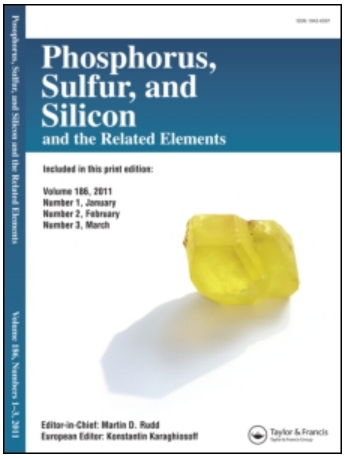

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Synthesis of Novel Maleonitrile Derivatives

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SYNTHESIS OF NOVEL MALEONITRILE DERIVATIVES

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The synthesis of four novel maleonitrile derivatives are described. New maleonitriles have been prepared by the reaction of different alkylhalides such as 3-bromopropionitrile, 1,3-dichloroacetone, α,α′-dibromoxylene, and p-nitrobenzylbromide with dithiomaleonitrile disodium salt. All novel compounds have cis-cyano groups and are characterized by IR, NMR spectroscopy, and elemental analysis.

Keywords: Cyclophane; ligands; macrocycle; maleonitrile; porphyrazine

Interest in synthesizing new derivatives of maleonitrile stems from their extensive use as precursors to porphyrazines.[1] The possibility to functionalize porphyrazines on the periphery can be achieved by addition of different groups to these unsaturated 1,2-dinitrile derivatives. A distinct advantage of preparing phthalocyanines over porphyrazines has been the relative difficulty in synthesising the starting compound in the latter; i.e., derivatization of phthalonitrile is much easier than maleonitrile.[2] Although a number of synthetic procedures to obtain maleonitrile derivatives (e.g., conversion of alkynes into alkyl and/or aryl-substituted unsaturated 1,2-dinitriles,[3] dimerization of arylmethyl cyanides with iodine,[4] etc.) have been reported, the products are usually a mixture of *cis* and *trans* isomers and isolation of the desired *cis* isomer from the mixture is usually cumbersome.

The rise in the frequency of porphyrazines reported recently has been a clear consequence of the practical procedure to obtain dialkylthiomaleonitrile from disodium salt of dithiomaleonitrile reported by Schramm and Hoffman.[5] In addition to ready solubility, electron donating thioether groups on the periphery of the porphyrazine

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enhance the electron density of the macrocycle leading to visible spectra comparable with those of phthalocyanines.[6] Parallel with the efforts of different research groups to derivatize dithiomaleonitrile (e.g., oxocrown-,[7,8] aza-crown-,[9] thiacrown-formation,[10,11] alkyl, or alkoxy groups of various lengths[12]), our group has been heavily engaged with the preparation of derivatives with additional functionalities such as, 2-hydroxyethyl-,[13] 2-dimethylaminoethyl-,[14] 2-tosylaminoethyl-,[15] 2-[(acetylbenzo-15-crown-5)yl]-dithiomaleonitrile.[16] Recently, heterocyclic products obtained by the addition reaction of disodium salt of maleonitrile to unsaturated reagents have been converted into porphyrazine derivatives.[17]

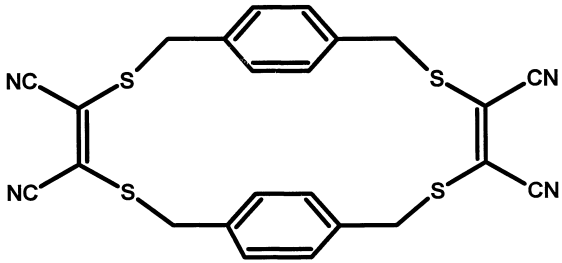
In the present work, we report the synthesis of a cyclophane structure with two dithiomaleonitrile units (**2**), a 7-membered heterocyclic product (**3**) and two open-chain derivatives (**4**, **5**) as potential starting materials for porphyrazines (Figure 1).

RESULTS AND DISCUSSION

The general procedure used to obtain the desired maleonitrile derivatives **2–5** has been alkylation of the dithiolate function in **1**. The alkylating agent R-X has been either a chloride or bromide derivative, i.e., 3-bromopropionitrile, 1,3-dichloroacetone, α,α'-dibromo-p-xylene, p-nitrobenzylbromide.

Cyclophane type compound **2** was obtained in two steps; first **1** and α,α'-dibromo-p-xylene were refluxed in methanol in 2:1 ratio and then the addition of the second portion of α,α'-dibromo-p-xylene to the reaction media was preferred. The reason for this two-step process was to reduce the formation of any oligomeric by-product to minimal amount. The IR spectrum of **2** shows aromatic (3010 cm^{-1}) and aliphatic (2815 cm^{-1}) CH vibrations in addition to a single intense C≡N vibration (2238 cm^{-1}). The ^1H NMR spectrum of the same compound support the proposed structure with chemical shifts of the protons in the SCH_2 group at 4.25 and the benzene protons at 7.24 ppm as two singlets.

The cyclization reaction between **1** and dichloroacetone gave a 7-membered dithiaheterocycle. The IR spectrum of **3** supported the expected structure by streching vibrations of CN, C=O and SCH_2 groups at 2225, 1626, 2937 cm^{-1} respectively. Elemental analysis also corresponded closely with the values calculated for $C_7H_4N_2OS_2$. In the ^1H NMR spectrum, there was only one chemical shift for SCH_2 at 4.28 ppm due to the symmetrical structure of the molecule.



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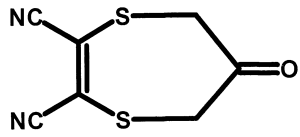

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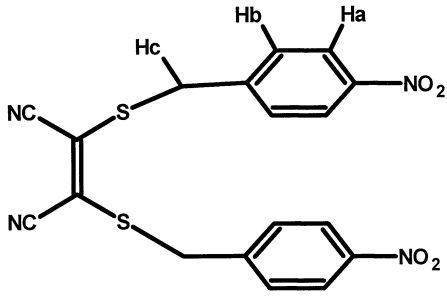

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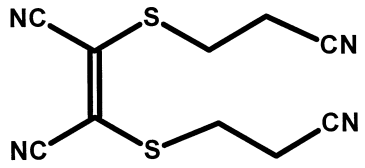

5

FIGURE 1 Maleonitrile derivatives **2–5** synthesized.

In the case of **4**, the substituents on the maleonitrile core are p-nitrobenzyl groups, so the alkylating agent has been p-nitrobenzylbromide. Vibrations at 2250 cm^{-1} for the CN group and at 1523 and 1313 cm^{-1} for Ar-NO_2 in the IR spectrum confirmed the structure of **4**. In the ^1H NMR spectrum two chemical shifts for the aromatic protons and another one for the SCH_2 group occur at 8.19, 7.61, and 4.58 ppm respectively.

Compound **5** is a maleonitrile derivative with alkylnitrile substituents. Its structure was verified with two chemical shifts corresponding to SCH_2 and CH_2-CN groups at 3.46 and 3.00 ppm, respectively, in the ^1H NMR spectrum. In the IR spectrum, the appearance of two streching vibrations located at 2229 and 2208 cm^{-1}, due to the presence of two different cyano groups, is remarkable.

Our interest in synthesizing new dithiomaleonitrile derivatives further stems from their use as precursors to porphyrazines rendering them different physico-chemical properties which will be the subject of interest for diverse application areas.

EXPERIMENTAL

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrophotometer using KBr pellets, elemental analyses were carried out by the Instrumental Analysis Laboratory of TÜBİTAK Marmara Research Centre. ^1H NMR spectra were recorded on a Bruker 250 MHz spectrometer using $SiMe_4$ as the reference. Disodium salt of dithiomaleonitrile (**1**) was prepared according to the reported procedure.[18]

Synthesis of 3,6,13,16-Tetrathia-tricyclo[16.2.2.$2^{8,11}$]-tetracosa-1(21),4,8,10,14,18(22),19,23-octaene-4,5,14,15-tetracarbonitrile (2, $C_{24}H_{16}N_4S_4$)

A mixture of **1** (0.372 g, 2 mmol) and α,α'-dibromo-p-xylene (0.264 g, 1 mmol) was refluxed in 160 ml of methanol for 1 h under N_2. Then, the second portion of α,α'-dibromo-p-xylene (0.264 g, 1 mmol) was added to the mixture and the reaction mixture was further refluxed for 7 h by stirring. At the end of 8 h, the mixture was filtered and the precipitate was dissolved in 20 ml of THF and cooled in the deep freeze overnight. It was heated to room temperature and the white crystalline precipitate was filtered, washed with diethyl ether, and dried in vacuo to yield 76 mg (17%) of **2**. M.p. 95°C(dec). Anal. Calc. for $C_{24}H_{16}N_4S_4$ (488): C, 59.01; H, 3.21; N, 11.47%; found C, 58.92; H, 3.11; N, 11.51. IR (KBr) cm^{-1}: 3010 (ArH), 2876, 2815 (CH_2), 2238 (C≡N), 1500 (C=C), 1437,

1187, 1125, 816, 712, 750, 787, 600. ^{1}H NMR ($CDCl_3$) ppm: 7.24 (8H, s, Ar-H), 4.25 (8H, s, CH_2).

Synthesis of 6-Oxo-6,7-dihydro-5H-[1,4]dithiepine-2,3-dicarbonitrile (3, $C_7H_4N_2OS_2$)

A mixture of dichloroacetone (0.635 g, 50 mmol) and **1** (0.930 g, 50 mmol) were refluxed in 130 ml of methanol under N_2 for 7 h. It was filtered while hot and the precipitate was dissolved in 30 ml of chloroform. To remove insoluble by products, the mixture was filtered again and the filtrate was evaporated to dryness. The brown oily residue was dissolved in a minimum amount of acetone (ca. 1 ml) and it was added dropwise into cool diethyl ether. After stirring for 5 min, the mixture was filtered and the precipitate was washed with diethyl ether and then dried in vacuo. M.p. 100°C (dec). Yield 0.380 g (38.77%) Anal. Calc. for $C_7H_4N_2OS_2$ (196): C, 42.86; H, 2.04; N, 14.28%; found C, 42.75; H, 2.13; N, 14.35%. IR (KBr) cm^{-1}: 2937, 2225 (C≡N), 1626 (C=O), 1563, 1437, 1370. ^{1}H NMR ($CDCl_3$) ppm: 4.28 (4H, s, CH_2).

Synthesis of bis(p-Nitrobenzylthio)maleonitrile (4, $C_{18}H_{12}N_4O_4S_2$)

1 (1.86 g, 10 mmol) and p-nitro-benzylbromide (4.32 g, 20 mmol) were stirred in 50 ml of methanol in an ice-bath for 5 h and then the mixture was filtered. The precipitate was dissolved in 25 ml of chloroform, filtered, and the filtrate was evaporated to dryness and the residue was recrystallized in 20 ml chloroform. Yield: 3.4 g (83%). Anal. Calc. for $C_{18}H_{12}N_4O_4S_2$ (412): C, 52.43; H, 2.91; N, 13.59%; found C, 52.28; H, 3.05; N, 13.42%. IR (KBr) cm^{-1}: 3190, 3180, 3063, 3000 (ArH), 2937 (SCH_2), 2250 (C≡N), 1586 (C=C), 1523, 1313 (NO_2), 1250, 1187, 1125, 1084, 787, 750, 670. ^{1}H NMR (DMSO-d_6) ppm: 8.19 (4H, s, Ha), 7.61 (4H, s, Hb), 4.58 (4H, s, Hc).

Synthesis of bis(2-Cyano-ethylthio)maleonitrile (5, $C_{10}H_8N_4S_2$)

A mixture of **1** (0.372 g, 20 mmol) and 3-bromopropionitrile (0.36 ml, 40 mmol) was refluxed in 25 ml of acetonitrile under N_2 for 7.5 h. At the end of reaction, the mixture was filtered. The filtrate was evaporated to dryness. The crude product was stirred with 25 ml of methanol and then the mixture was filtered. The filtrate was left at 5°C overnight. It was warmed to room temperature and filtered. The precipitate was washed with diethyl ether and dried in vacuo. M.p. 90°C (dec). Yield.

0.254 g (51.20%). Analysis: Calc. for $C_{10}H_8N_4S_2$ (248): C, 48.39; H, 3.23; N, 22.58%; found C, 48.55; H, 2.94; N, 22.85. IR (KBr) cm^{-1}: 2913, 2879 (CH_2), 2208 (CH_2–C≡N), 2229 (C≡N), 1500, 1437, 1374, 1250, 1184, 1124, 687 cm^{-1}. ^1H NMR (DMSO-d_6) ppm: 3.46 (4H, t, CH_2–CN), 3.00 (4H, t, SCH_2).

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