraging result led us to examine the possibility of using a *substituted* 1-imino-3-methylthioisoindolenine in the *exclusive* formation of 2,9,16,23-tetrasubstituted phthalocy-anines as one isomer. Treatment of 4-neopentoxyphthalonitrile (**8**) with hydrogen sulfide (12) gave a mixture of 1-imino-6-neopentoxy-3-thioisoindoline (**9**) and 1-imino-5-neopentoxy-3-thioisoindoline (**10**), separable by flash chromatography (13). In separate experiments pure **9** and **10** were treated with iodo-methane to give 1-imino-3-methylthio-6-neopentoxyisoindol-enine (**11**) and 1-imino-3-methylthio-5-neopentoxyisoindol-enine (**12**) respectively. In separate experiments, compounds **11** and **12** self-condensed spontaneously *at room temperature* to 2,9,16,23-tetraneopentoxyphthalocyanine (**1**), *as a mixture*
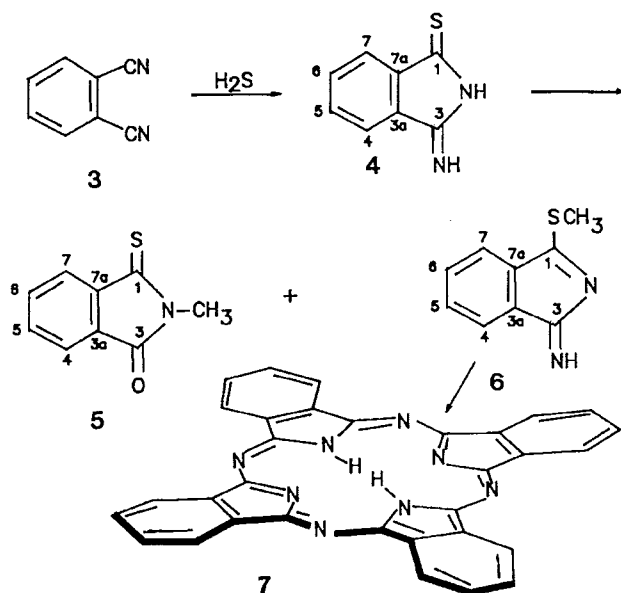
SCHEME 1

of isomers as analyzed previously by ^{1}H nmr spectroscopy (7). In addition a mixture of purple coloured compounds (**13–16**) could be recovered by flash chromatography. The assignments of the structures of compounds **13–16** remain tentative and are based on mass spectroscopy, high resolution mass spectroscopy, nmr, and uv/vis spectroscopy. Mass spectroscopy of this mixture of purple compounds could be accounted for by a mixture of compounds (**13–16**) exhibiting parent ions for all of the compounds. Further purification gave small quantities of pure **13** and **14**, whose structures are consistent with their exact high resolution mass spectra (see Experimental). Interestingly, the ^{1}H nmr spectra of **13** and **14** were consistent with the assigned structures but the absorptions for the neopentoxy substituents indicated that **13** and **14** were formed as one isomer each and that mixtures of isomers in which the position of the neopentoxy groups was different in each benzo ring were not obtained. Alternatively, the absorptions of the different positional isomers of **13** and **14** could have been coincident but this possibility is unlikely.

We were interested in characterizing the precursors **4–6** and **9–11** by ^{13}C nmr spectroscopy but found that it was necessary to obtain ^{13}C nmr spectra of pure 1,3-diimino-5-neopentoxy-isoindoline (**17**) (see Experimental) and monoiminophthalimide (**18**) (**14**) (Fig. 1). Using the ^{13}C nmr of **17** and **18** it was possible to assign the absorptions of **4–6** and **9–11** (Table 1). In addition, the uv spectra of **4–6**, **9–11**, and **17** are recorded in Table 2.

It is well known that aromatic thioamides undergo condensation to isoindigo dyes (12), so that the formation of **13–16** is not too surprising. The presence of the neopentoxy substituents of **13–16** solubilized these normally poorly soluble compounds and allowed us to effect a separation to isolate pure **13** and **14**. The uv/vis spectra of **13** and **14** are unique and neither resembles phthalocyanines nor isoindigos. In a recent paper Fujiki *et al.* (15) describe the preparation of a hydroxygermanium(IV) α,β,γ-triazabenzcorrole formed by a ring contraction of dichlorogermanium phthalocyanine. Illumination of this corrole derivative is reported (15) to give a red compound whose uv/vis is identical to **13** and **14**. These authors propose three structures **19–21** for their red compound, none of which would be consistent with the carbon–carbon double bond structure of

13 and **14**. In light of our results a possible structure for their red compound could be illustrated below.

A representation of their red compound by the structure **22** in Fig. 2 would be likely and would not involve cleavage of a carbon–carbon double bond. Repetition of the work of Fujiki *et al.* (15) using neopentoxy-substituted phthalocyanines would give soluble derivatives of their red compound that could be purified and adequately characterized.

Condensation of **11** or **12** at −20°C in dimethylformamide (DMF) and using Zn(OAc)$_2$ as a template for macrocycle formation gave **2** directly and a mixture of purple compounds, likely **13–16**. In two experiments, condensation of **11** or **12** led to 2,9,16,23-tetraneopentoxyphthalocyanine **2** as mainly one isomer when examined by ^{1}H nmr spectroscopy (Table 3), but larger scale preparations of this reaction again led to **2**, but only as a mixture of isomers. Of course, both 2,9,16,23-tetraneopentoxyphthalocyanine (**1**) and 2,10,16,24-tetraneopentoxyphthalocynanine should exhibit only one peak for the *tert*-butyl groups and the method of synthesis should favour **1**, but the formation of the latter isomer cannot be entirely excluded. It should be pointed out that the mixture of isomers thus obtained was not identical to the statistical distribution of isomers of **2** previously reported (7) (Table 3).

In summary, we have demonstrated the remarkable low temperature formation of phthalocyanines from iminomethylthioisoindolenines, have aided in the characterization of the coloured by-products formed in these as similar reactions, and have initiated experiments directed towards the isolation of pure isomers of tetrasubstituted phthalocyanines.

Experimental

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (nmr) spectra for carbons and protons were recorded on a Bruker AM300 nmr spectrometer using deuterochloroform as a solvent and tetramethylsilane as the internal standard unless otherwise stated. The positions of the signals are reported in δ units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).)

The visible–ultraviolet spectra (uv) were recorded on a Hewlett Packard HP8451A Diode Array spectrophotometer. Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode.

Melting points (mp) were determined using a Kofler hot stage melting point apparatus and are uncorrected. Thin-layer chromatography (tlc) was performed using silica gel G as the adsorbent. Flash chromatography was performed using silica gel of particle size 20–45 μm. All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

Purification of 5-neopentoxy-1,3-diiminoisoindoline (17)

The crude 5-neopentoxy-1,3-diiminoisoindoline obtained from 134 mg of 4-neopentoxyphthalonitrile (0.63 mmol) by standard procedure (6) was dissolved in ethyl acetate, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the ethyl acetate and recrystallization from ethyl acetate/hexanes gave in 68% yield 98 mg of pure 5-neopentoxy-1,3-diiminoisoindoline as white crystals, mp 200–203°C; ir (cm^{-1}): 3260 (NH), 3200 (NH), 1695, 1650, 1620–1600, 1540, 1450, 1440, 1315, 1240, 1140, 1065, 1020, 885, 820; ^{1}H nmr δ: 7.59 (d, *J* = 8.4, 1H), 7.24 (br, 1H), 7.12 (dd, *J* = 8.4, 2.1, 1H), 3.70 (s, 2H, CH_2O), 1.06 (s, 9H, (CH_3)$_3$C); ms *m/z*: 231 (M$^+$, 25), 161 (M$^+$ − 70, 80), 71 (38), 57 (47), 43 (100). *Anal.* calcd. for C$_{13}$H$_{17}$N$_3$O: C 67.51. H 7.41, N 18.17; found: C 68.01, H 7.74, N 18.05.
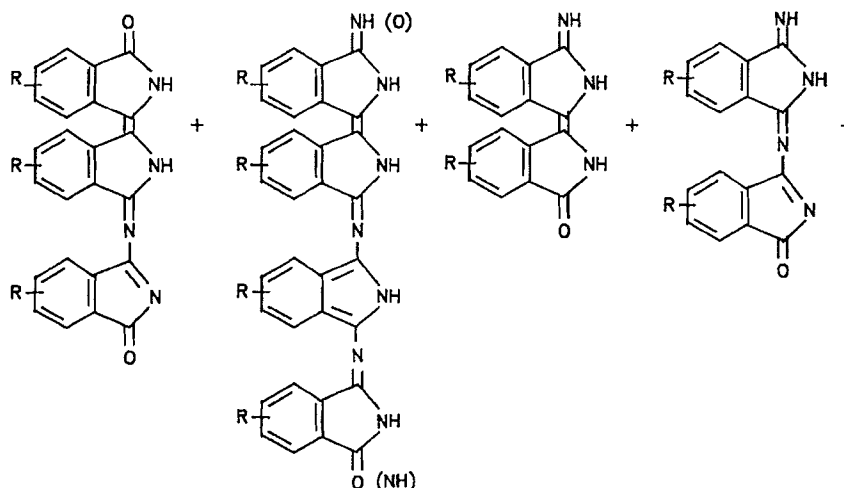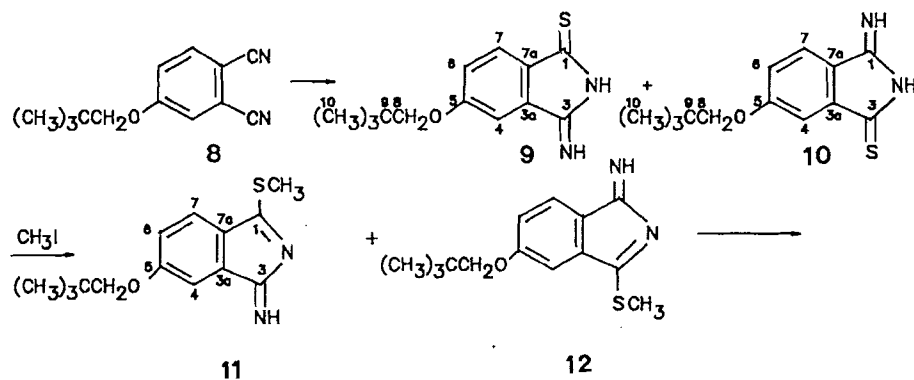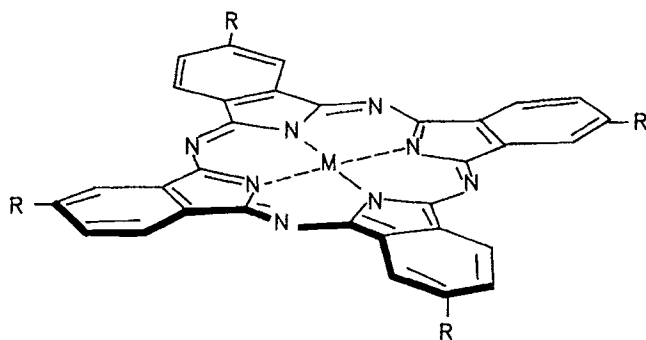
SCHEME 2

1-Imino-3-thioisoindoline (4)

The 1-imino-3-thioisoindoline was prepared from phthalonitrile and sodium hydrogen sulfide according to the procedure of Baguley and Elvidge (12), mp 220°C (dec.) (lit. (12) mp 218°C); ir (cm^{-1}): 3160 (NH), 1665, 1465, 1390, 1290, 1270, 1240, 1080, 910, 765, 675; ^{1}H nmr (DMSO-d_6) δ: 10.88 (vbr. 2H, NH), 7.99 (d, J = 7.3, 1H), 7.81–7.67 (m, 3H); ms m/z: 162 (M$^+$, 100), 146 (20), 135 (30), 129 (92), 76 (47).

1-Imino-3-methylthioisoindolenine (6) and N-methylmonothio-phthalimide (5)

A solution of 101 mg of 1-imino-3-thioisoindoline (0.63 mmol) in 1 mL ethanol was methylated with dimethyl sulfate according to the procedure of Baguley and Elvidge (12). The crude product was pre-cipitated from water, filtered, and washed with water to give in 65% yield, 71 mg of 6. An attempt to recrystallize 6 resulted in decomposi-tion, accompanied by phthalocyanine formation, mp 86–90°C (dec.)

TABLE 1. ^{13}C nuclear magnetic resonance chemical shifts (in ppm (δ), in $CDCl_3$) of some imino and thioanalogs of phthalimide

| | Carbon | | | | | | | | | | | | |
Compound	1	3	3a	4	5	6	7	7a	8	9	10	N—CH₃	S—CH₃
4[a]	199.92[b]	164.97[b]	134.00	121.72	132.54[c]	132.34[c]	123.02	137.80	—	—	—	—	—
5	197.36	169.79	127.38	123.64	134.02	133.08	122.69	137.06	—	—	—	27.54	—
6	182.37	171.52	140.45	122.75	131.12[c]	130.97[c]	119.86	136.64	—	—	—	—	13.25
9[a]	197.85	163.31[d]	131.67	106.91	163.27	118.83	124.90	130.69	77.99	31.59	26.24	—	—
10[a]	165.26[b]	200.23[b]	140.25	107.67	162.53	118.98	123.32	122.01	77.78	31.54	26.22	—	—
11	n.o.[e]	n.o.	n.o.	108.12	162.13	117.54	121.27	n.o.	77.83	31.58	26.24	—	12.92
17[a]	169.17	169.17	138.80	106.89	161.56	116.70	122.21	128.51	77.76	31.60	26.30	—	—
18[a,f]	172.9[b]	164.5[b]	134.2[b]	122.0	132.9	132.3	122.5	133.1	—	—	—	—	—

[a]Taken in DMSO-d_6.
[b]Broadened.
[c]These values may be interchanged.
[d]Signal overlap with C5.
[e]n.o.: not observed due to low concentration. Sample should not be heated to dissolve.
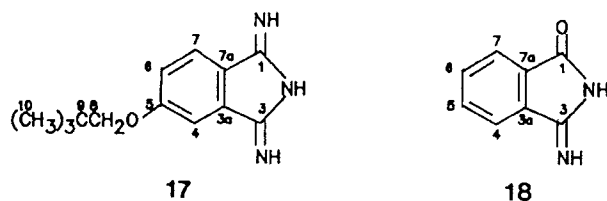[f]Data taken from ref. 14.

FIG. 1. Compounds used in aiding assignments of ^{13}C nmr spectra (Table 1).

TABLE 2. Ultraviolet spectra of iminothioisoindolines and related compounds in $CHCl_3$ at 24°C

Compound	λ_{max}(nm) (log ϵ)
4[a]	234(4.29), 310(4.13), 345(3.90)
5	242(3.75), 300(4.16), 332(4.01)
6[a]	285(3.98), 436(2.72)
9	258(4.24), 340(4.23)
10	256(4.40), 326(4.28)
11[b]	254(4.36), 298(4.18), 366(3.42)
17	244(4.24), 266(4.24), 312(sh) (4.12)

[a]Data taken from ref. 12.
[b]This compound is not very stable.

(lit. (12) mp 98–100°C); ir (cm⁻¹): 3180 (NH), 1655, 1480, 1360, 1265, 1240, 1040, 960, 770, 760, 685; ¹H nmr δ: 9.49 (br, 1H), 7.93 (br, 1H), 7.55–7.43 (m, 3H), 2.74 (s, 3H, S—CH₃); ms m/z: 176 (M⁺, 35), 129 (100).

When left overnight the filtrate deposited orange needles, which were filtered off to give in 9% yield 10 mg of N-methylmonothiophthalimide, mp 97–98°C (lit. (16) mp 97°C, 86–87°C); ir (cm⁻¹): 1740 (C═O), 1470, 1375, 1340, 1325, 1075, 990, 770, 700; ¹H nmr δ: 7.96 (m, 1H), 7.77 (m, 1H), 7.69 (m, 2H), 3.48 (s, 3H, N—CH₃); ms m/z: 177 (M⁺, 100), 117 (80).

1-Imino-6-neopentoxy-3-thioisoindoline (9) and 1-imino-5-neopentoxy-3-thioisoindoline (10)

A suspension of 15.1 g of sodium sulfide nonahydrate (62.9 mmol) in 5 mL of water was saturated with a slow stream of hydrogen sulfide gas for 1 h. The suspension became cloudy and the stream of H_2S was increased for a further 45 min. The grey solution was then added to a solution of 4.2 g of 4-neopentoxyphthalonitrile (6) (19.6 mmol) in 11 mL of 95% ethanol and the mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with 200 mL of water and the

precipitate was filtered and washed with water to yield 3.9 g of crude product. Further purification was done by flash chromatography (13) on silica gel, using ether/petroleum ether (3:2) as eluant. The first 100 mL consisted of dark impurities and a trace of 5-neopentoxydithiophthalimide (11). Continued elution gave a yellow moving band consisting of 1-imino-6-neopentoxy-3-thioisoindoline. Evaporation of the eluant gave in 17% yield 0.84 g of pure 9 as very light brown crystals, mp 126–130°C (dec.); ir (cm⁻¹): 3280–3180 (NH), 1660, 1610, 1490, 1480–1460, 1365, 1255, 1105, 830; ¹H nmr (acetone-d_6) δ: 7.83 (d, J = 8.4, 1H), 7.53 (br, 1H), 7.26 (dd, J = 8.4, 2.3, 1H), 3.82 (s, 2H, CH₂O), 1.06 (s, 9H, (CH₃)₃C); ms m/z: 248 (M⁺, 100), 178 (82), 71 (27), 43 (28). *Anal.* calcd. for $C_{13}H_{16}N_2OS$: C 62.87, H 6.49, N 11.28; found: C 62.95, H 6.70, N 11.42.

Continued elution of the silica gel gave a second yellow moving band consisting of 1-imino-5-neopentoxy-3-thioisoindoline. Evaporation of the eluant gave in 20% yield 0.97 g of pure 10 as golden crystals, mp 189–191°C (dec.); ir (cm⁻¹): 3250 (NH), 1660, 1610, 1495, 1380, 1365, 1325, 1280, 1200, 1050, 1020, 865, 830, 820, 730; ¹H nmr (acetone-d_6) δ: 7.88 (d, J = 8.5, 1H), 7.37 (d, J = 2.2, 1H), 7.32 (dd, J = 8.5, 2.2, 1H), 3.83 (s, 2H, CH₂O), 1.07 (s, 9H, (CH₃)₃C); ms m/z: 248 (M⁺, 42), 178 (80), 71 (52), 43 (100). *Anal.* calcd. for $C_{13}H_{16}N_2OS$: C 62.87, H 6.49, N 11.28; found: C 63.09, H 6.75, N 11.22.

1-Imino-3-methylthio-6-neopentoxyisoindolenine (11) and 1-imino-3-methylthio-5-neopentoxyisoindolenine (12)

A solution of 64.4 mg of 1-imino-6-neopentoxy-3-thioisoindoline (0.26 mmol), 1 mL ethanol, and 0.22 mL of 1.25 N sodium hydroxide (0.28 mmol) was diluted with 1 mL of water and stirred while 0.02 mL of methyl iodide (0.32 mmol) was added dropwise at room temperature. After 45–60 min, ice-cold water was added and the product was filtered and washed with water to give in 82% yield 56 mg of 1-imino-3-methylthio-6-neopentoxyisoindolenine as brown crystals. Compound 11 was used directly in the next step, mp 115–117°C (turned green); ir (cm⁻¹): 3260–3180 (NH), 1660, 1605, 1480–1460, 1360, 1250, 1100, 825; ¹H nmr δ: 9.34 (br, 1H), 7.46 (br, 1H), 7.35 (d, J = 8.2, 1H), 7.00 (d, J = 8.2, 1H), 3.69 (s, 2H, CH₂O), 2.72 (s, 3H, SCH₃), 1.05 (s, 9H, (CH₃)₃C); ms m/z: 262 (M⁺, 10), 192 (23), 71 (65), 57 (48), 43 (100). *Anal.* calcd. for $C_{14}H_{18}N_2OS$: C 64.09, H 6.92, N 10.68; found: C 64.06, H 7.02, N 11.05.

Similarly a solution of 101 mg of 1-imino-5-neopentoxy-3-thioisoindoline was methylated with methyl iodide at 0°C for 3 min to give a dark oily product. The crude product was extracted with ether and the organic layer was washed thoroughly with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated to give in 75% yield 80 mg of a very dark oil. Compound 12 is very unstable and therefore it is used directly in the next step. An attempt to purify 12 by flash chromatography caused decomposition, hydrolysis of the
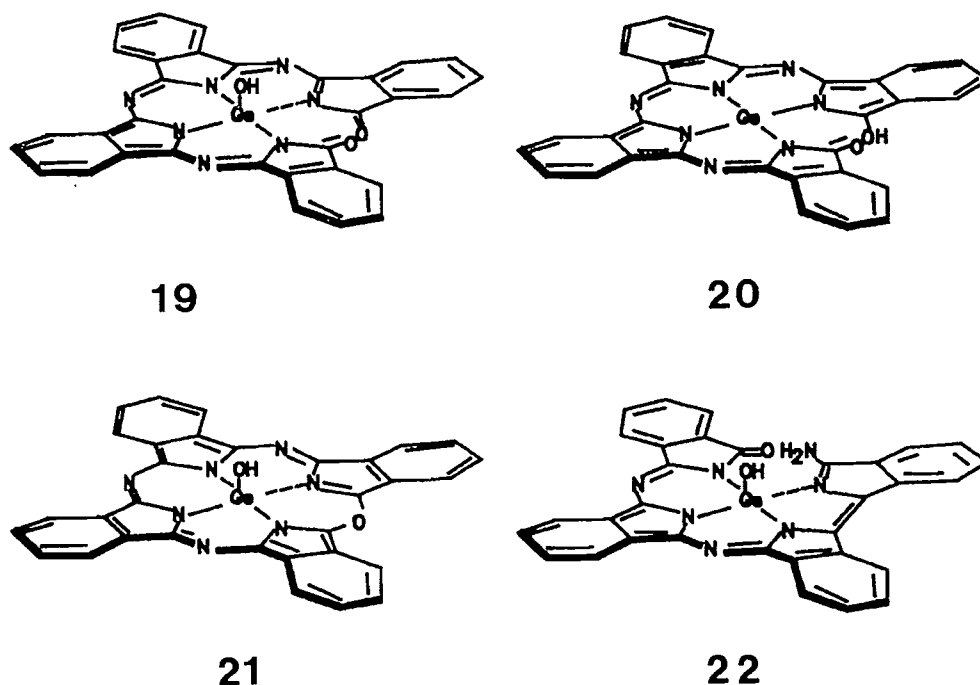
19   **20**

21   **2 2**

FIG. 2. Reported and new suggested structures for the red compound.

TABLE 3. ^{1}H nuclear magnetic resonance chemical shifts (in ppm (δ), of 2,9,16,23-tetraneopentoxyphthalocyanine (**1**) and its Zn derivative (**2**) for different methods of preparation

Phthalocyanine	Precursor	Reaction conditions	$(CH_3)_3C$	NH
1	**17**	160°C, DMAE[a]	1.27, 1.26, 1.25, 1.232, 1.226	−4.94, −5.12, −5.21, −5.64
1	**11**	60°C, DMAE	1.29, 1.26, 1.25, 1.24, 1.23	−2.62, −4.98, −5.14, −5.27
1	**11**	24°C, DMAE	1.28, 1.27, 1.222, 1.218	−2.30, −2.48
1	**12**	24°C, DMAE	1.30, 1.28, 1.27, 1.24, 1.23	−2.73, −3.27
2	**1** via **17**	100°C, Zn(OAc)$_2$	1.27, 1.26, 1.25, 1.22, 1.21	—
2	**11**	−18°C, Zn(OAc)$_2$	1.26, 1.20	—
2	**12**	−20°C, Zn(OAc)$_2$	1.26	—

[a]N,N-Dimethylaminoethanol.

imino group, and phthalocyanine formation; ^{1}H nmr δ: 7.64 (d, $J = 9$, 1H), 7.44 (d, $J = 3$, 1H), 6.97 (dd, $J = 9, 3$, 1H), 3.73 (s, 2H, CH_2O), 2.81 (s, 3H, SCH_3), 1.06 (s, 9H, $(CH_3)_3C$); ms m/z: 262 (M$^+$, 31), 247 (M$^+$ − 15, 9), 215 (M$^+$ − SCH$_3$, 40), 192 (M$^+$ − 70, 14), 145 (95), 71 (98), 43 (100).

Phthalocyanine formation from 11

Compound **11** obtained from 100 mg of **9** (0.40 mmol) in 1–2 mL of N,N-dimethylaminoethanol underwent self-condensation under argon at room temperature for 60 h. The crude reaction product was purified as previously described (6) to give, after flash chromatography, in 5–18% yield, 2,9,16,23-tetraneopentoxyphthalocyanine (**1**) as a mixture of isomers. From the ^{1}H nmr it seemed that some isomers were more selectively formed than others, but complete selectivity was not obtained. If during the self-condensation the argon is bubbling directly inside the reaction mixture, to remove the ammonia that is formed during the reaction, the desired phthalocyanine is not formed at room temperature. Raising the temperature to 60°C (oil bath) increased the yield but reduced the selectivity of the formation of isomers. Phthalocyanine formation was observed to take place when a solution of **11** in ether was left at room temperature overnight or when a sample

of **11** was left partially dissolved in DMSO-d_6 inside an nmr tube. In both cases no selectivity towards the formation of one isomer was detected by ^{1}H nmr. During the purification of **1** by flash column chromatography it was observed that some purple material was left on the top of the column. At room temperature the purple colour became very intense. Therefore, after all of **1** was eluted with toluene, the solvent system was changed to 2-methoxyethanol/toluene (1:50). Several fractions were collected and, after evaporation of the solvent, it was found that some fractions contained mixtures of only **13** and **14**. The spectral data of this mixture is given as follows: ir (cm^{-1}): 3400 (NH), 2940, 1765, 1730, 1610, 1490, 1365, 1230, 1045, 1010, 745; uv (ether): 582, 542, 510, 346 nm; ^{1}H nmr δ: 7.75 (d, $J = 8.3$ Hz), 7.32 (d, $J = 2.0$ Hz), 7.20 (dd, $J = 8.2$ and 2.0 Hz), 3.71 (s, CH_2O), 1.06 (s, $(CH_3)_3C$); ^{13}C nmr δ: 168.00, 167.93, 164.83, 135.24, 125.18, 124.27, 120.66, 108.57, 78.80, 31.88, 29.66, 26.44. Further purification on a few mg was achieved by preparative tlc using the same eluting solvent as above to give **13** and **14** in estimated yields of 5% and 7% respectively; ms (high resolution) m/z, calcd. for C$_{39}$H$_{44}$N$_4$O$_5$, **13**, (M$^+$): 648.35404; found: 648.3555; calcd. for C$_{52}$H$_{61}$N$_7$O$_5$, **14**, (M$^+$): 863.47337; found: 863.4696.

Compounds of related structure were discussed by Fujiki *et al.* (15).

Phthalocyanine formation from 12

Compound **12** obtained from 116 mg of **10** (0.47 mmol) in 1–2 mL of *N,N*-dimethylaminoethanol underwent self-condensation under argon at room temperature for 18 h. The crude reaction product was purified as previously described (6) to give, after flash chromatography, in 8% yield, 8 mg of 2,9,16,23-tetraneopentoxyphthalocyanine as a mixture of isomers; some isomers were more selectively formed than others, in comparison with the isomers formed from the self-condensation of 5-neopentoxy-1,3-diiminoisoindoline (**17**) at 150°C. Further elution of the column with 2-methoxyethanol/toluene (1:50) gave purple/red material consisting of **13–16** as analyzed by mass spectroscopy. The physical and spectral data of **1** (except for the ^{1}H nmr) were identical to the ones previously reported (6).

2,9,16,23-Tetraneopentoxyphthalocyanine zinc(II) (2)

A mixture of 20 mg of **11** (0.076 mmol) and 5.7 mg (0.031 mmol) of zinc acetate was cooled in the freezer to −15°C. Cold DMF (−15°C) was added (1 mL); the mixture turned green and was left in the freezer for 1 week. The crude product was purified by flash column chromatography in a cold room (3°C). The column was packed a day in advance and was left in the cold room overnight. The crude product was applied to the column as is, and was eluted with cold toluene at 3°C to give 1 mg of **2** (5% yield); ^{1}H nmr (C$_6$D$_6$) δ: 1.26, 1.20; ms *m/z*: 922 (M$^+$, 100), 851 (*M$^+$* − 71, 40), 460 (*M^{+2}* − 1, 65). Similarly a mixture of **12** derived from 102 mg of **10** (0.41 mmol) underwent self-condensation in the presence of zinc acetate in DMF at −15 − −18°C. Purification as above gave a mixture of **2** contaminated by **13** and **14**. Further purification by preparative tlc using 2-methoxyethanol/toluene (1:50) as eluting solvent followed by flash column chromatography gave 10.8 mg of **2** in 11% yield uncontaminated by **13** and **14**; ^{1}H nmr (C$_6$D$_6$) δ: a major peak at 1.26 and 2 small peaks at 1.23 and 1.21 ppm. This experiment was repeated at −40°C and gradually the temperature was raised to +5°C. Purification as above gave a trace of the desired product as indicated by a faint blue spot on tlc; ^{1}H nmr (C$_6$D$_6$) δ: 1.26 ppm. A control experiment using **11** in 2-*N,N*-dimethylaminoethanol showed that metal-free phthalocyanine formation did not take place at temperatures below 10°C.

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