Hexakis(alkylthio)-Substituted Unsymmetrical Phthalocyanines

Salih Dabak[a], Ahmet Gül[a,b], and Özer Bekaroğlu*[b]

Department of Chemistry, TUBITAK Marmara Research Center[a],
P.O. Box 21, 41470 Gebze, Kocaeli, Turkey

Department of Chemistry, Technical University of Istanbul[b],
Maslak, Istanbul, Turkey

Received March 25, 1994

Key Words: Phthalocyanines, unsymmetrical, soluble / Boron complex / Phthalonitrile derivatives

Cyclotrimerization of 4,5-bis(hexylthio)phthalodinitrile (**1**) in 1-chloronaphthalene in the presence of BCl_3 leads to the subphthalocyanine **4**. Unsymmetrical phthalocyanines (**5**, **6**) with six alkylthio substituents on three of the benzenoid units are synthesized by the reaction of **4** with an diiminoisoindoline derivative (R' = H or NO_2). These extremely soluble compounds are characterized by IR, ^{1}H- and ^{13}C-NMR as well as UV/Vis spectra.

The intense interest in soluble phthalocyanines originates predominantly from the suitability of these compounds as materials with novel electrical, optical, catalytic, and mesogenic properties[1,2]. The attractive and challenging characteristics of the phthalocyanines are their great variety, chemical stability, the relative ease with which they can be prepared and purified and the strong dependence of their properties on peripheral and axial substitution patterns[3]. The search for new materials possessing large optical nonlinearities also comprises these compounds with completely conjugated 18-π electron systems[3]. Phthalocyanines show large second-order polarizibilities as do numerous other conjugated π donor-acceptor organic molecules and some coordination compounds[4]. Although symmetrical or pseudosymmetrical derivatives are sufficient for many applications, unsymmetrical ones are especially required for a second-order NLO effect[4].

Although at first glance it appears possible to obtain unsymmetrically substituted phthalocyanines by cyclotetramerization of a mixture of two or more phthalonitrile derivatives with different substituents, isolation of each isomer is hardly possible, and the yield of the desired product might be very low[5–7]. Therefore, efficient synthetic routes to each isomer are required. In this context two methods for the preparation of disubstituted phthalocyanines by crossed condensation of an iminoisoindoline derivative either with 1,3,3-trichloroisoindolenine[8] or with another sterically crowded iminoisoindoline are noteworthy[9]. Preorganization of three phthalonitrile units as a subphthalocyanine of boron[10,11] and subsequent conversion into an unsymmetrical phthalocyanine by reaction with various substituted iminoisoindolines has proven to be the most efficient way of obtaining unsymmetrical phthalocyanines with indentical substituents on three of the benzene units and a different substituent on the fourth one[12–14]. In connection with the intensive research on the thio-substituted phthalocyanines as near-IR absorbers[15–18] and as a part of our research in the field of soluble phthalocyanines with substituents carrying different donor groups[19–22], we have isolated a boron complex of a hexakis(alkylthio)-substituted subphthalocyanine which can be used as an intermediate to obtain unsymmetrical phthalocyanines. In this paper we report also on the synthesis and characterization of two unsymmetrical phthalocyanines which carry two peripheral hexylthio substituents each on three of the benzenoid groups while the fourth one is unsubstituted or bears a nitro substituent.

Results and Discussion

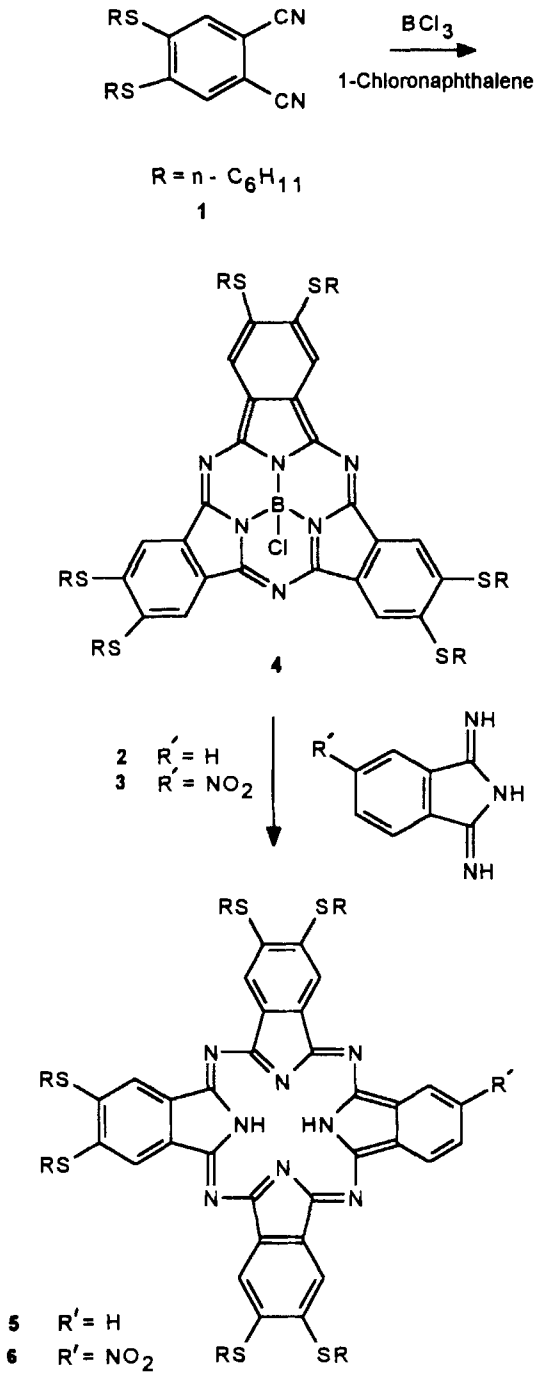
4,5-Bis(hexylthio)phthalodinitrile (**1**), obtained from 4,5-dichlorophthalic acid by a multistep reaction sequence[16], was used for the preparation of the subphthalocyanine **4** by cyclotrimerization in the presence of boron trichloride (Scheme 1). In contrast to the unsubstituted analog which was synthesized at much higher temperatures (i.a. at reflux temperature of 1-chloronaphtalene)[10], the reaction leading to **4** was complete at 100°C. The boron complex **4** is extremely soluble in apolar solvents such as hexane, heptane, benzene, toluene, diehtyl ether, tetrachloromethane, chloroform, and dichloromethane. Protic solvents such as ethanol, methanol or DMF, DMSO were the few solvents from which **4** could be precipitated unchanged.

The reaction of **4** with iminoisoindoline derivatives was accomplished at low temperatures as in the case of other similar ring expansion reactions[13,14]. Here the excess of iminoisoindoline derivatives resulted in the formation of the corresponding symmetrical metal-free derivatives of the iminoisoindoline reactant together with the desired unsymmetrical phthalocyanines **5** or **6**, but they were easily separated by column chromatography. The hexakis(hexylthio)-substituted phthalocyanines **5** and **6** are extremely soluble in apolar solvents like the subphthalocyanine **4** or the symmetrically octakis(alkylthio)-substituted phthalocyanines[16].

The relatively weak absorption at 955 cm^{-1} in the IR spectrum of **4** can be assigned to B–Cl bond, and it disap-

  0009–2940/94/1010–2009 $ 10.00+.25/0

Scheme 1. Synthesis of the unsymmetrical phthalocyanines **5** and **6**



pears after the phthalocyanine formation. Although the X-ray results of the unsubstituted subphthalocyanine have shown that this molecule is composed of three symmetrically oriented iminoisoindoline units[11], the ^{1}H- and ^{13}C-NMR spectra of the subphthalocyanine **4** reveal that this bowl-shaped molecule no longer exhibits 3*m* symmetry. The signal of the aromatic protons at δ = 8.5 is split into a doublet. In the ^{13}C-NMR spectrum, aromatic carbon atoms appear as four groups as expected, but each group is split into two or three signals which may be attributed to the disruption of the symmetry. The FAB-mass spectrum of **4** also brings new lights into this discrepancy (Figure 1). While the M^+ ion is observed at *m/z* 1128 as the most intense peak, $[M + Cl]^+$ is also present at 1163 which might be interpreted as a consequence of the partial chlorination of peripheral positions. Since insertion of one chlorine atom in up to 25% of the molecules does not cause an appreciable change in the elemental analysis results, the presence of some peripherally chlorinated impurities might be another reason for splitting observed in the NMR spectra of **4**.

The quasiaromatic conjugated π system of the 14-membered inner core shows an optical absorption at higher energy than the phthalocyanines[1,18]. The intense absorption around 590–600 nm is very similar to the Q band of the phthalocyanines and is also affected by the changes in the polarity of the solvent (i.e. λ_{max} 600 nm in $CHCl_3$, 596 nm in toluene and 593 nm in tetrachloromethane).

The ^{1}H-NMR spectra of the unsymmetrical phthalocyanines **5** and **6** are in excellent agreement with the proposed structures. The aromatic protons of the alkylthio-substituted benzene units appear as two singlets at δ = 7.74 and 7.62 corresponding to the different positions with respect to the unsubstituted benzene in **5**. The protons of the latter appears at δ = 8.38 and 8.0 as singlets. In the case of **6**, the effect of the nitro group on the aromatic protons is a broadening of the peaks together with a shift to higher field. The strongly shielded cavity protons absorb at δ = −4.91 for **5** and at −6.10 for **6**, and the signals disappear by deuterium exchange. The alkyl carbon atoms are observed as six signals in ^{13}C-NMR spectra for both **5** and **6** as expected. The number of weaker signals for aromatic carbons also meets the expectations.

The electronic spectra of the unsymmetrical phthalocyanines show the features of both metal-free phthalocyanine and alkylthio substitution (Figure 2). The latter is characterized by a shift of the Q band to lower energy. While a split Q band at 723 and 691 nm is observed for **5** in chloroform, the introduction of a polar nitro substituent as in the case of **6** causes a drastic change in the Q absorption which is extremely sensitive to the solvent used. As shown in Figure 3, the spectrum of **6** in toluene is split into two peaks, but those in chloroform or CCl_4 exhibit an intense absorption with a shoulder; however, the shoulder is on the lower energy side in CCl_4, while in chloroform it is on the higher energy side. The intensity of Soret band acceeds that of Q band in **6** as a result of this new substitution pattern with electron-donating and and-accepting groups in the same molecule.

Experimental

IR: Perkin-Elmer 983, CH_2Cl_2, sodium chloride Cell. – ^{1}H and off-resonance-decoupled ^{13}C NMR: Bruker 200-MHz. – UV/Vis: Varian DMS 90. – FAB MS: VG-ZAB-SPEC spectrometer. – Elemental analyses: Instrumental Analysis Laboratory of TÜBITAK Marmara Research Centre. – 4,5-Bis(hexylthio)phthalodinitrile (**1**)[18], 1,3-dihydro-1,3-diiminoisoindoline (**2**)[23], and 1,3-dihydro-1,3-diimino-6-nitroisoindoline (**3**)[23] were prepared according to literature procedures.

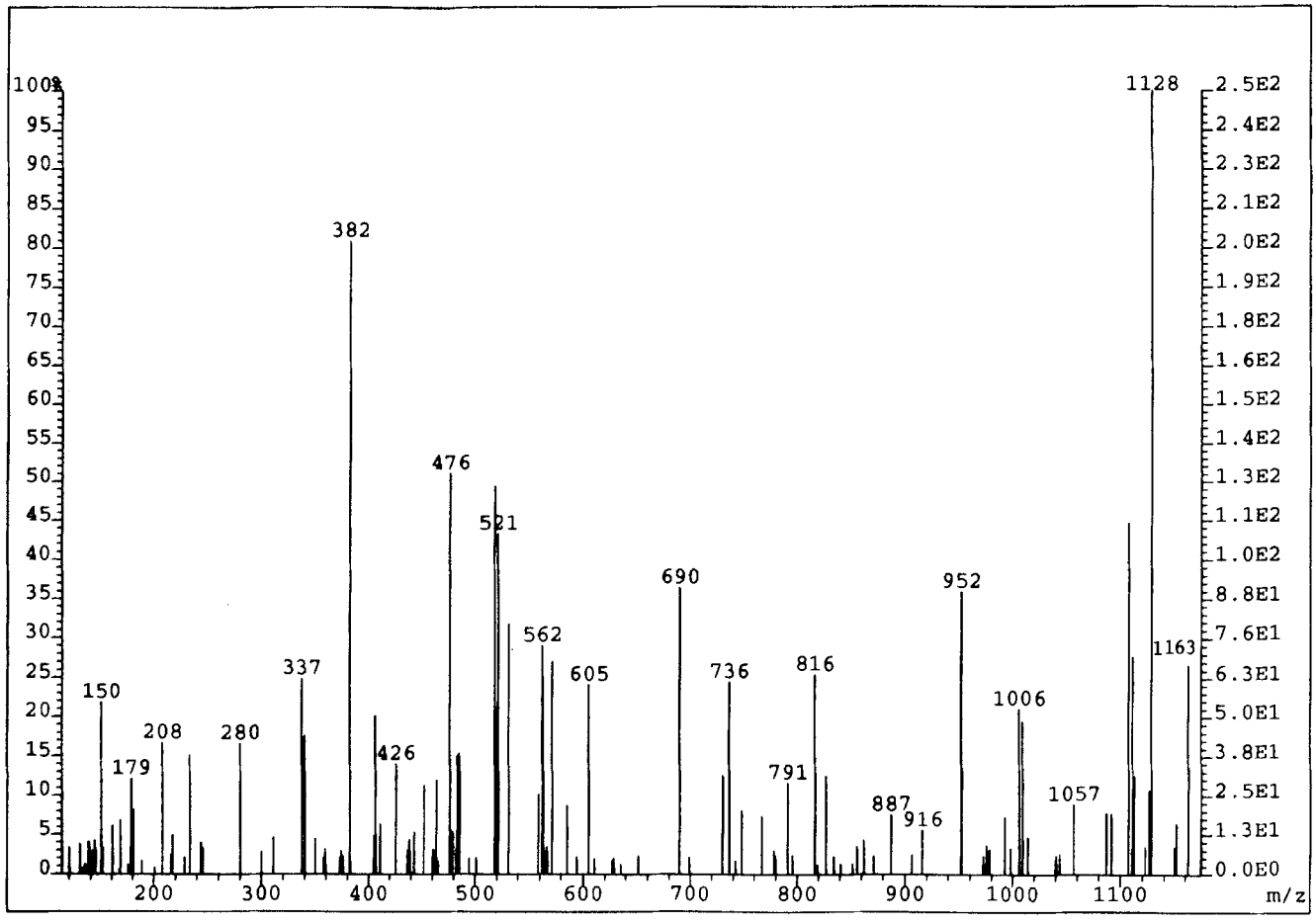


Figure 1. FAB-Mass spectrum of **4**

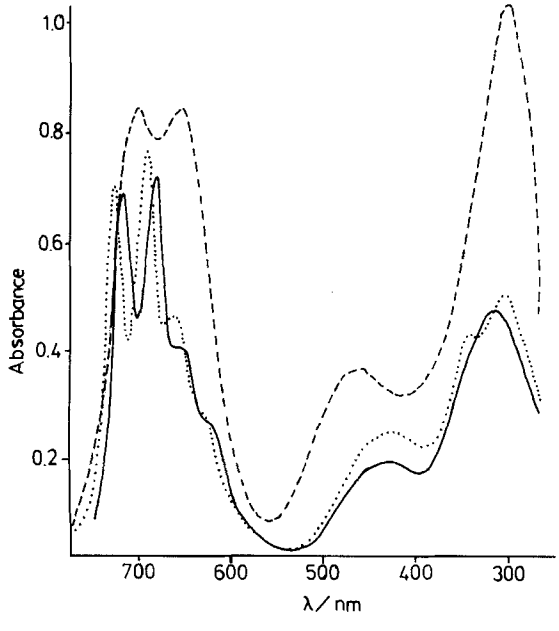


Figure 2. UV/Vis spectra of octakis(alkylthio)phthalocyanine (···), **5** (—), and **6** (– – –) in toluene

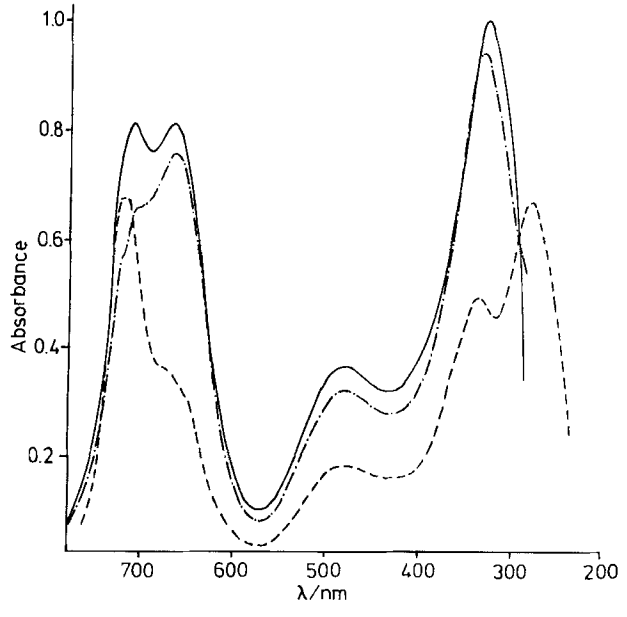


Figure 3. UV/Vis spectra of **6** in toluene (—), chloroform (– – –), and tetrachloromethane (—·—·—)

Chloro[2,3,9,10,16,17-hexakis(hexylthio)-7,12,14,19-diimino-21,5-nitrilo-5H-tribenzo[c,h,m][1,6,11]triazacyclopentadecinato-(2−)-N^{22},N^{23},N^{24}]-(T-4)-boron (**4**): Compound **1** (2.0 g, 5.55 mmol) was dissolved in anhydrous 1-chloronaphthalene (4 ml) under Ar. After cooling of the solution in an ice bath a solution of boron trichloride (0.217 g, 1.85 mmol) in anhydrous 1-chloronaphthalene was added. The mixture was stirred at 0°C for 10 min and then heated to 100°C. This temp. was maintained for 4 h. After cooling to room temp. the dark purple mixture was diluted with ethanol (50 ml), and the waxy precipitate was centrifugated. This treatment was carried out several times. The crude product was dissolved in dichloromethane and precipitated from the solution by the addition of ethanol, then centrifugated to obtain a bronze-colored product. This compound was soluble in CH_2Cl_2, $CHCl_3$, CCl_4, diethyl ether, hexane, toluene, benzene; yield: 0.59 g (28%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2960–2850 cm^{-1}, 1600, 1525, 1460–1365, 1220–1190, 1110–1040, 980, 955 (B–Cl), 860, 820, 790, 760, 710. – UV/Vis (chloroform): λ_{max} (lg ε) = 600 nm (5.17), 550 (4.69), 396 (4.71), 302 (5.08). – ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, 18H, CH_3), 1.38 (m, 24H, $CH_2CH_2CH_3$), 1.65 (m, 12H, $SCH_2CH_2CH_2$), 1.86 (p, 12H, SCH_2CH_2), 3.25 (t, 12H, SCH_2), 8.56 (d, 6H, J = 3.2 Hz, aromatic CH). – ^{13}C NMR ($CDCl_3$): δ = 14.04 (CH_3), 22.56, 28.43, 28.62, 31.47 (CH_2), 33.64 (SCH_2), 119.38, 127.07, 128.30, 139.37, 140.16, 140.65, 149.00, 149.53, 150.70 (aromatic C). – MS (FAB), *m/z* (%): 1163 (27) $[M + Cl]^+$, 1128 (100) $[M]^+$, 1057 (9), 1006 (21), 952 (36), 916 (6), 887 (8), 816 (25), 791 (12), 736 (25), 690 (37), 605 (24), 562 (29), 521 (43), 476 (51), 426 (14) $[M - 6 \times (C_6H_{13}S_2)]^+$, 382 (81), 337 (25), 280 (17), 208 (17), 179 (12), 150 (22). – $C_{60}H_{84}BClN_6S_6$ (1127.9): calcd. C 63.89, H 7.51, N 7.45, S 17.05; found C 63.85, H 7.21, N 7.66, S 16.46.

Unsymmetrical Phthalocyanines

2,3,9,10,16,17-Hexakis(hexylthio)phthalocyanine (**5**): A mixture of **2** (0.18 g, 1.24 mmol), **4** (0.2 g, 0.177 mmol), anhydrous 1-chloronaphthalene (0.5 ml), and anhydrous dimethyl sulfoxide (1 ml) was heated at 80°C under Ar for 4 h. After cooling to room temp. the reaction mixture was diluted with ethanol (30–40 ml), and the waxy precipitate was separated. It was heated with ethanol and centrifuged to remove impurities. The crude green product was purified by column chromatography (silica gel, CH_2Cl_2). This compound was soluble in CH_2Cl_2, $CHCl_3$, CCl_4, diethyl ether, hexane, heptane, etc. Yield: 20 mg (10%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3300 cm^{-1}, 2980–2880, 1600, 1500, 1460, 1430–1400, 1380, 1330, 1265, 1080, 1025, 940, 870, 800, 745–720. – UV/Vis (chloroform): λ_{max} (lg ε) = 723 nm (5.12), 691 (5.12), 660 (4.66), 448 (4.53), 340 (4.81). – ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, 18H, CH_3), 1.25–1.99 (m, 48H, CH_2), 3.16 (t, 12H, SCH_2), 7.62 (s, 2H, aromatic CH), 7.74 (s, 4H, aromatic CH), 8.00 (s, 2H, aromatic CH), 8.38 (s, 2H, aromatic CH), −4.91 (s, 2H, NH). – ^{13}C NMR ($CDCl_3$): δ = 14.21 (CH_3), 22.72, 28.69, 29.15, 31.78, 33.70 (CH_2), 119.65, 121.95, 128.67 (aromatic CH), 132.37, 138.08, 140.30 (aromatic C). – $C_{68}H_{90}N_8S_6$ (1211.8): calcd. C 67.40, H 7.48, N 9.24, S 15.87; found C 67.00, H 7.65, N 9.00, S 15.50.

2,3,9,10,16,17-Hexakis(hexylthio)-23-nitrophthalocyanine (**6**) was synthesized similar to **5** by starting with **3** (0.236 g, 1.24 mmol) and **4** (0.20 g, 0.177 mmol). The crude product was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane, 3:2). Yield: 15 mg (7%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3300 cm^{-1}, 2980–2880, 1600, 1520, 1460, 1340, 1260, 1110–1020, 800, 740. – UV/Vis (toluene): λ_{max} (lg ε) = 707 nm (4.72), 646 (4.72), 479 (4.40), 326 (4.81). – ^{1}H NMR ($CDCl_3$): δ = 1.03 (t, 18H, CH_3), 1.80–1.25 (m, 48H, CH_2), 2.95 (SCH_2), 6.8–8.2 (m, 9H, aromatic CH), −6.10 (s, 2H, NH). – ^{13}C NMR ($CDCl_3$, APT): δ = 14.20 (CH_3), 22.69, 28.39, 29.10, 31.79, 33.52 (CH_2), 115.85, 117.39, 118.87., 120.27 (aromatic CH), 139.31, 141.02, 141.48, 146.26 (aromatic C). – $C_{68}H_{89}N_9O_2S_6$ (1256.8): calcd. C 64.98, H 7.14, N 10.03, S 15.05; found C 65.66, H 7.22, N 9.65, S 15.32.

[1] N. Kobayashi in *Phthalocyanines Properties and Applications* (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, Weinheim, **1993**, vol. 2, chapter 3.
[2] F. H. Moser, A. L. Thomas, *The Phthalocyanines*, CRC, Boca Raton, **1983**, vol. 1 and 2.
[3] H. Schultz, H. Lehman, M. Rein, M. Hanack, *Struct. Bonding (Berlin)* **1991**, *74*, 41–146.
[4] D. F. Eaton, *Science* **1991**, *253*, 281–287.
[5] C. C. Leznoff, A. B. P. Lever (Eds.), *Phthalocyanines Properties and Applications*, VCH, Weinheim, **1989**, vol. 1.
[6] C. C. Leznoff, C. R. McArthur, Y. Qin, *Can. J. Chem.* **1993**, *71*, 1319–1326.
[7] C. Piechocki, J. Simon, *J. Chem. Soc., Chem. Commun.* **1985**, 259–260.
[8] J. G. Joung, W. Onyebuagu, *J. Org. Chem.* **1990**, *55*, 2155–2159.
[9] J. Yang, T. C. Rogers, M. R. Van De Mark, *J. Heterocyclic Chem.* **1993**, *30*, 571–573.
[10] A. Meller, A. Ossko, *Monatsh. Chem.* **1972**, *103*, 150–155.
[11] H. Kietaibl, *Monatsh. Chem.* **1974**, *105*, 405–418.
[12] M. Ando, M. Mori (Toyo Ink Mfg. Co., Ltd.), Jpn. Kokai Tokkyo Koho JP 02 09, 882 [90 09.882], **1990**; *Chem. Abstr.* **1990**, *113*, P25558c.
[13] [13a] N. Kobayashi, R. Kondo, S. Nakajima, T. Osa, *J. Am. Chem. Soc.* **1990**, *112*, 9640–9641. – [13b] K. Kasuga, T. Idehara, M. Handa, K. Isa, *Inorg. Chim. Acta* **1992**, *196*, 127–128.
[14] E. Musluoğlu, A. Gürek, V. Ahsen, A. Gül, Ö. Bekâroğlu, *Chem. Ber.* **1992**, *125*, 2337–2339.
[15] [15a] H. Matsuda, S. Okada, A. Masaki, H. Nakanishi, Y. Suda, K. Shigehara, Y. Yamada, *Proceedings of SPIE, Nonlinear Optical Properties of Organic Materials III*, **1990**, *1337*, 105–113. – [15b] Y. Suda, K. Shigehara, A. Yamada, H. Matsuda, S. Okada, A. Masaki, H. Nakanishi, *Proceedings of SPIE, Nonlinear Optical Properties of Organic Materials IV*, **1991**, *1560*, 75–83.
[16] D. Wöhrle, M. Eskes, K. Shigehara, A. Yamada, *Synthesis* **1993**, 194–196.
[17] I. Gürol, V. Ahsen, Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.* **1994**, 497–500.
[18] A. Gqrek, Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.*, in press.
[19] [19a] A. R. Koray, V. Ahsen, Ö. Bekâroğlu, *J. Chem. Soc., Chem. Commun.* **1986**, 932–933. – [19b] V. Ahsen, E. Yilmazer, M. Ertaş, Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.* **1988**, 401–406.
[20] [20a] V. Ahsen, A. Gürek, E. Musluoğlu, Ö. Bekâroğlu, *Chem. Ber.* **1989**, *122*, 1073–1074. [20b] E. Musluoğlu, V. Ahsen, A. Gül Ö. Bekâroğlu, *Chem. Ber.* **1991**, *124*, 2531–2536.
[21] [21a] M. Koçak, A. Cihan, A. I. Okur, and Ö. Bekâroğlu, *J. Chem. Soc., Chem. Commun.* **1991**, 577–578. – [21b] A. Gürek, V. Ahsen, A. Gül and Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.* **1991**, 3367–3371.
[22] M. Koçak, A. I. Okur, Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.* **1994**, 323–326.
[23] P. J. Brach, S. J. Grammatica, O. A. Osanna, L. Weinberger, *J. Heterocycl. Chem.* **1970**, *7*, 1403–1405.

[127/94]